OCN 401 Biogeochemical Systems (10.24.17)

(Schlesinger: Chapter 9)

# Part 2. Oceanic Carbon and Nutrient Cycling

## Lecture Outline

1. Net Primary Production (NPP)
   a) Global Patterns
   b) Fate of NPP

2. Sediment Diagenesis
   a) Diagenesis of Organic Matter (OM)
   b) Biogenic Carbonates

# Net Primary Production: Global Patterns

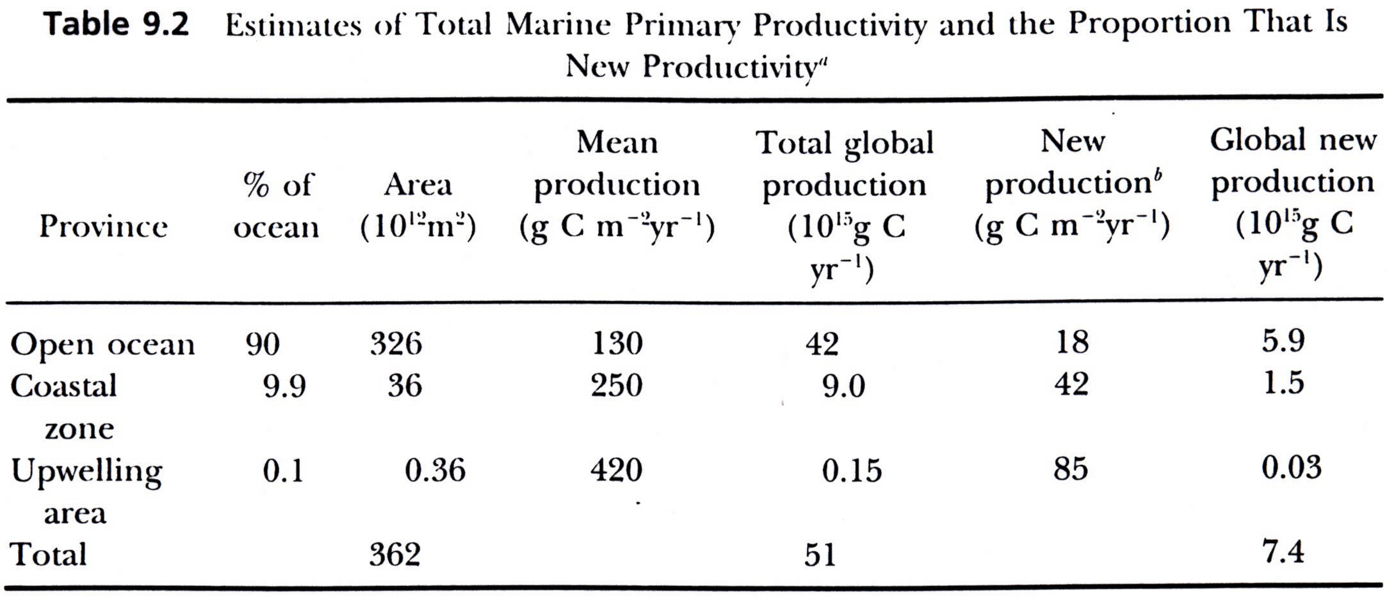


**Table 9.2** Estimates of Total Marine Primary Productivity and the Proportion That Is New Productivity[a]

| Province | % of ocean | Area $(10^{12} m^2)$ | Mean production $(g\ C\ m^{-2} yr^{-1})$ | Total global production $(10^{15} g\ C\ yr^{-1})$ | New production[b] $(g\ C\ m^{-2} yr^{-1})$ | Global new production $(10^{15} g\ C\ yr^{-1})$ |
|---|---|---|---|---|---|---|
| Open ocean | 90 | 326 | 130 | 42 | 18 | 5.9 |
| Coastal zone | 9.9 | 36 | 250 | 9.0 | 42 | 1.5 |
| Upwelling area | 0.1 | 0.36 | 420 | 0.15 | 85 | 0.03 |
| Total | | 362 | | 51 | | 7.4 |

[a]From Knauer (1993); [b]New productivity defined as C-flux at 100 m

- Oceanic NPP is ≈ 50% of total NPP on Earth
    - mostly as phytoplankton (microscopic plants) in surface mixed layer
    - macrophytes (seaweed) accounts for only ≈ 0.1%.
- NPP range: 130 - 420 gC/m$^2$/yr
    - lowest in open ocean
    - highest in coastal zones
- Terrestrial forests range: 400-800 gC/m$^2$/yr
    - deserts average 80 gC/m$^2$/yr.

# Water Column Vertical Profiles Reflect Impact of PP

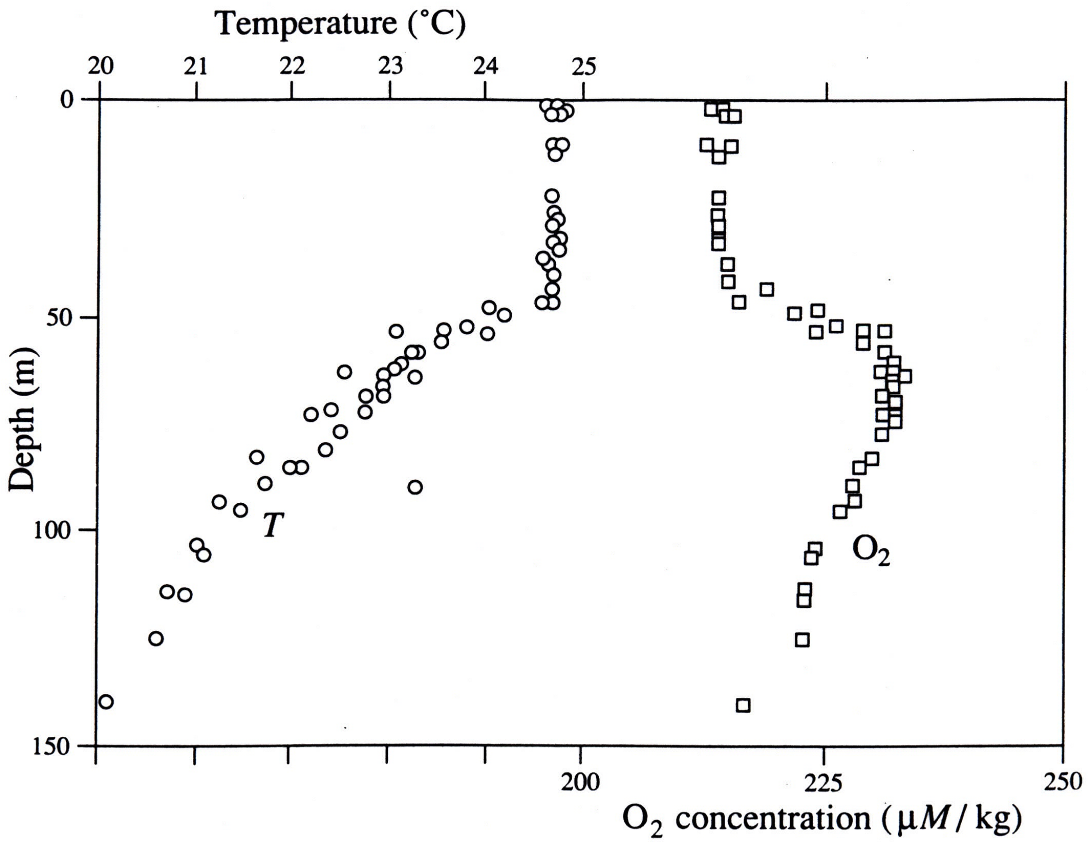


**Figure 9.5** Distribution of temperature and $O_2$ with depth in the North Pacific Ocean. The peak in $O_2$ at 50 m is not unusual; it reflects the frequent observation that maximum photosynthesis does not occur at the surface, but at a lower level of the euphotic zone where there is maximum nutrient remineralization. From Craig and Hayward (1987). See also Fig. 9.19 for the distribution of $O_2$ to 1700 m.

- $O_2$ distribution → indirect measure of photosynthesis: $CO_2 + H_2O = CH_2O + O_2$
- NPP is usually measured using $O_2$-bottle or $^{14}C$-uptake techniques.
- $O_2$ bottle measurements >> $^{14}C$-uptake rates in the same waters.

# Uncertainties in Estimates of Net Primary Production

- Discrepancies in methods for measuring NPP

  - estimates range from 27 to 51 x $10^{15}$ gC/yr.

- $O_2$ bottle measurements >$^{14}$C-uptake rates

  - large biomass of picoplankton pass through filters used in the $^{14}$C technique
    - ○ 1979: Synechococcus discovered (1 µm)
    - ○ 1980s: Prochlorococcus discovered (0.5 – 0.7 µm)

  - picoplankton may account for up to 50% of oceanic production.

  - DOC produced by phytoplankton, a component of NPP, passes through filters.

  - Problems with contamination of $^{14}$C-incubated samples with toxic trace elements depress NPP.

# Net Primary Production: Global Patterns

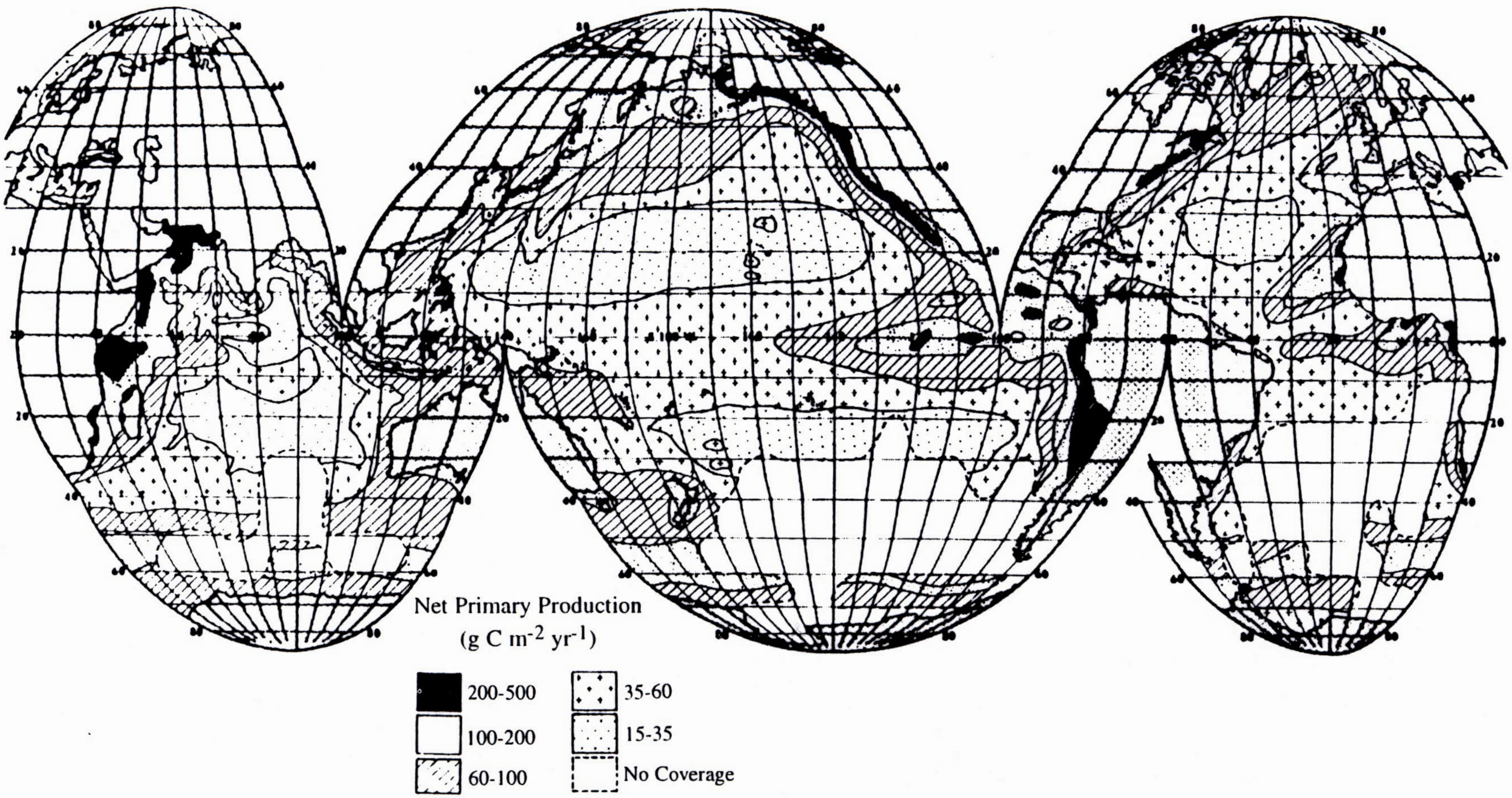
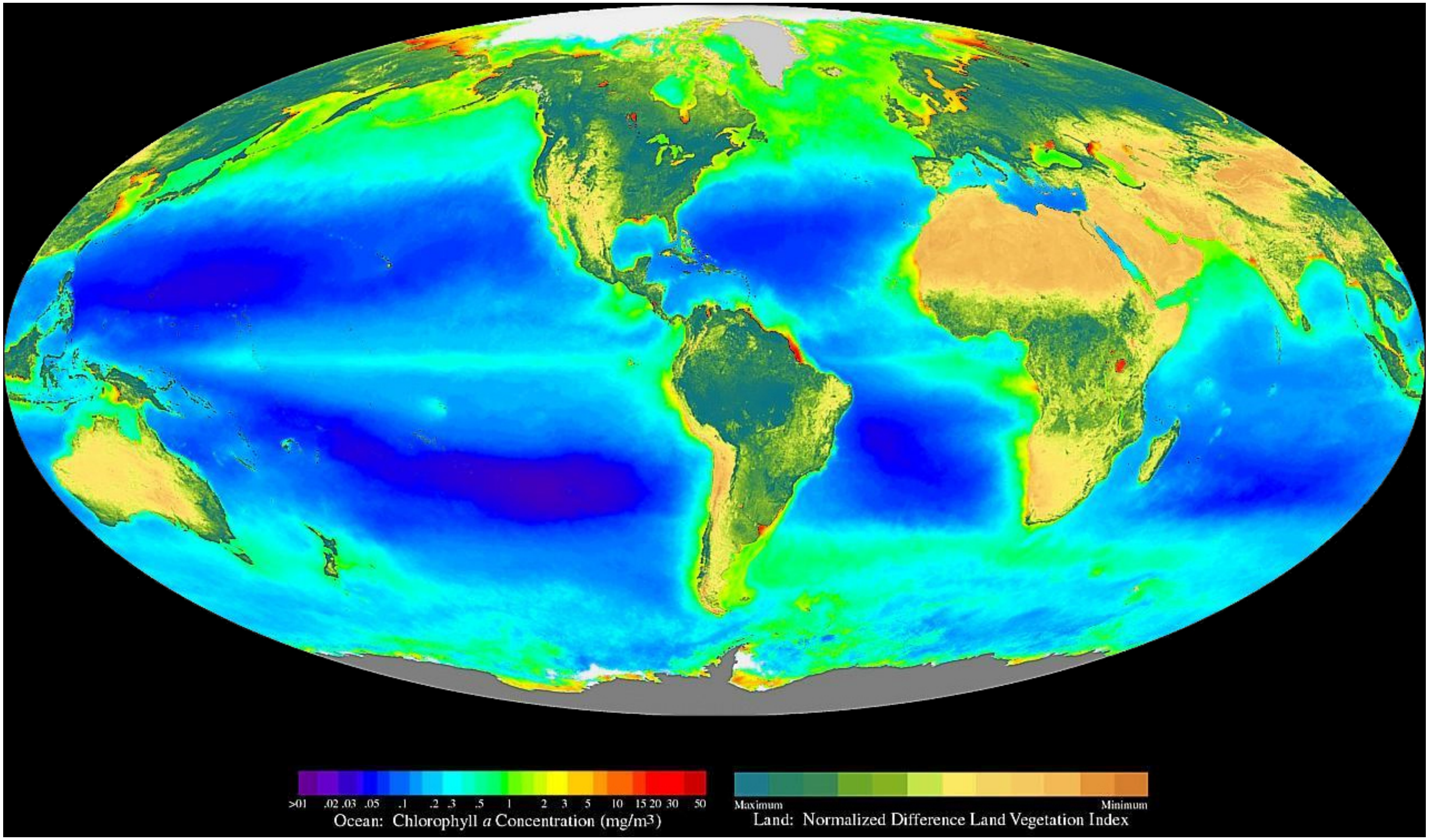


**Figure 9.6** Net primary production in the world's oceans in units of g C $m^{-2}$ $yr^{-1}$. From Berger (1989). Compare to Fig. 5.12, which shows the distribution of net primary production on land.

Despite disagreement on absolute magnitude of global NPP, there is consensus on the global distribution of NPP.

# Net Primary Production:  Global Patterns (cont’d.)

Satellite remote sensing allows quantification of chlorophyll (chl-a), a for photosynthetic biomass



*http://www.gsfc.nasa.gov*

# Chlorophyll: a proxy for PP

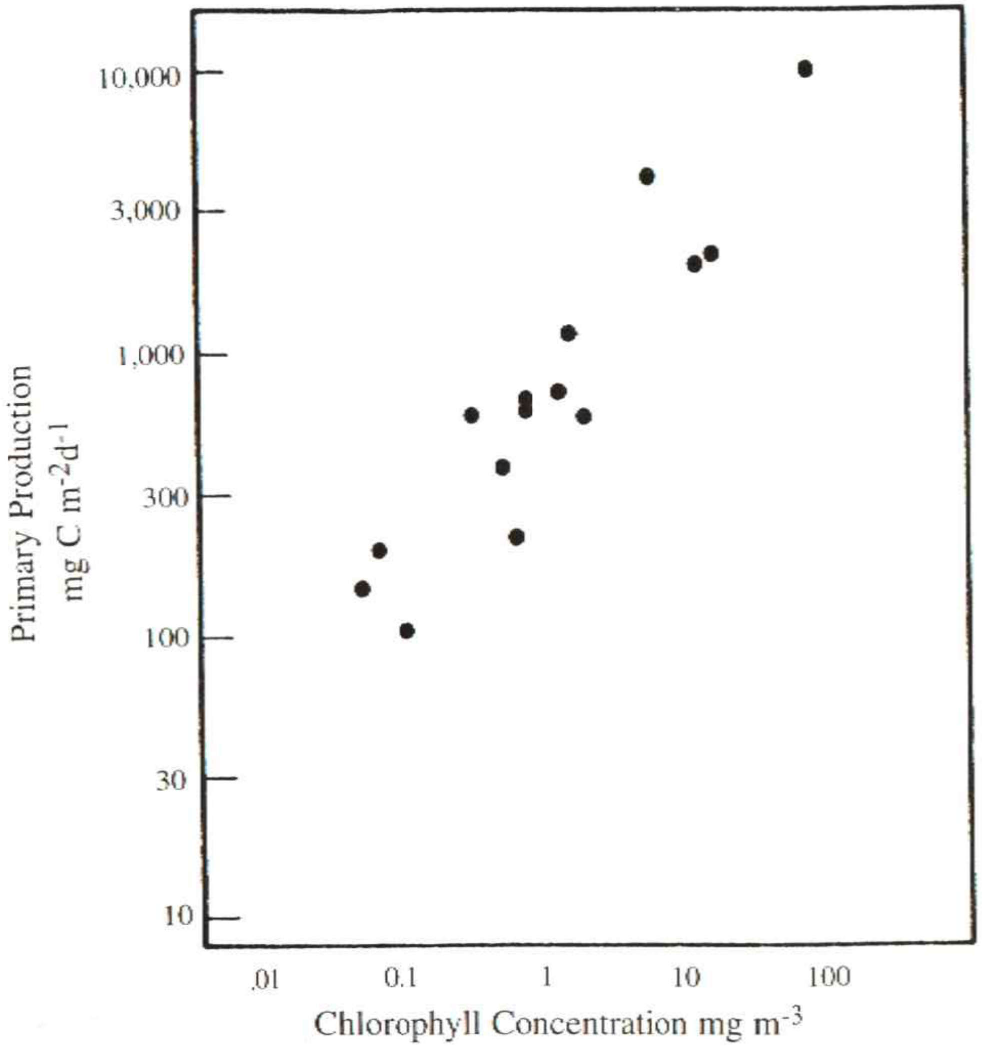


**Figure 9.7** Net primary productivity as a function of surface chlorophyll in waters of coastal California. From Eppley et al. (1985).

# Fate of Net Primary Production: Decomposition and Recycling in Surface Waters

- Most NPP (80-90%) is consumed in the surface ocean by zooplankton and free-floating bacteria (bacterioplankton).

- Bacterial decomposition >> zooplankton consumption of POM

- Bacteria respire 30-70% of NPP

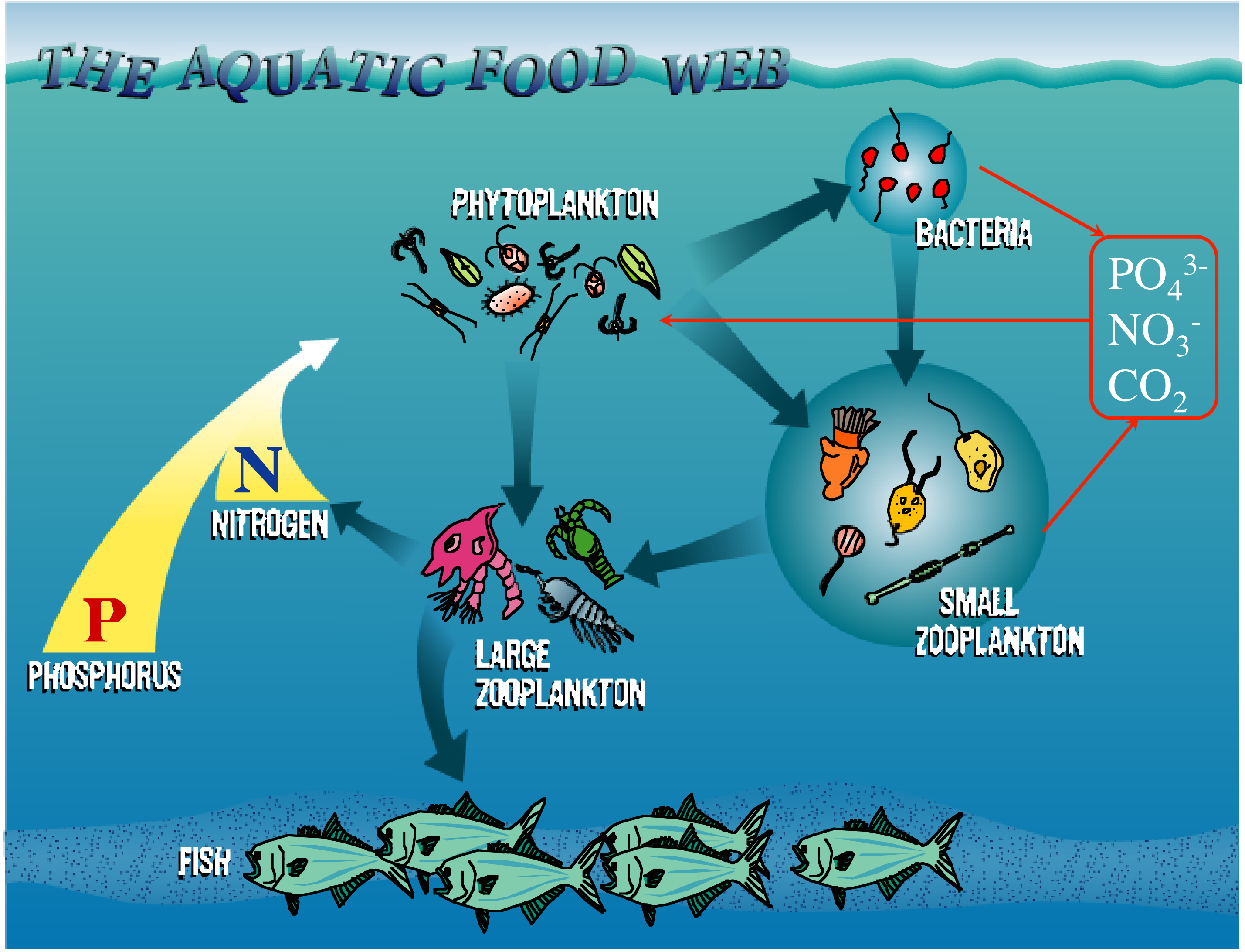
- Zooplankton are the 1st step in a trophic chain that leads to larger animals

- In contrast, bacteria are consumed by bacteriovores, who mineralize nutrients (converting POP and PON to $PO_4^{3-}$ and $NO_3^-$) and release $CO_2$ to surface waters.

- When bacteria are abundant, a large fraction of the C fixed by NPP is not passed to higher trophic levels.

- Bacterial #s are depressed in cold waters, where more NPP can be passed up the food chain.

# Aquatic Food Web:
# Recycling & Decomposition in Surface Waters



# Fate of Net Primary Production: *Export* of NPP out of Surface Waters to the Deep Sea

- 80-90% of NPP is degraded to inorganic compounds ($PO_4^{3-}$, $NO_3^-$, $CO_2$ ) in surface waters.

- The remaining 10-20% sinks below the euphotic zone to the deep ocean.

- POM *exported* from the photic zone sinks at ≈ 350 m/d, so the average particle spends ≈ 10 days in transit to the bottom.

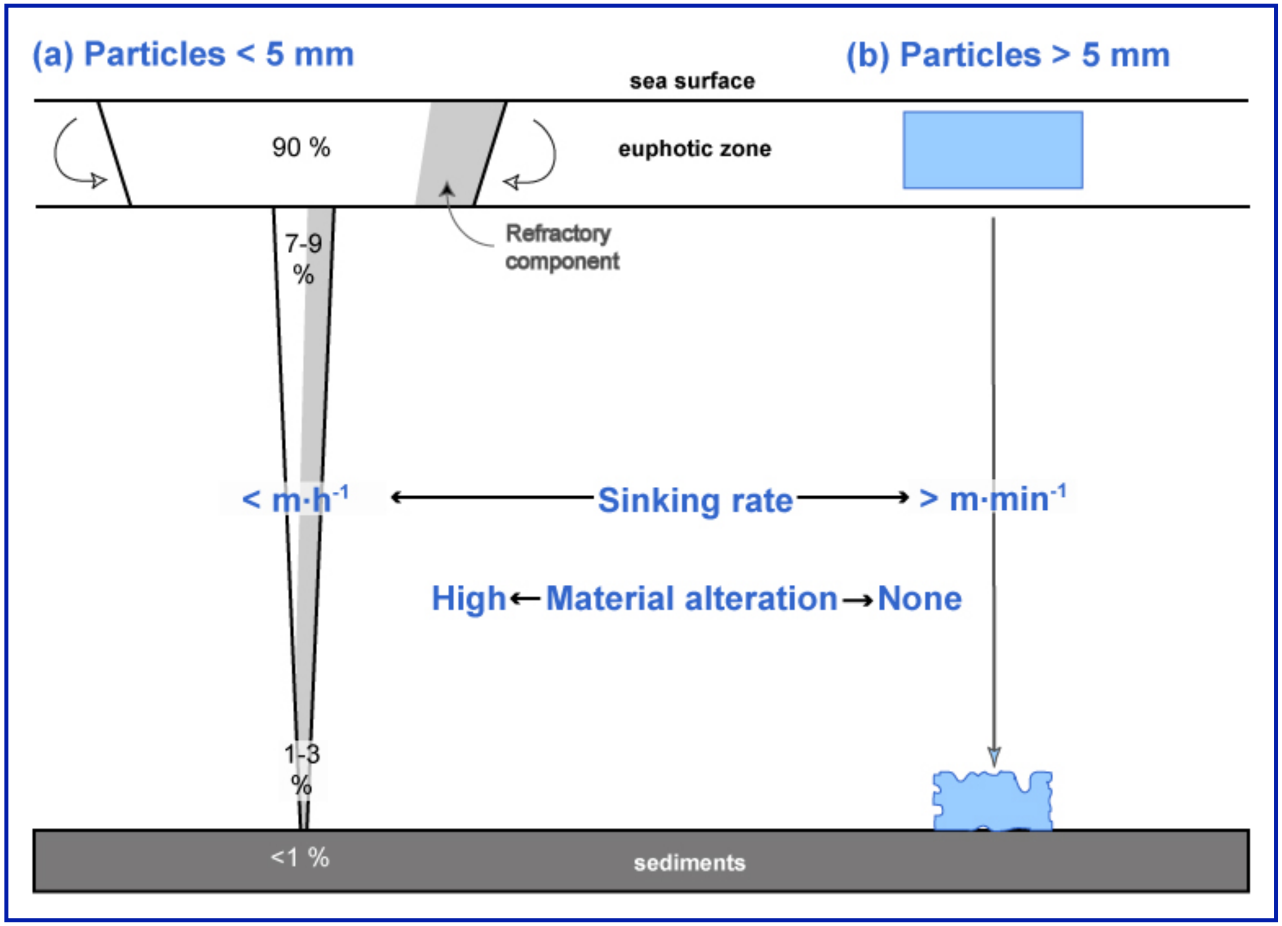
- Bacteria continue to decompose POM as it sinks, consuming $O_2$ and producing $CO_2$ in deep waters; rates are limited by the cold temperatures.

- Most POM (95%) is remineralized by 3000 m depth; only small quantities reach the sediments of the deep ocean.

- Comparison of rates of NPP and OM incorporation in deep sea sediment suggests ≈ 98% of POM is degraded in the deep sea water column.

- Burial in sediments is <1% of NPP (estimated 0.085 to 0.126 x $10^{15}$ gC/yr).

# Fate of NPP - Deep ocean



*Hannides (2008)*

# Global patterns of NPP in surface waters

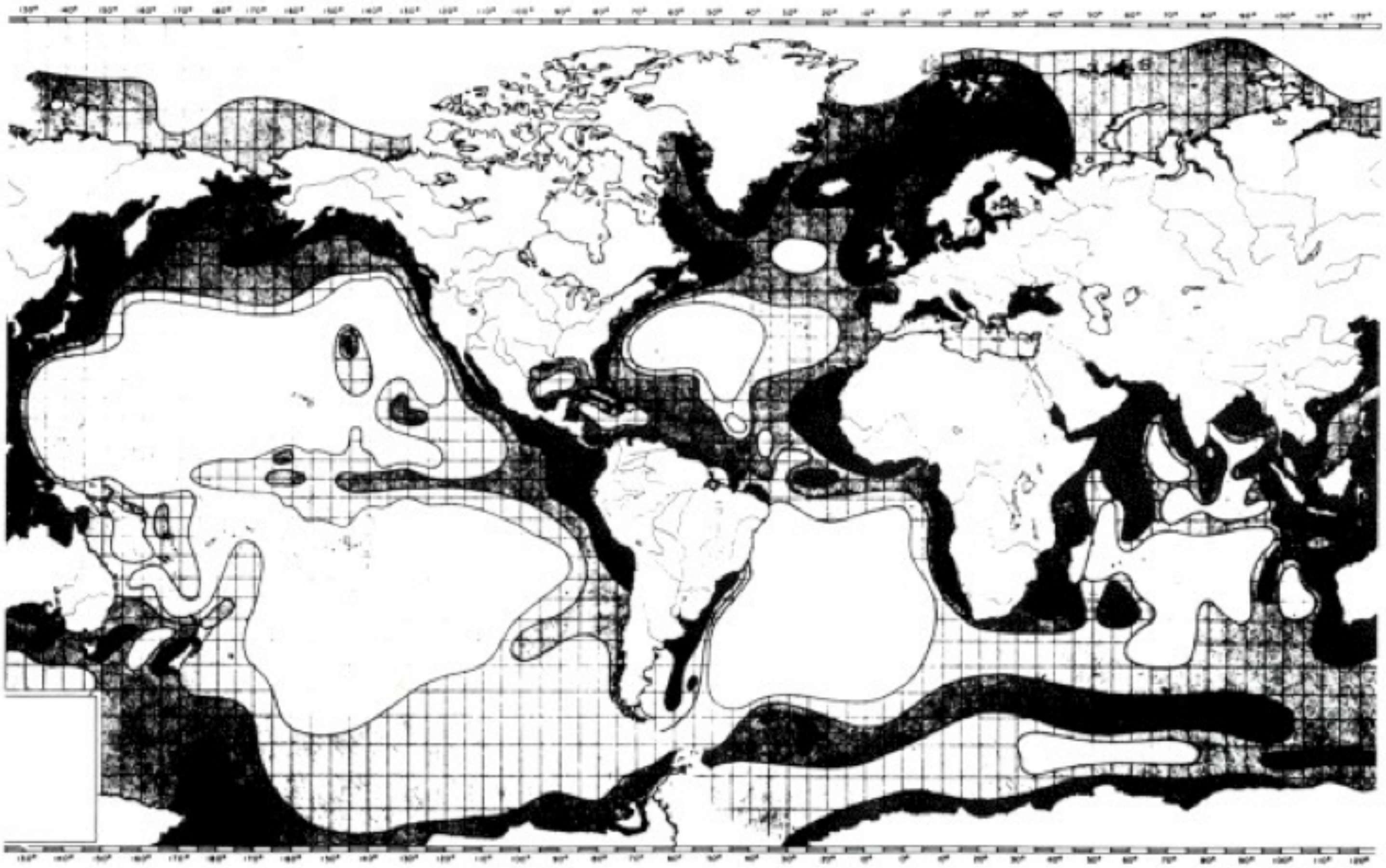


**Figure 14.1** The global distribution of phytoplankton primary production (mg C $m^{-2}$ $day^{-1}$ ) in five categories of > 500, 250-500, 150-250, 100-150, and <100 (after Koblentz-Mishke et al., 1970). (Reproduced with permission.). **www.icsu-scope.org/.../ scope35/chapter14.html**

# Zooplankton abundance correlates with NPP

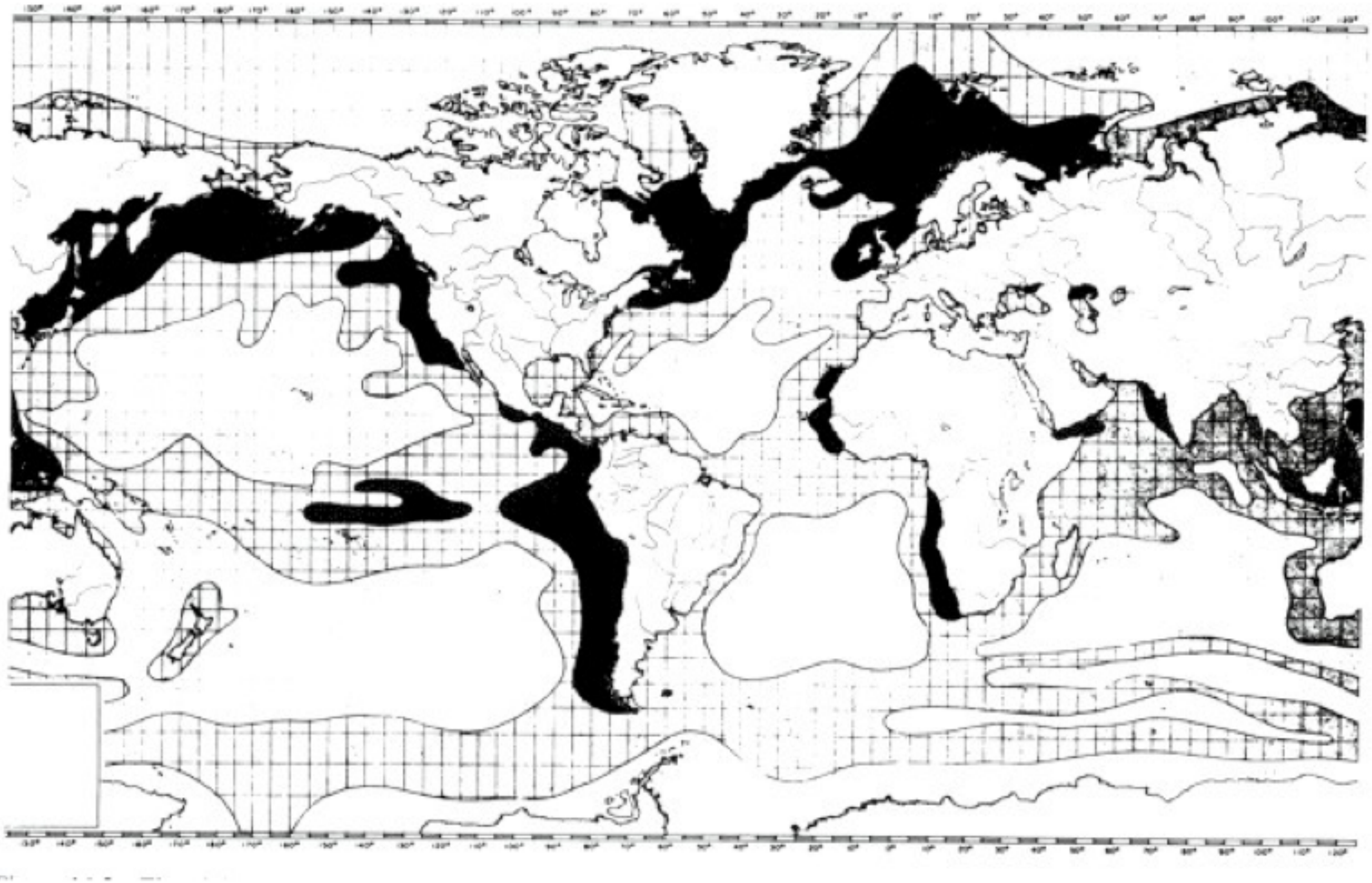


**Figure 14.2** The global distribution of zooplankton abundance (mg m$^{-3}$ ) over the upper 100 m of the water column in four categories of >500, 201-500, 51-200, and <50 (after Bogorov et al., 1968). (Reproduced with permission.). **www.icsu-scope.org/.../ scope35/chapter14.html**

# Sediment OM Distribution similar to NPP

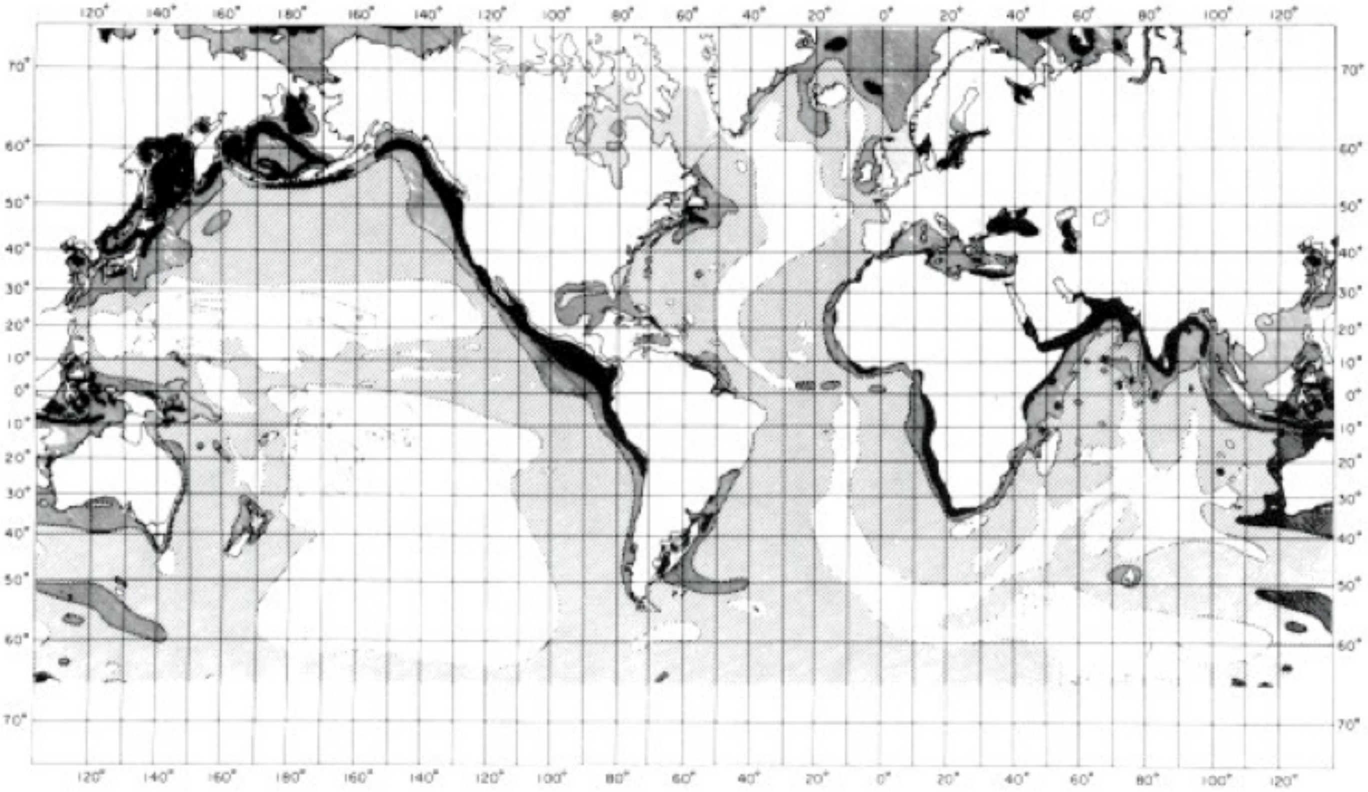


**Figure 14.3** The global distribution of organic carbon (% dw) within surface sediments in five categories of $> 2.00$, 1.01-2.00, 0.51-1.00, 0.25-0.50, and $< 0.25$ (after Premuzic et al., 1982). (Reprinted with permission from *Organic Geochemistry*, 4, 1982, Pergamon Journals Ltd.). **www.icsu-scope.org/.../ scope35/chapter14.html**

# *Autochthonous* vs. *Allochthonous* Organic Matter

- River-borne organic carbon is respired in the ocean.
- Proportion of terrestrial OM declines from coastal and shelf areas to the deep sea: $\delta^{13}C$ of bulk sediment OM (Hedges & Parker, 1976)
- Compound specific $\delta^{13}C$ analysis indicates that terrestrial OM is transported to deep waters as fine-grained, old soil OM (Goñi et al. 1997).
- Total respiration of OC in the ocean >> authochthonous OC production (e.g., NPP), which suggests that the ocean is net heterotrophic.

# Heterotrophic Metabolism: Organic Matter Decomposition

- Suite of microbial metabolic reactions
- Aerobic respiration dominates most Earth surface environments
- Anaerobic metabolism occurs in oxygen-deficient environments

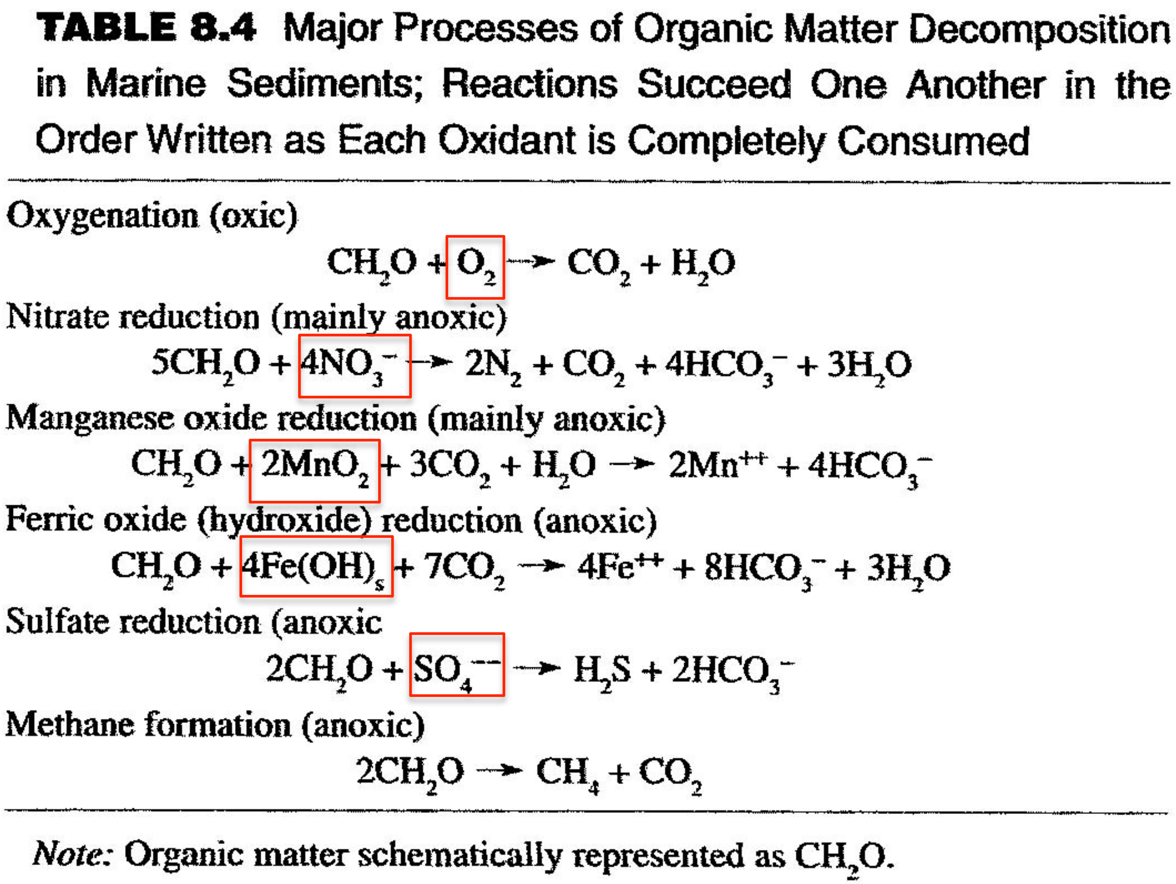


**TABLE 8.4** Major Processes of Organic Matter Decomposition in Marine Sediments; Reactions Succeed One Another in the Order Written as Each Oxidant is Completely Consumed

Oxygenation (oxic)

$$CH_2O + \boxed{O_2} \rightarrow CO_2 + H_2O$$

Nitrate reduction (mainly anoxic)

$$5CH_2O + \boxed{4NO_3^-} \rightarrow 2N_2 + CO_2 + 4HCO_3^- + 3H_2O$$

Manganese oxide reduction (mainly anoxic)

$$CH_2O + \boxed{2MnO_2} + 3CO_2 + H_2O \rightarrow 2Mn^{++} + 4HCO_3^-$$

Ferric oxide (hydroxide) reduction (anoxic)

$$CH_2O + \boxed{4Fe(OH)_s} + 7CO_2 \rightarrow 4Fe^{++} + 8HCO_3^- + 3H_2O$$

Sulfate reduction (anoxic

$$2CH_2O + \boxed{SO_4^{--}} \rightarrow H_2S + 2HCO_3^-$$

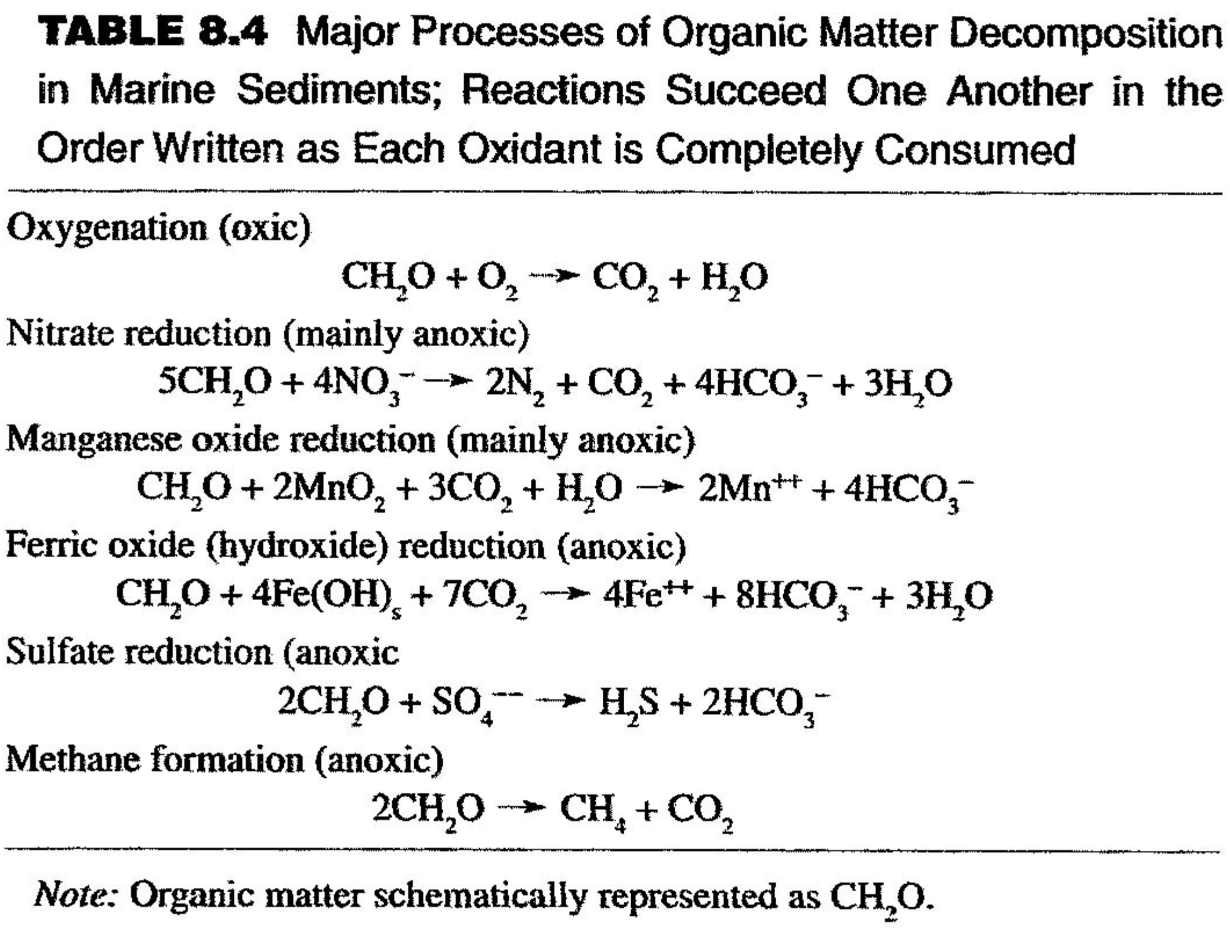
Methane formation (anoxic)

$$2CH_2O \rightarrow CH_4 + CO_2$$

*Note:* Organic matter schematically represented as $CH_2O$.

# Sediment Diagenesis: Organic Matter Respiration

- Suite of biogeochemical reactions that occur after deposition in sediments are called *diagenetic reactions*: *Sediment Diagenesis*.
- Most diagenetic reactions are microbially mediated, following the same hierarchy of respiration reactions seen in soils, lakes and estuaries.



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Methane formation (anoxic)

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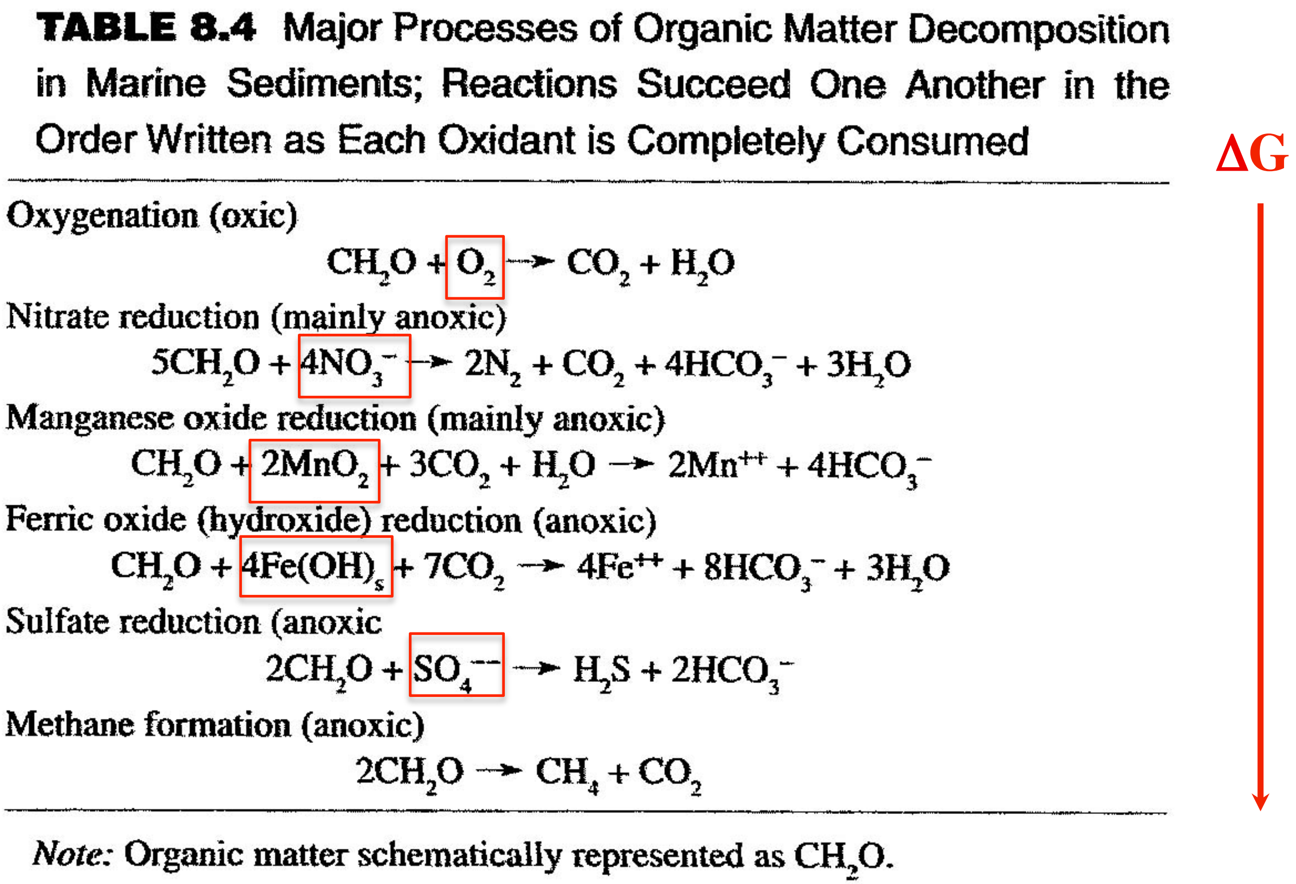
# Why do Metabolic Reactions Occur in Sequence?

- Sequence controlled by free energy yield per mole of organic carbon oxidized by the electron acceptor
- Oxidant that provides the greatest free-energy yield is utilized first; the others occur in sequence as the more favorable oxidant is consumed.



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Methane formation (anoxic)

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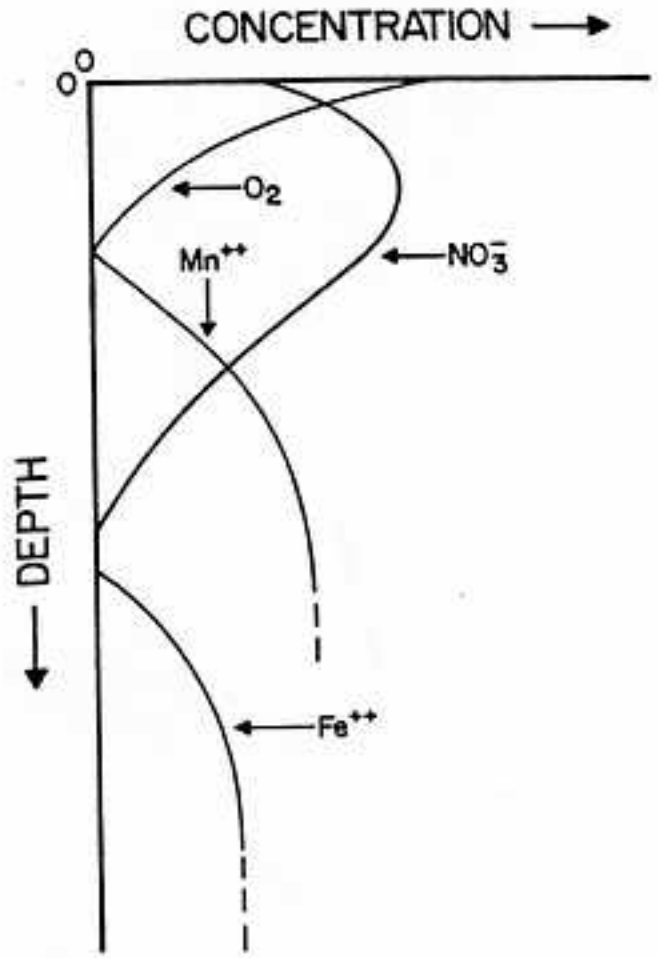
*Note:* Organic matter schematically represented as $CH_2O$.

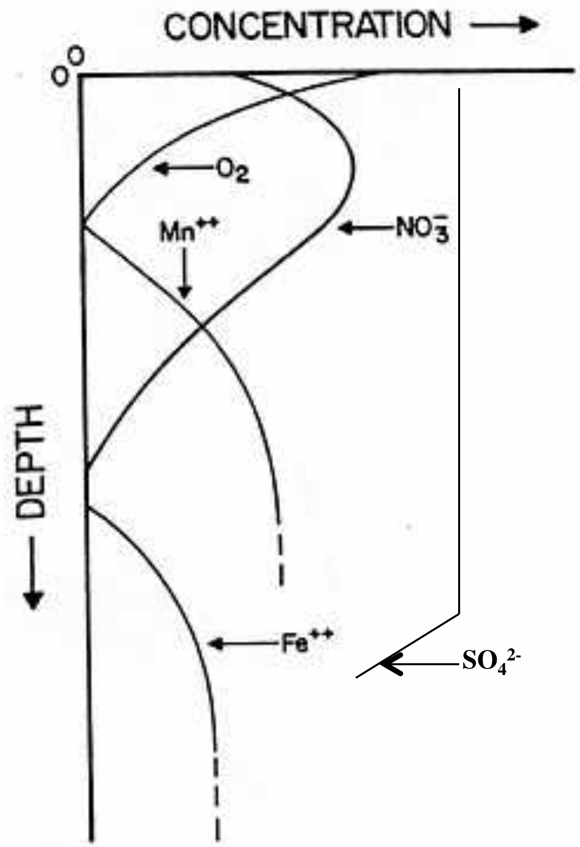
# Sediment Diagenesis: Pore water profiles reflect sequence of microbial respiration reactions



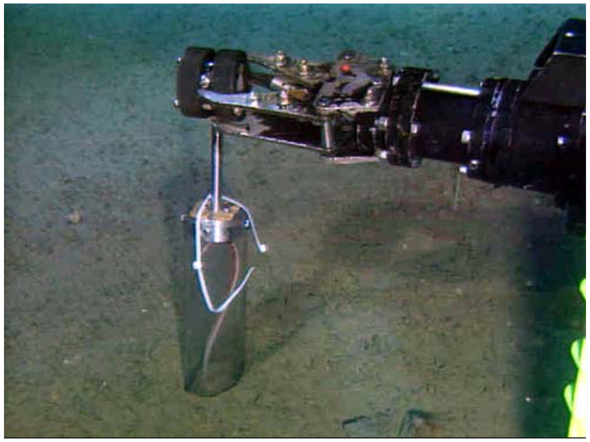
*Froelich et al. 1979*

# Redox Zonation in Sediments Reflects Sequence of Microbial Metabolic Reactions

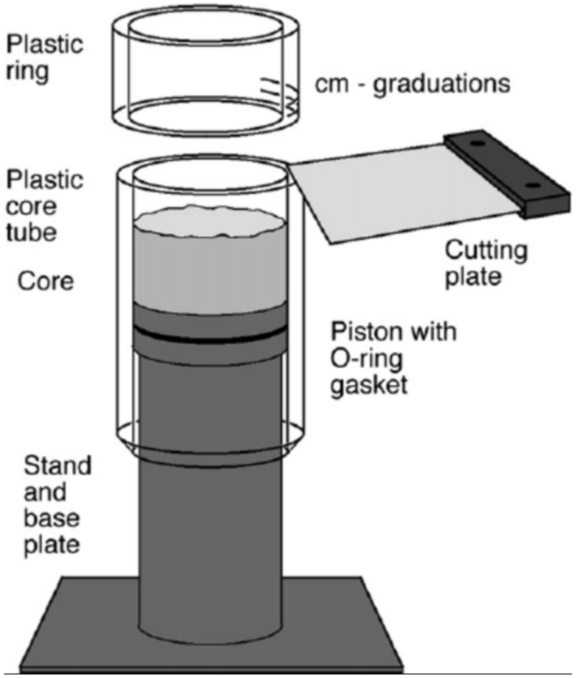
**Pore Water Profiles**



| Zone | Process | Electron Acceptor | $\Delta G°$ (J/mol C) |
|---|---|---|---|
| **Oxic** | Aerobic Respiration | $O_2$ | -471 |
| **Suboxic, Postoxic** | Denitrification | $NO_3^-$ | -444 |
| | Mn-ox reduction | $Mn^{4+}$ | -397 |
| | Fe-ox reduction | $Fe^{3+}$ | -131 |
| **Anoxic** | Sulfate reduction | $SO_4^{2-}$ | -76 |



# Sediment core retrieval, description, sectioning, and archiving



# Sedimentary Diagenesis: Organic Matter Respiration

- ≈14% of sedimentary organic matter (SOM) is oxidized through anaerobic respiration, especially sulfate reduction.

- Sulfate reduction is an important pathway in marine sediment diagenesis because of the high concentrations of $SO_4^{2-}$ in seawater (28 mM).

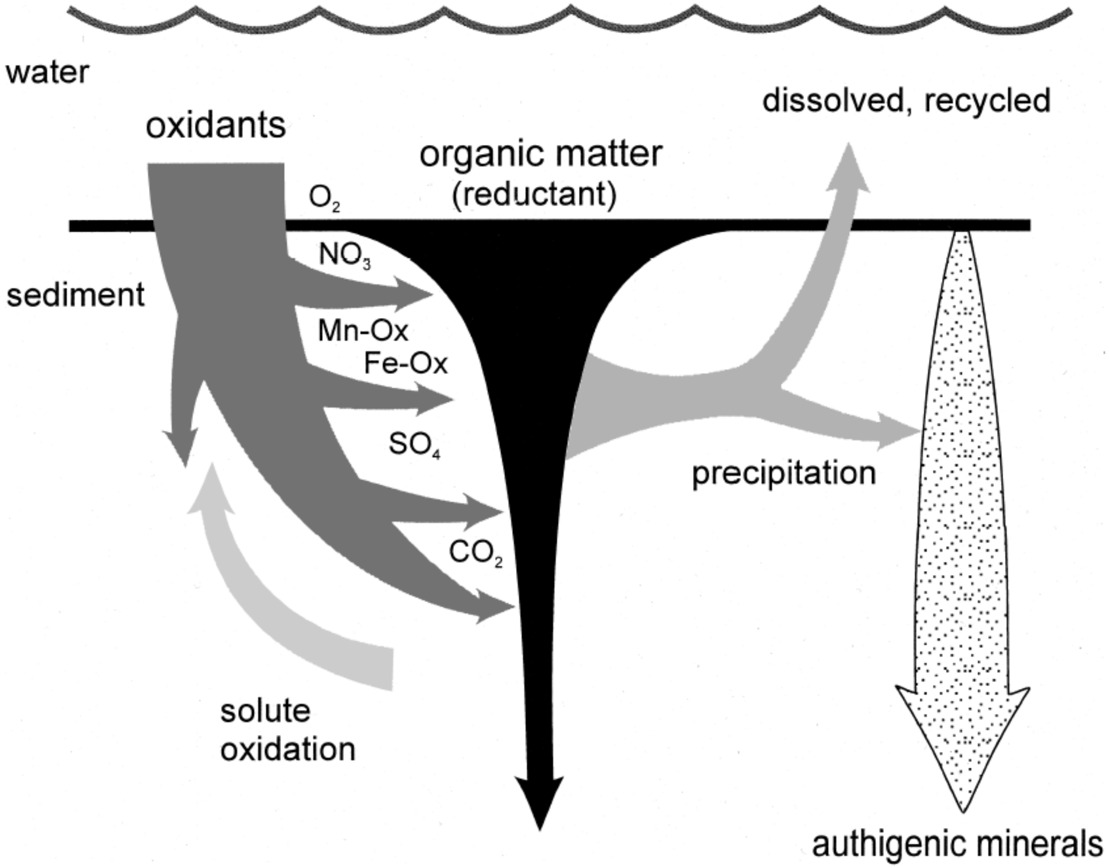
- Sulfate reduction in sediments leads to production of reduced S and pyrite formation:

$$2H^+ + SO_4^{2-} + 2CH_2O \longrightarrow 2CO_2 + H_2S + H_2O \qquad (7.17)$$

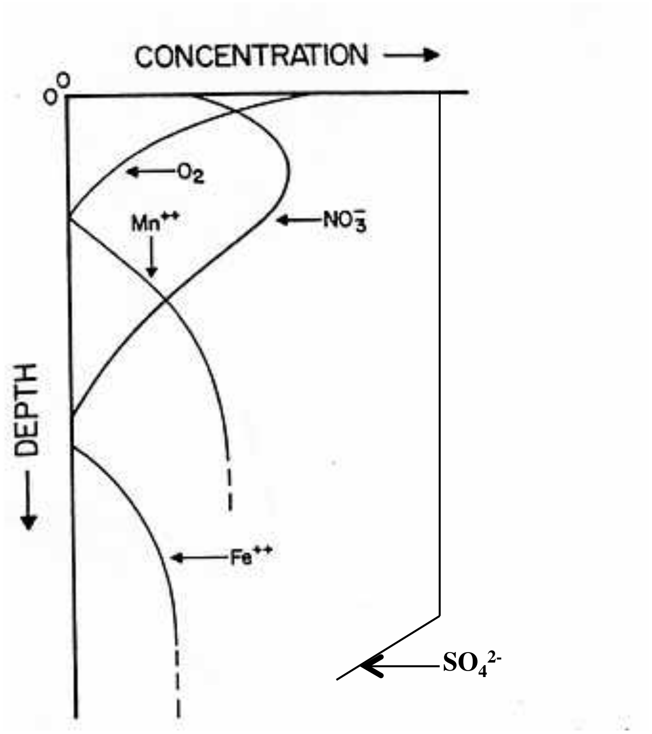
$$2Fe(OH)_3 + 2H_2S + 2H^+ \longrightarrow FeS_2 + 6H_2O + Fe^{2+} \qquad (7.19)$$

- Pyrite formation is often limited by available Fe; excess $H_2S$ escapes to upper layers of sediment where it is re-oxidized to $SO_4^{2-}$.

# Hierarchy of Oxidants Dictates Sequence of Diagenetic Reactions and is reflected in Pore Water and the Solid Phase



*Aller 2004*



*Froelich et al. 1979*

# OM Burial Rate Correlates with Sediment Burial Rate

- $SO_4$ reduction in near shore sediments >>> pelagic sediments
  - NPP in overlying water is high
  - Flux of OM to sediments is high.
  - Burial of OM is rapid due to high sedimentation rates

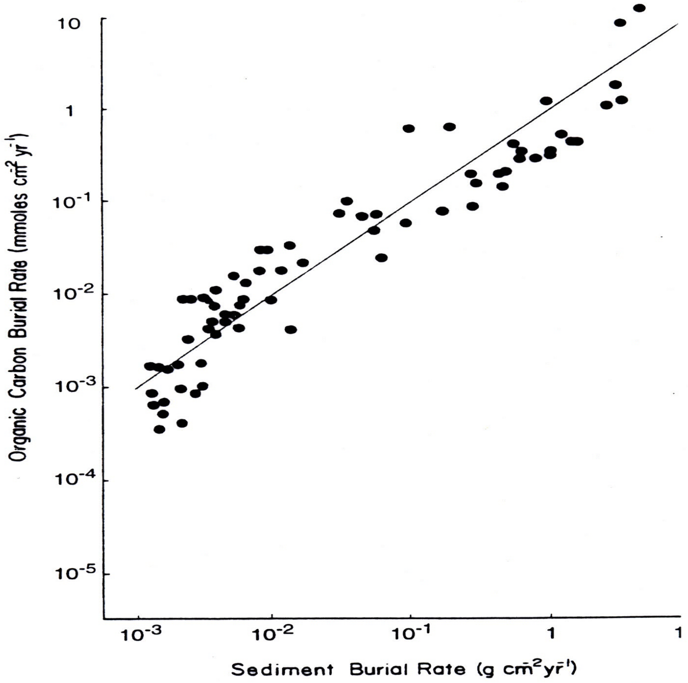
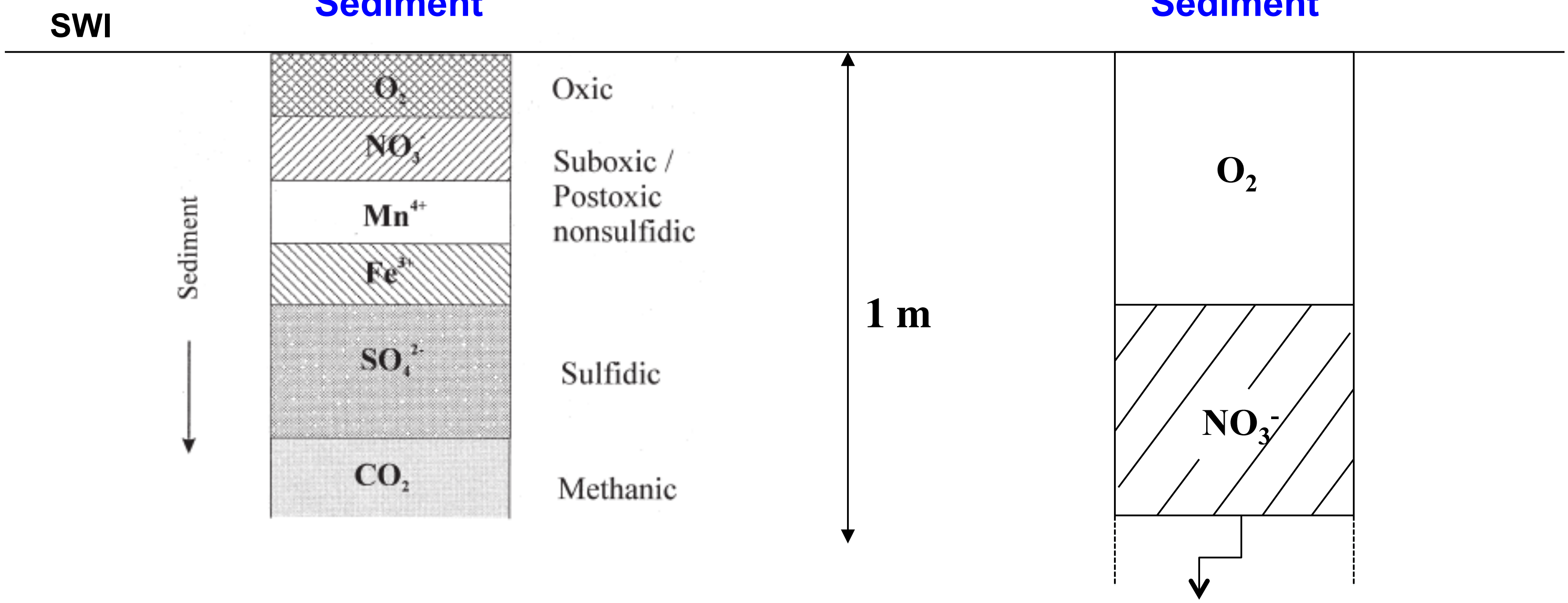


**Figure 9.9** Burial of organic carbon in marine sediments as a function of the overall rate of sedimentation. From Berner and Canfield (1989).

# Lability and Quantity of OM is Primary Driver of Vertical Distribution of Redox Zones in Sediments



- Rate of consumption of oxidants in nearshore sediments >>> rate in pelagic sediments
  - Slower sediment accumulation rate in pelagic sediments
  - Lower flux of OM to pelagic sediments
  - Lower reactivity of OM at SWI in pelagic sediments

# Long-Term Burial of OM and Pyrite

- Permanent burial of reduced compounds (OC, $FeS_2$) results in release of $O_2$ to the atmosphere.

$$CO_2 + H_2O \longrightarrow CH_2O + O_2$$

$$8FeO + 16CH_2O + 16\,SO_4^{2-} \longrightarrow \underset{\downarrow}{8FeS_2} + 16HCO_3^- + 8H_2O + 15O_2$$

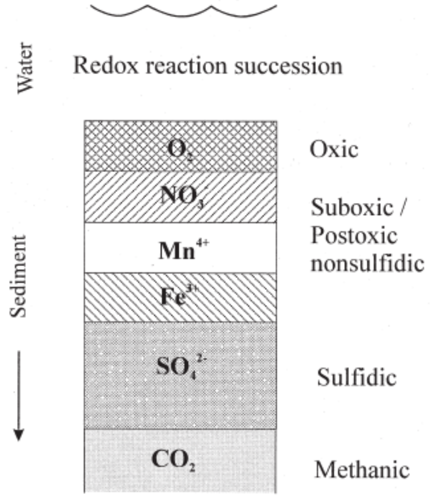
- Over geologic time, $FeS_2$ burial may account for ≈20% of the $O_2$ in the atmosphere.

- Atmospheric $O_2$ levels are regulated by burial of reduced substances throughout geologic time (The Walker *Negative Feedback*, J.C.G. Walker, 1980).

  - During periods of rapid continental uplift, erosion and sedimentation, large quantities of OM were buried, and atmospheric $O_2$ increased.

  - Rising atmospheric $O_2$ increased aerobic decomposition of organic matter, consuming $O_2$ and preventing further increases in atmospheric $O_2$.

# Locus of Methanogenesis in Marine Sediments and its Fate



- The zone of methanogenesis underlies the zone of sulfate reduction.
  - Sulfate reducing bacteria out-compete methanogens for reduced C substrates.
- Because the oceans have high $SO_4^{2-}$ concentrations (28 mM), methanogenesis is uncommon.
- Most methane released from sediments is oxidized in the water column, and never makes it to the surface ocean.
- Methane flux to the atmosphere from the oceans is <10 x $10^{12}$ g/yr
  - by comparison, anthropogenic activity releases 376 x $10^{12}$ g/yr

# Sediment Diagenesis: Biogenic Carbonates

- Many marine organisms precipitate carbonate as skeletal and protective tissues via the reaction:

$$Ca^{2+} + 2HCO_3^- \longrightarrow \underset{\downarrow}{CaCO_3\,(s)} + H_2O + CO_2 \qquad (9.2)$$

- foraminifera, pteropods, other small zooplankton
- coccolithophores, marine algae

- The deep ocean accumulates $CO_2$ produced from degradation of POM that sinks from surface waters, and is supersaturated with respect to $CO_2$ because it is isolated from the surface.

- $CO_2$ is more soluble at low T and high P of the deep ocean.

- High $CO_2$ makes the deep ocean undersaturated with respect to $CaCO_3$ due to the formation of carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \qquad (9.3)$$

# Corrosion of Biogenic Carbonates in Deep Waters

- When the skeletal remains of $CaCO_3$-producing organisms sink to the deep sea, they dissolve:

$$CaCO_3\,(s) + H_2CO_3 \longrightarrow Ca^{2+} + 2HCO_3^- \qquad (9.4)$$

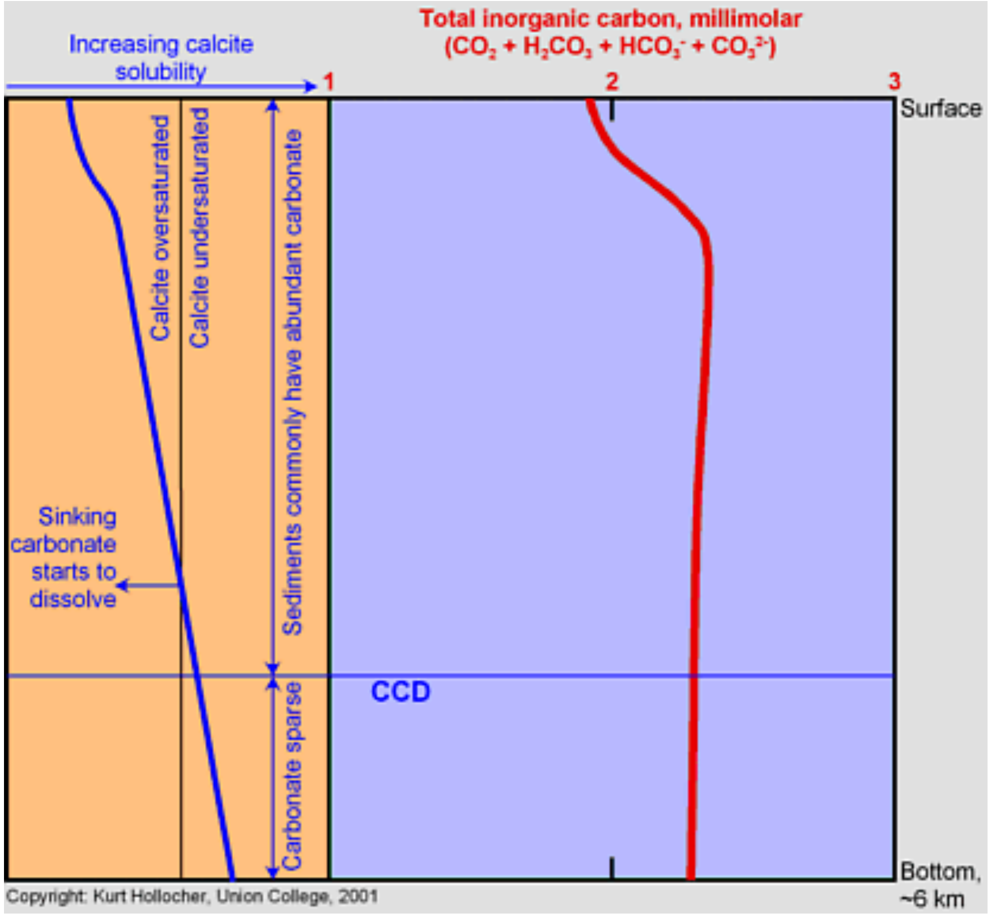
- *Lysocline* = depth at which dissolution begins, increasing alkalinity

- *Carbonate compensation depth (CCD) =* depth below which carbonate dissolution is complete

  - CCD occurs at ≈ 4200-4500 m in the Pacific

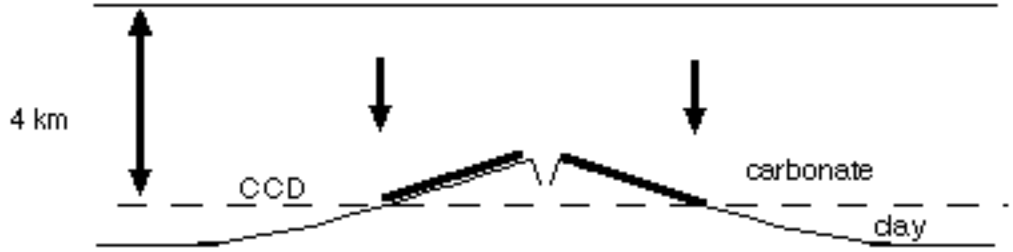
  - CCD occurs at ≈ 5000 m in the Atlantic

  - shallower CCD in the Pacific is due to its older age, having had a longer time to accumulate $CO_2$ from oxidized OM.



www.union.edu/.../ kth/illustrations_page.htm

- Aragonite (an alternate form of $CaCO_3$) dissolves more easily and at shallower depths than does calcite.
- Little dolomite (Ca, Mg)$CO_3$ forms in the modern ocean due to inhibition by $SO_4^{2-}$.
- Dolomite does form below the zone of sulfate reduction, where $HCO_3^-$ is high and $SO_4^{2-}$ is low.
- Dolomite was an important $Mg^{2+}$ sink in geologic past.



http://www.ic.ucsc.edu/~eart1/Notes/Lec6.html

**Calcite compensation depth (CCD) -level below which there is no carbonate accumulation (preservation)**

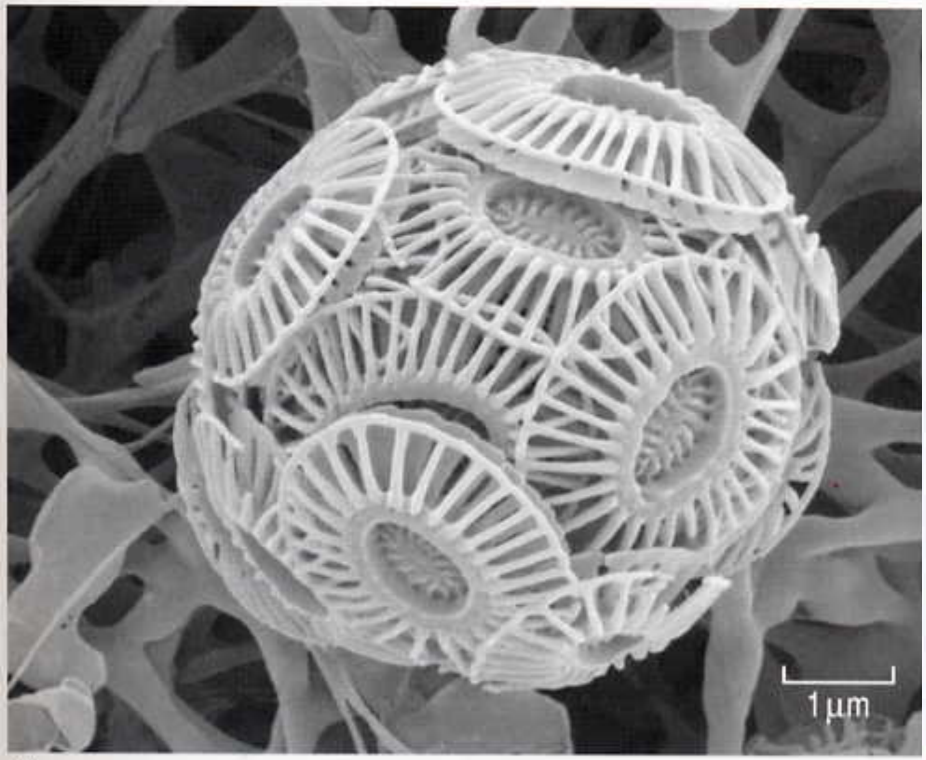


Fig 1.5 (a) Coccosphere of the coccolithophore *Emiliania huxleyi*. These algae are responsible for a large amount of $CaCO_3$ deposited on the sea floor of the open ocean -- coccolith oozes.

Fig 1.5 (b) Satellite image of a coccolithophore (*Emiliania huxleyi*) bloom in the English Channel off the south coast of Cornwall, 24 July 1999.

# Planktonic Foraminiferans

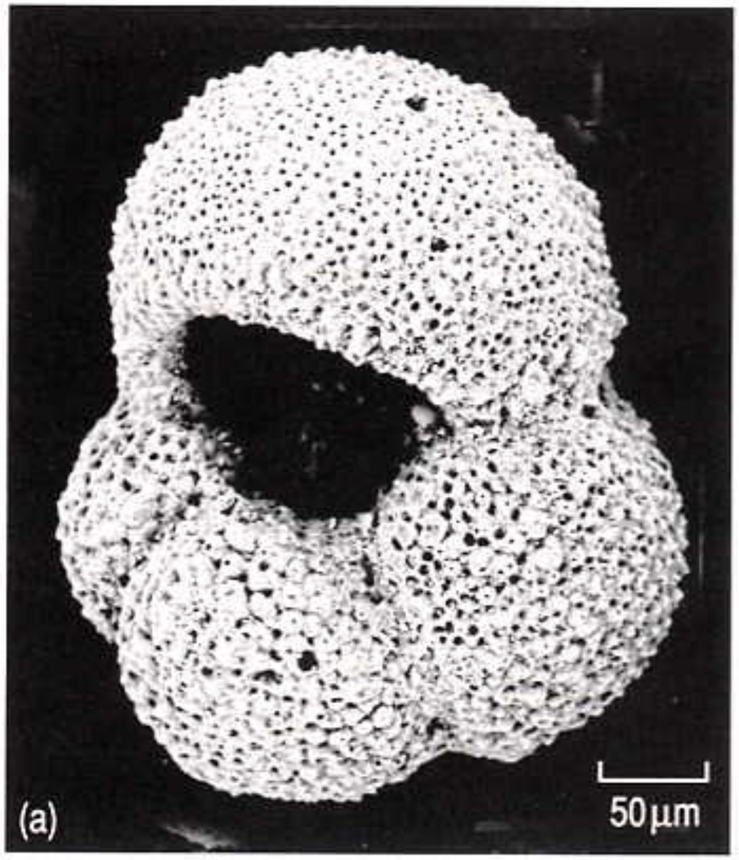


Fig 1.6 (a) *Globigerina bulloides*. This species is mainly found in subpolar waters, and also in regions of upwelling. The calcite skeleton consists of four spherical chambers, and has an open, arched aperture.

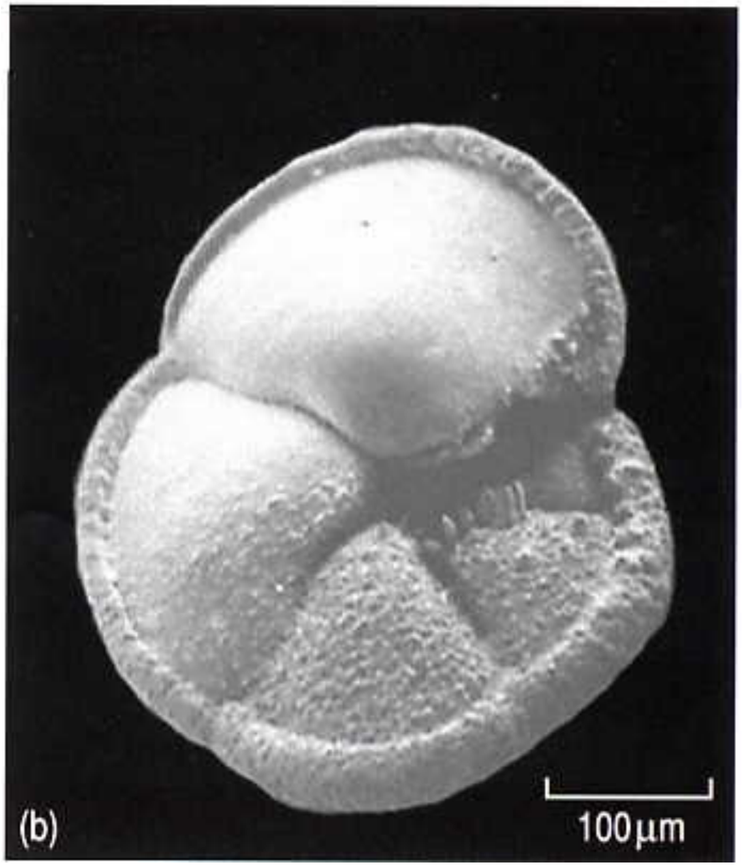


Fig 1.6 (b) *Globorotalia menardii*. This species is mainly found in subtropical waters. The calcite skeleton consists of five or six wedge-shaped chambers, and has a prominent outer crust known as a ‘keel’.

# Living Pteropod Molluscs

Fig 1.7 (a) *Candida atlanta*. This marine snail has a transparent shell, and paired muscular swimming wings protrude from its body.

Fig 1.7 (b) Venus slipper {*Cymbula* sp.). The Venus slipper lacks a true shell; instead, it has an internal skeletal structure. Like all pteropods, it swims by means of the paired wings that can clearly be seen on either side

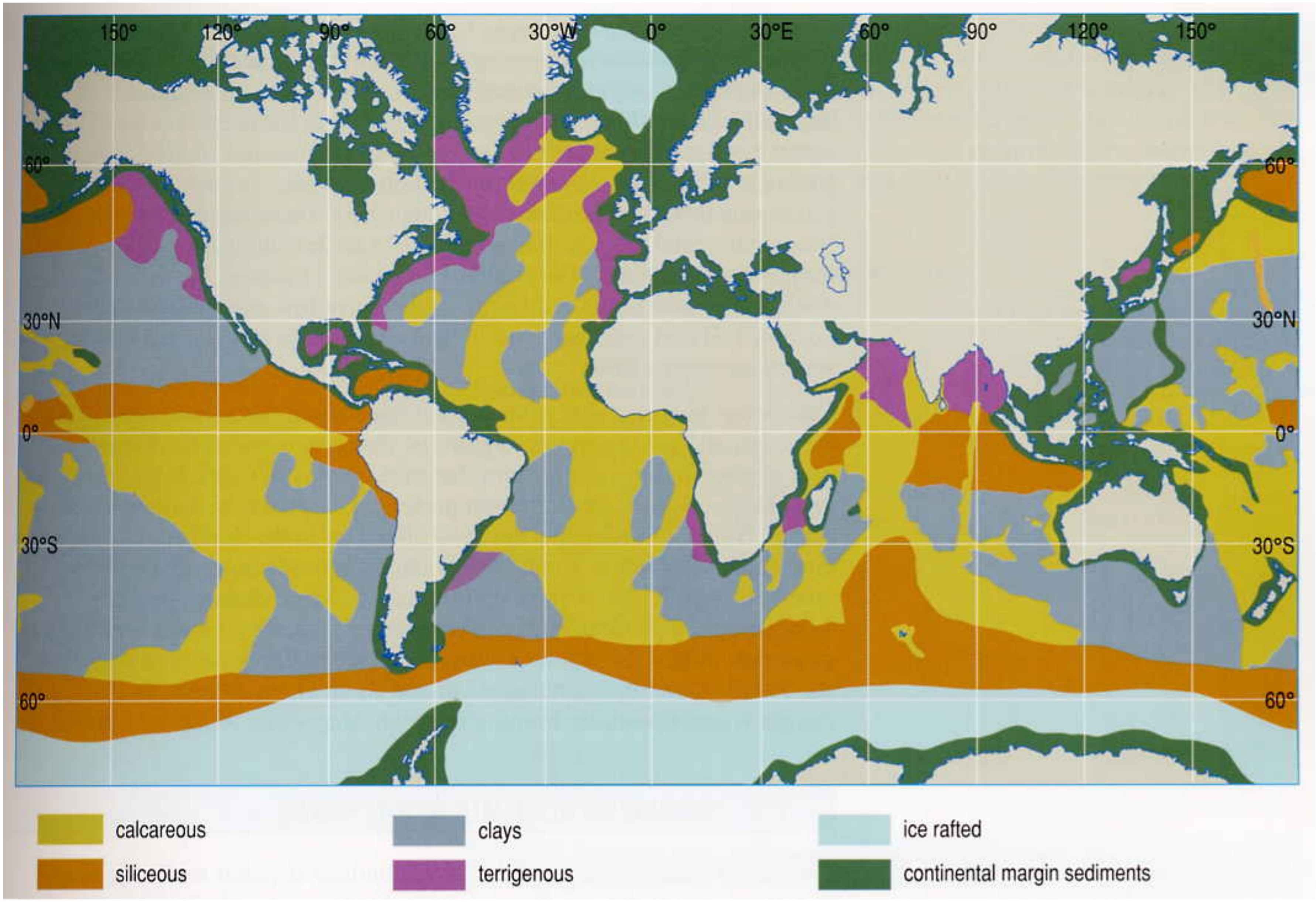
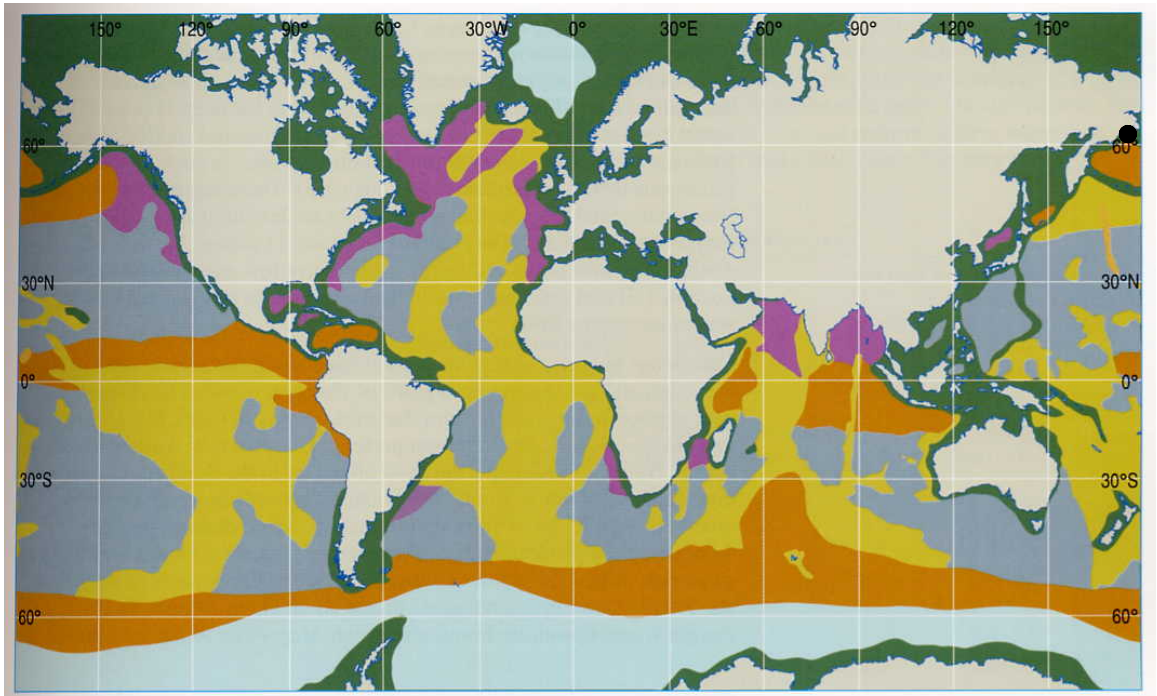


Fig 1.12 Distribution of dominant sediment types on the floor of the present-day oceans. Note that clays are mostly ‘terrigenous’. (Open University Series, Marine Biogeochemical Cycles)

# Relationship between distribution of sediment type and sea floor physiography



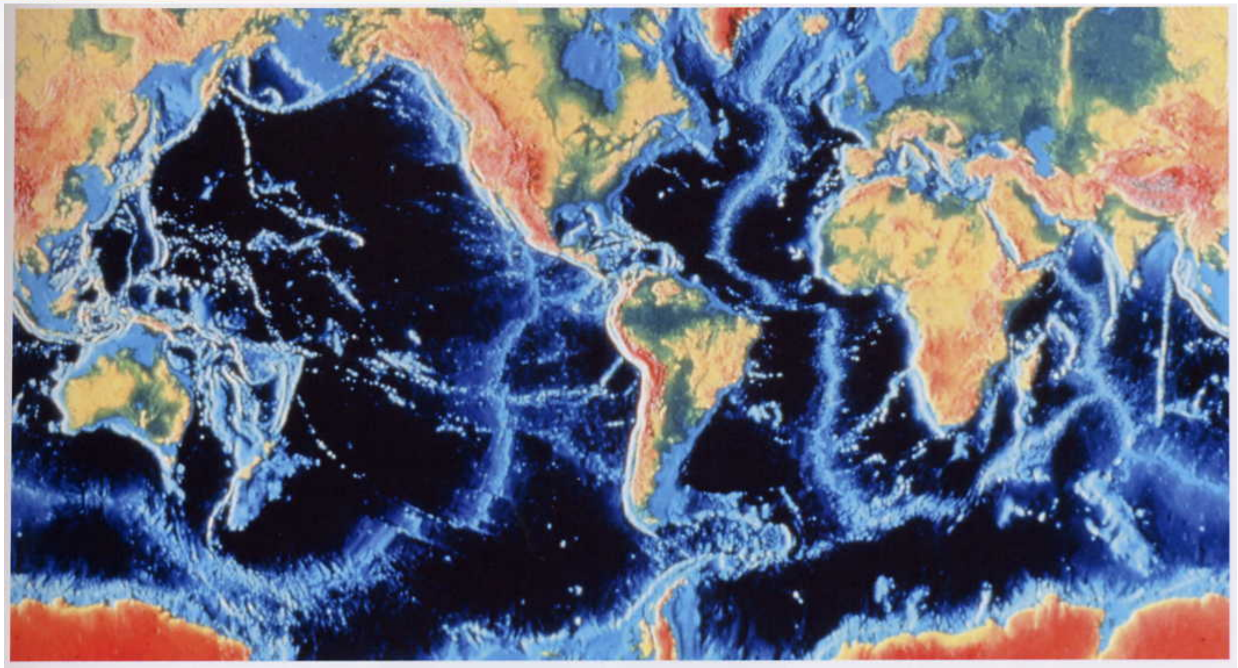
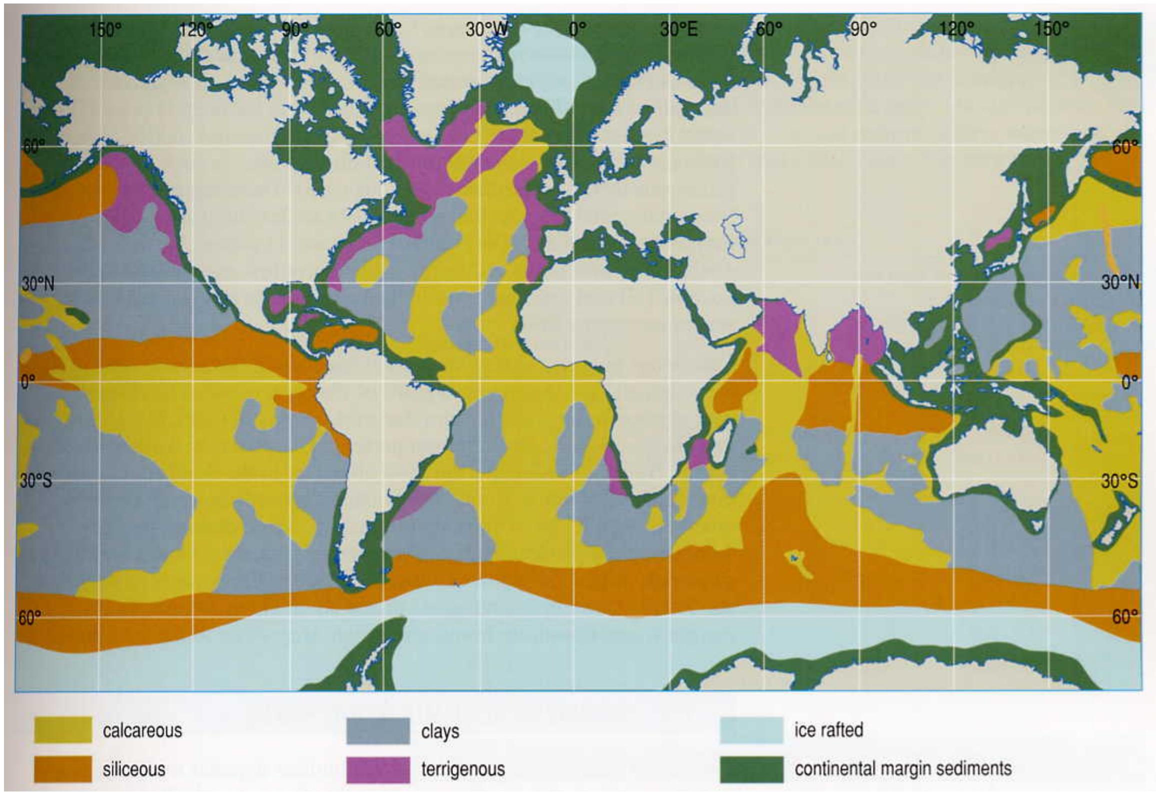


Fig 1.13 Physiography of oceanic basins, deeper blue = deeper water.



- Calcareous sediment dominates along oceanic ridges
- Shallowest regions of the oceans

- Carbonates are restricted to shallow waters:
  - More biogenic rain
  - Chemistry of waters at shallow depths
  - Distance from continental margins (minimal dilution)
- Siliceous sediments: Southern Ocean and upwelling regions

# Global ocean biogenic $CaCO_3$ sediment distribution and the Ca budget

- Calcareous sediments found only in shallow ocean basins where conditions minimize dissolution

- No $CaCO_3$ present over much of the abyssal plains (depths > 4500 m)

- $CaCO_3$ production in surface waters ≈ $5.3 \times 10^{15}$ g/yr

- $CaCO_3$ preserved in shallow calcareous sediments ≈ $3.2 \times 10^{15}$ g/yr

- Burial of Ca exceeds riverine supply, implying that the Ca budget in the ocean today is not at steady state.

# Summary

- Global NPP patterns follow nutrient distributions in the ocean.

- Most NPP is respired by bacteria, vs. consumed by zooplankton.

- Most NPP is recycled in surface waters, only a small amount is exported below the thermocline, and an even smaller fraction is buried in sediments.

- Thermodynamic hierarchy of redox reactions in marine sediments; $SO_4$ reduction is more important than in freshwater and terrestrial systems

- Burial of reduced substances (S and C) has had an important impact on atmospheric $O_2$ over geologic time.

- Carbonate distribution in ocean sediments is controlled by production and solubility, as are the resultant depths of the lysocline and CCD.