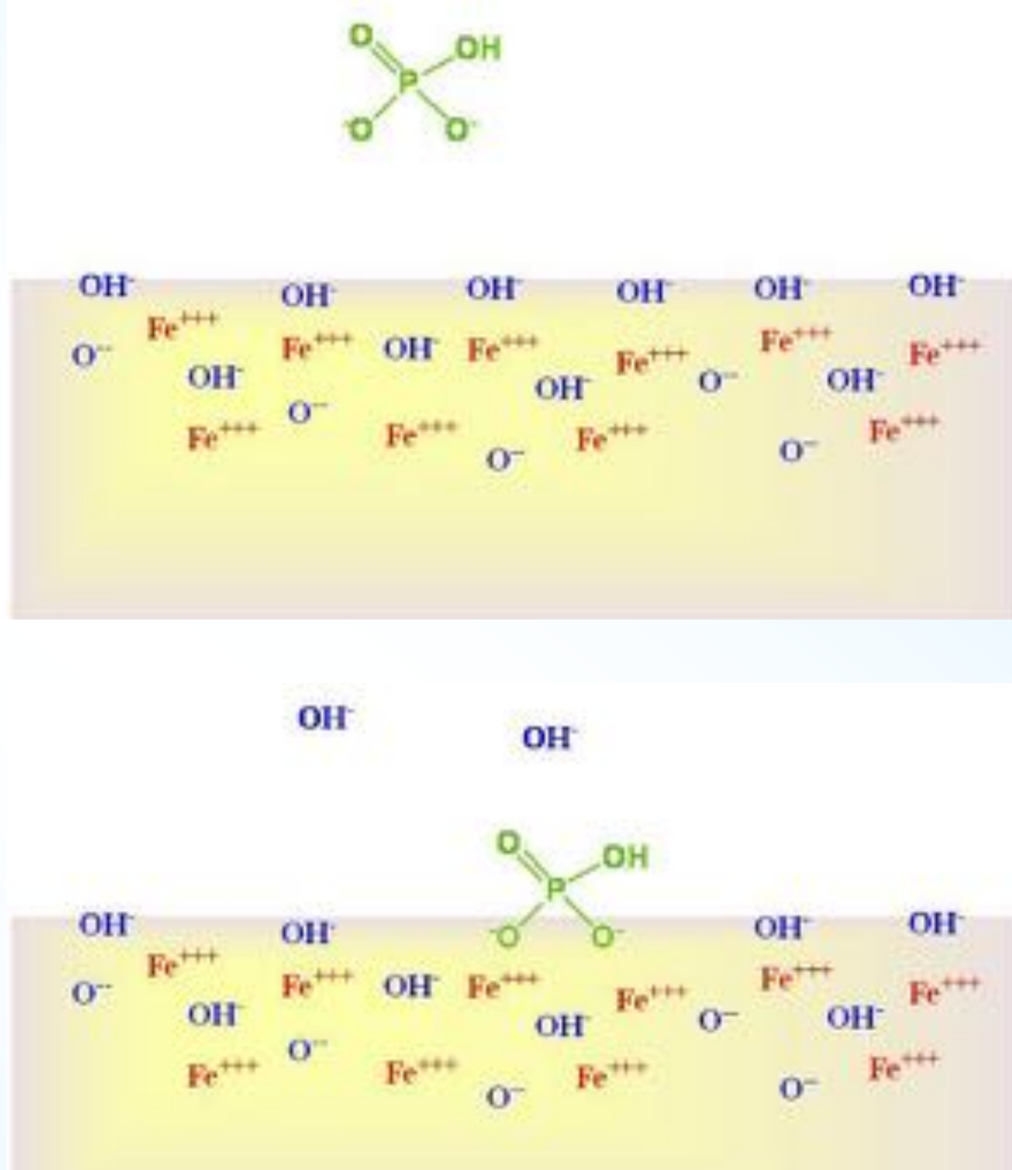
from last time…

- Iron (oxy)hydroxide binding phosphate
  - *Phosphate (HPO_4^{2-}) dissolved in seawater*
  - *Granular ferric oxide surface*
  - *Two ionic bonds at surface, displacing hydroxide*
  - *What about other ions?*



from last time…

- Fe-S-O-P recap
  - Phosphate release during respiration
  - Mineralization or sorption onto labile ferric oxyhydroxides
  - Reductive dissolution releases phosphate
  - Can lead to elevated bioavailable P levels in overlying water

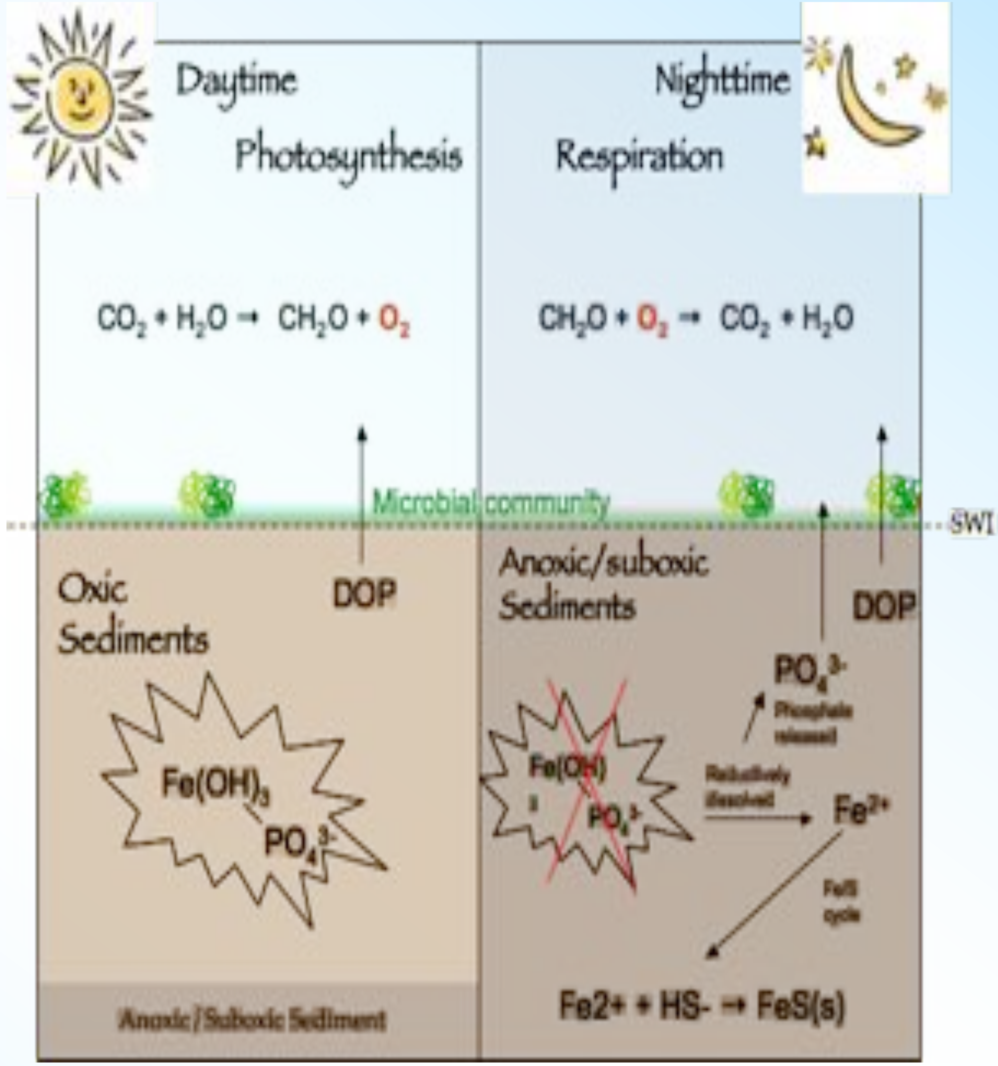


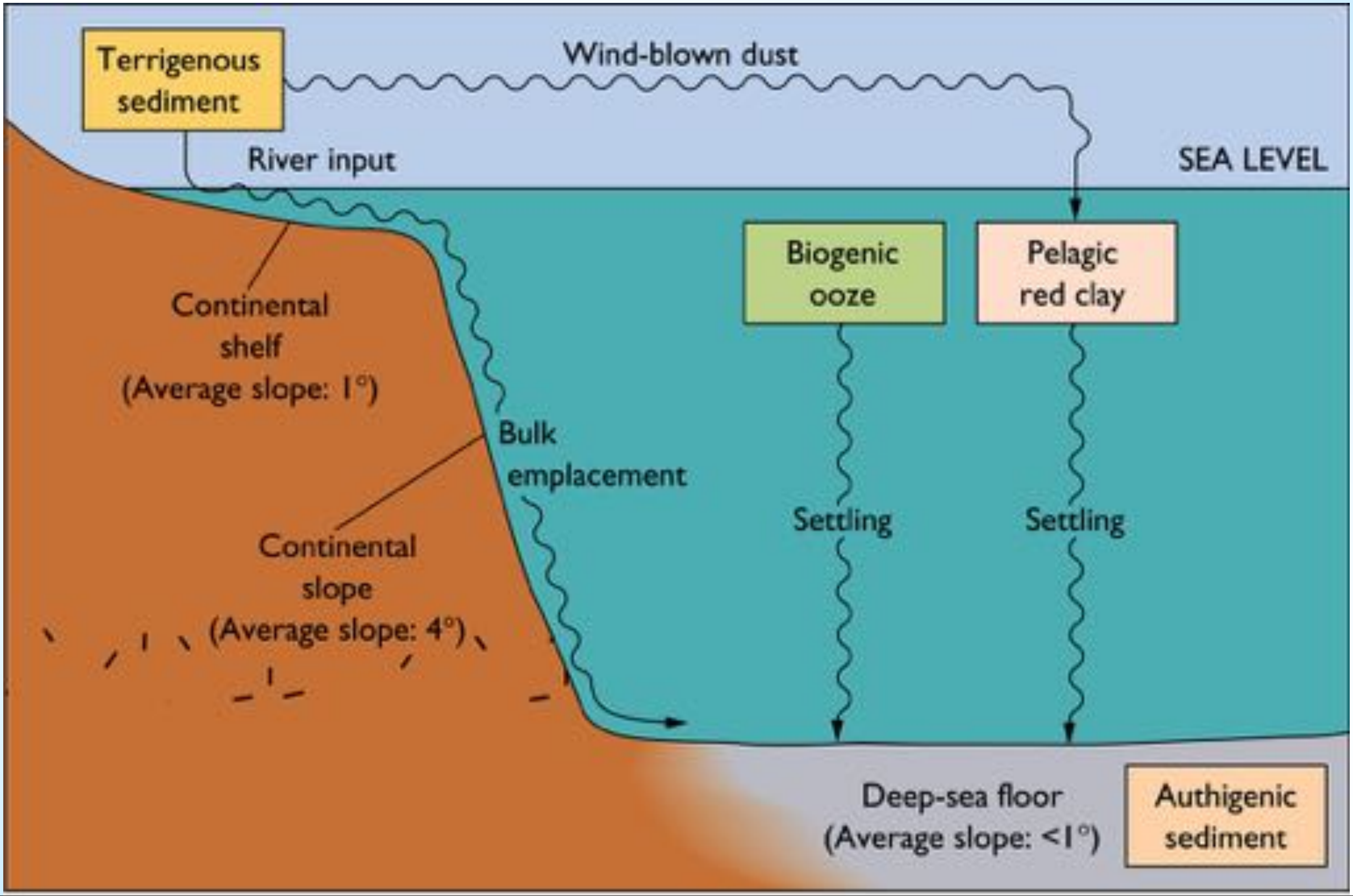
Figure 1: Proposed diel (day-night) trapping or release of porewater phosphate, DOP, and iron as a consequence of diurnal shifts between benthic photosynthesis and respiration.

Biogenic Production, Carbonate Saturation and Sediment Distributions

OCN 623 – Chemical Oceanography

Reading: Libes, Chapters 15 and 16

I. Deep Sea Sedimentation



Major Sediment Types:

Detrital ***Authigenic*** ***Biogenic***

1. Detrital Sediments

- Most voluminous component
- From chemical or mechanical weathering of continental material
- Typically occur as aluminosilicates
- Transported by rivers, wind, volcanoes,
- Accumulate most rapidly near continental margins
- Deep-sea detrital sediment is predominantly ***red clay***

Red Clay…

- ***Red clay*** (brown clay or pelagic clay) consists of very fine, weathered particles of (mostly) wind-blown terrigenous clays and extraterrestrial dust.

  - Accounts for 38% of deep-sea sediments

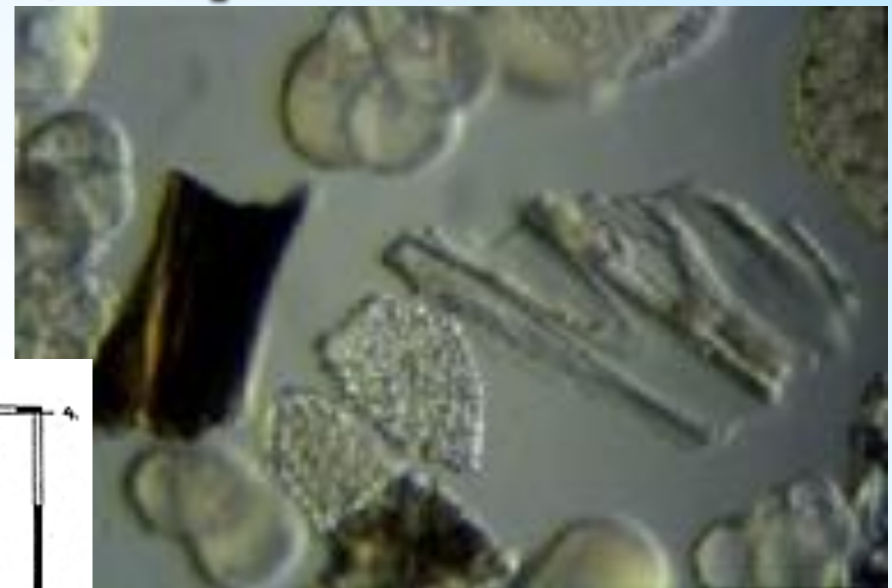
- Clay composition is climate-controlled, consisting mainly of ***kaolinite*** in the tropics and subtropics and ***chlorite*** in the polar and subpolar regions

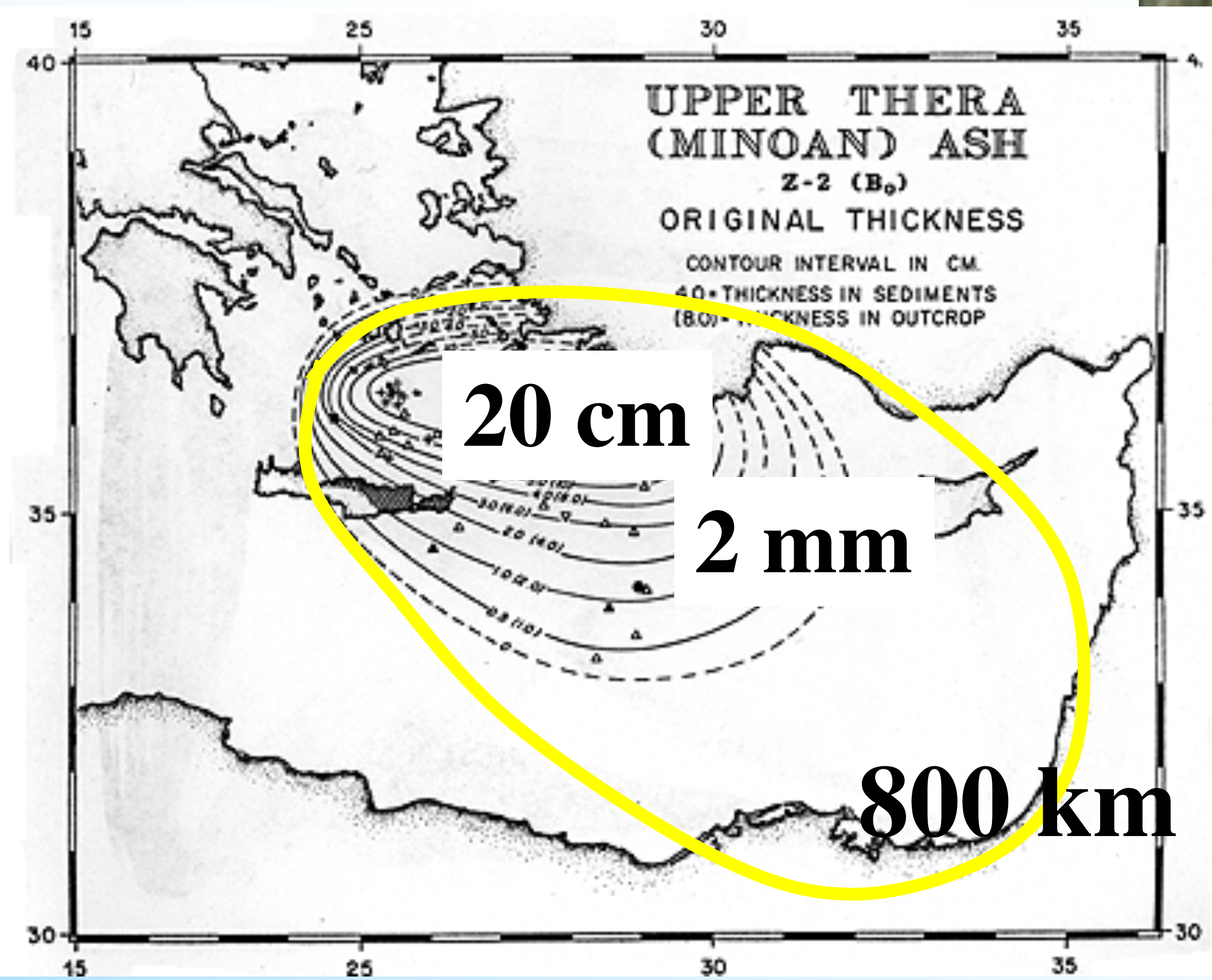
Detrital Aluminsolicates

Table 2-1. Mineralogy of alumino-silicate detritus transported from the continents into the sea via rivers and air.

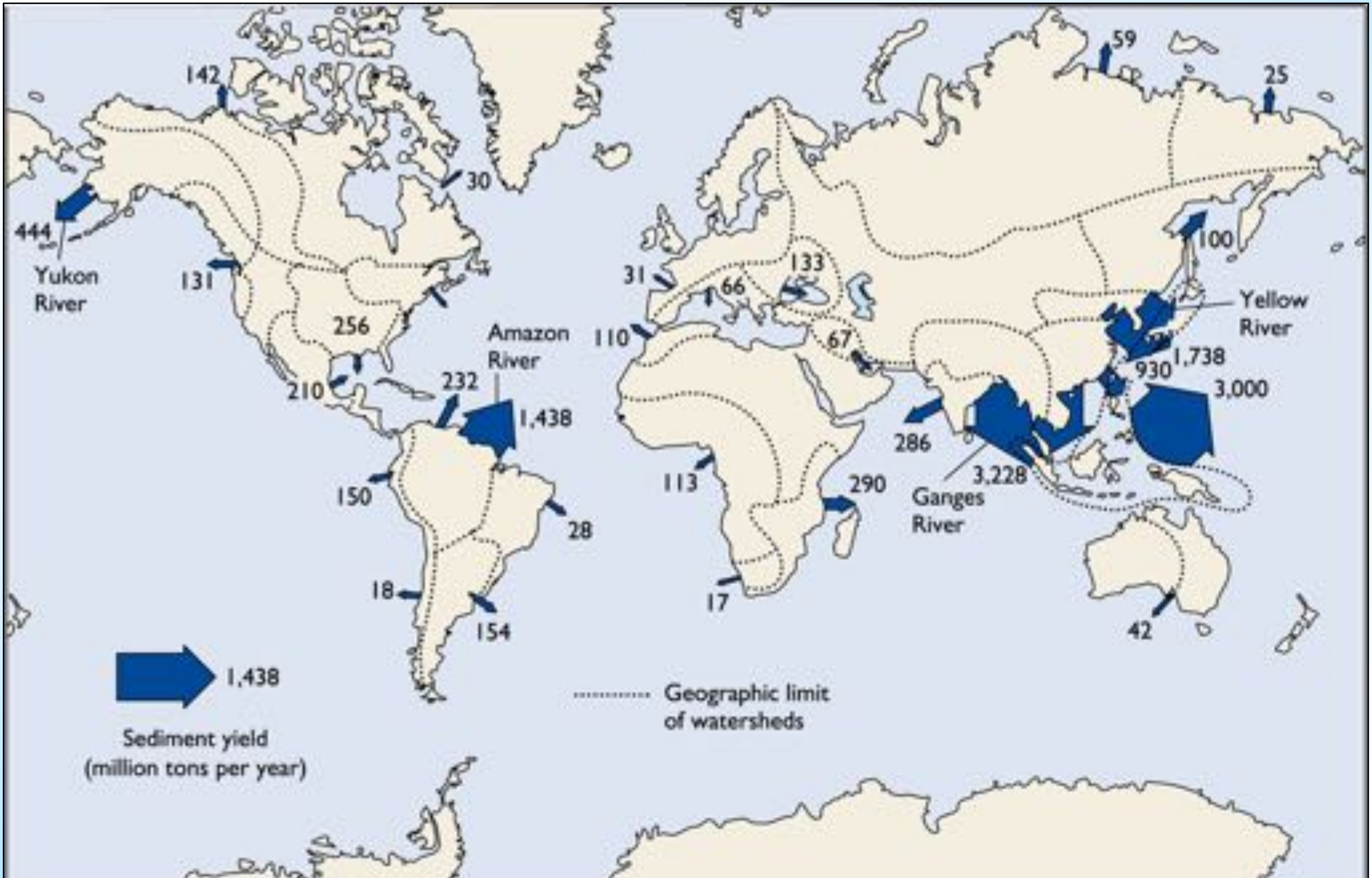
Mineral	Chemical Composition
Quartz	SiO_2
Orthoclase	$KAlSi_3O_8$
Plagioclase	$xNaAlSi_3O_8 + (1-x)CaAl_2Si_2O_8$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Illite	$KAl_3Si_3O_{10}(OH)_2$
Smectite	$Al_2Si_4O_{10}(OH)_2.xH_2O$
Chlorite	$(Mg,Fe,Al)_6(Al,Si)_4O_{10}(OH)_8$
Vermiculite	$Mg_3Si_4O_{10}(OH)_2 \cdot xH_2O$

Volcanic ash, tephra



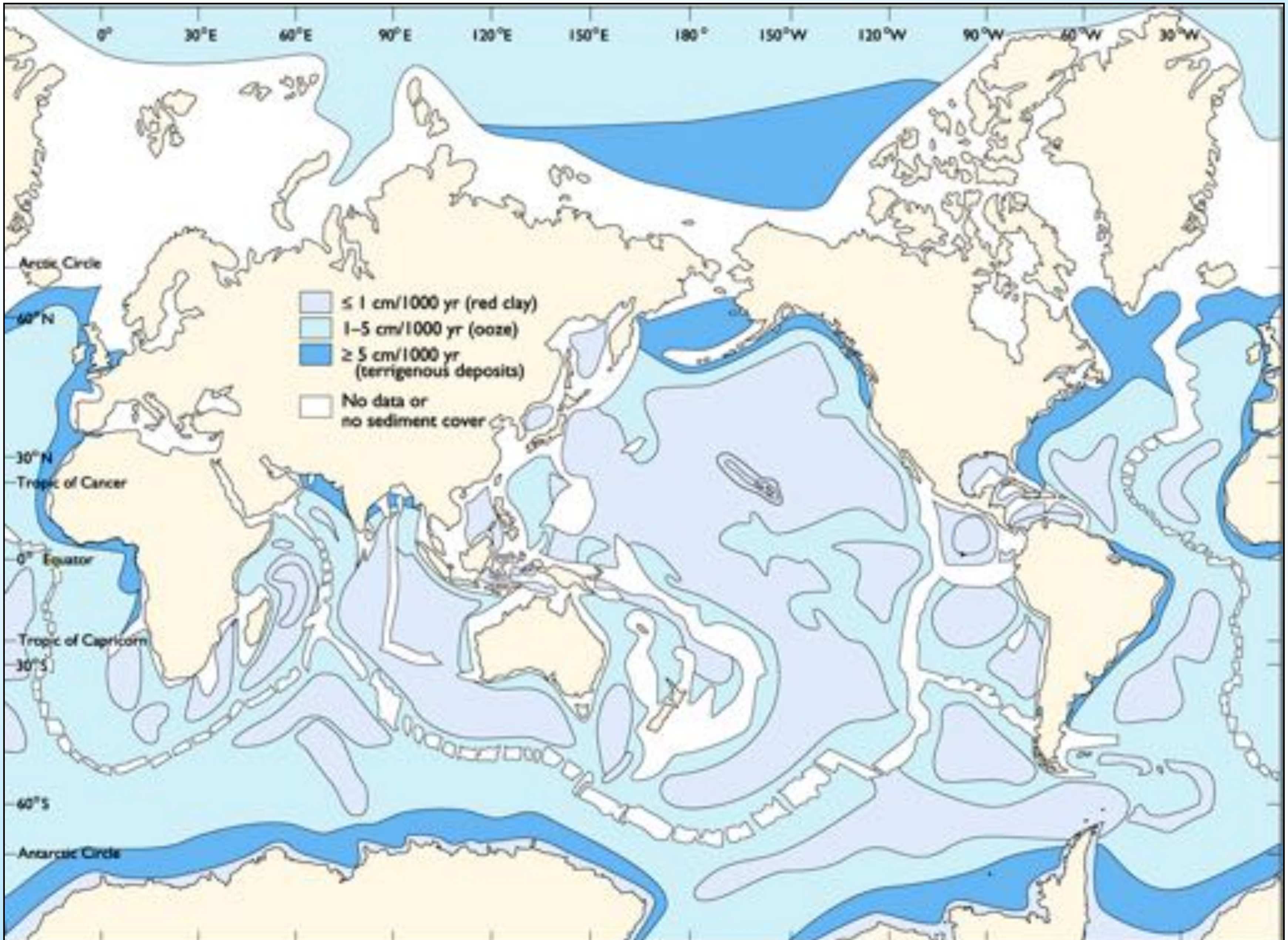


Riverine Sediment Inputs



(b) RIVER INPUT OF SILT TO OCEANS

Sediment Deposition Rates

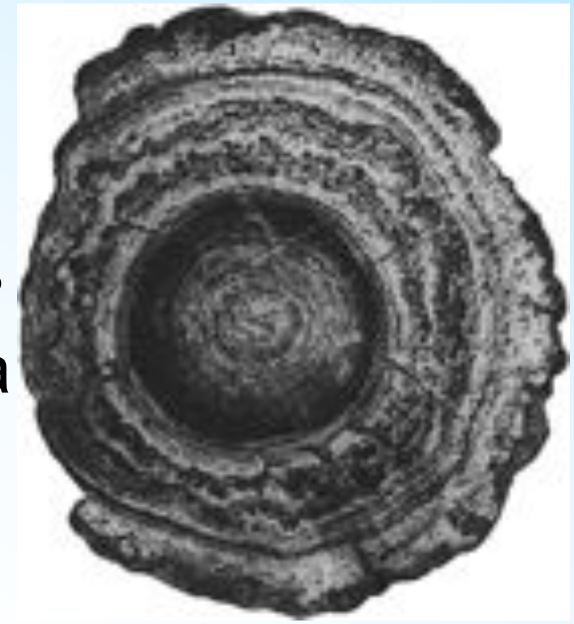


(b) SEDIMENTATION RATES

2. Authigenic Sediments

- Formed by crystallization within sediment or water column (latter referred to as *hydrogenous*)
- Fe-Mn oxides are the most important
- Make up small fraction of total sediment
- Form through reduction of metals in sediment column coupled with upward diffusion to oxic waters where they precipitate
- Also produced by hydrothermal activity

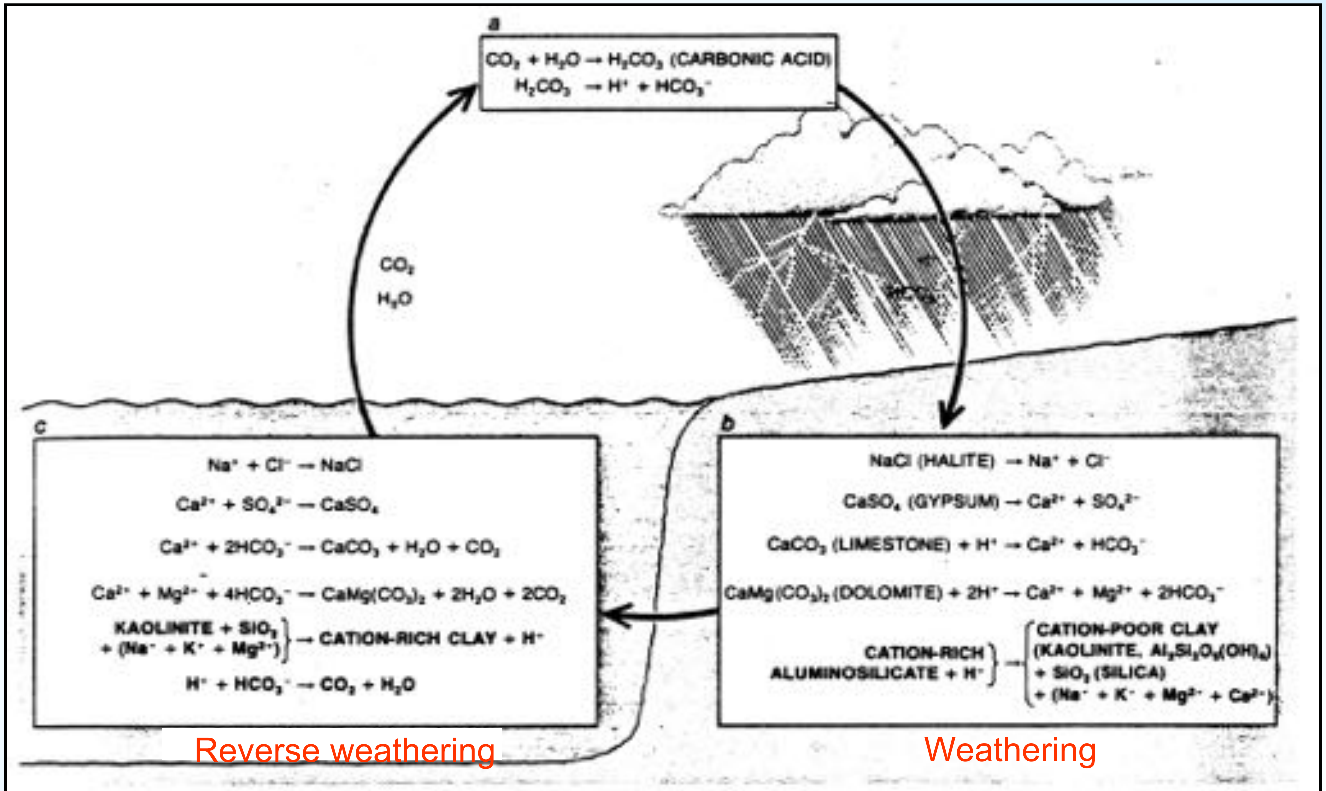
Major Authigenic Sediments



- **Ferromanganese nodules**
  - Deep-sea deposits
  - Concentric layers of metallic compounds
  - Precipitated by a combination of bacteria foraminifera, and inorganic chemical reactions

- **Phosphorites**
  - Continental shelf P-rich deposit
    - *Apatite* = $Ca_5(PO_4)_3(OH,F,Cl)$
  - Formed where upwelling of nutrient-rich water generates high biological productivity
  - Results from high sediment concentrations of P-rich organic debris

Review of reverse weathering



CHEMICAL BALANCE between the atmosphere, the continents and the oceans was hypothesized in the 1950's by Lars Gunnar Sillén of the Royal Institute of Technology in Stockholm and worked out in detail by Frederick T. Mackenzie and Robert M. Garrels of Northwestern University. In the atmosphere (*a*) carbon dioxide is dissolved in water vapor as carbonic acid. The water rains or snows on the continents (*b*), where hydrogen ions from the acid solution leach cations (positive ions) such as calcium, magnesium, sodium and potassium out of the continental rocks. Rivers carry the results of the continental weathering to the oceans (*c*). In the oceans, which are poor in hydrogen ions, the reactions reverse, creating sedimentary rock rich in cations and restoring carbon dioxide to the atmosphere.

Silica + degraded aluminous clays + iron oxide + organic carbon + soluble cations + bicarbonate

↓

New clay material + Carbon dioxide + water

3. Biogenic Sediments

- Produced from hard parts of plankton (plant/animal) in surface ocean
- Soft tissue residues are rarely important, yet a good correlation exists between sediment accumulation rate and sediment OC %

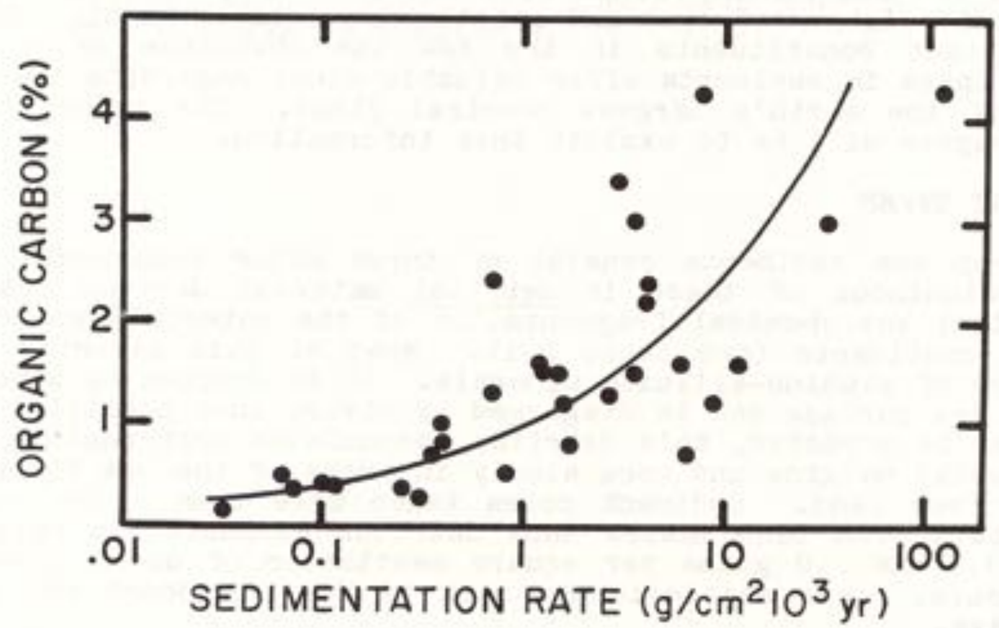


Figure 2-1. Organic carbon content of marine sediments as a function of bulk sediment accumulation rate. Results summarized by Ross Heath and his colleagues (531).

Composition of Biogenic Sediments

Biogenic oozes are fine-grained sediments -- at least 30% is shells of micro-organisms

Classified by their composition:

A. ***Calcareous oozes*** consist of the $CaCO_3$ shells of:

Foraminifera (animals, protozoa)

Pteropods (planktonic gastropods)

Coccoliths (algae)

Ostraracods (planktonic crustaceans)

- Pteropod shells are made of ***aragonite*** (more soluble), others are made of ***calcite***
- Calcareous oozes account for about 48% of deep-sea sediment

B. ***Siliceous oozes*** consist of the shells of:

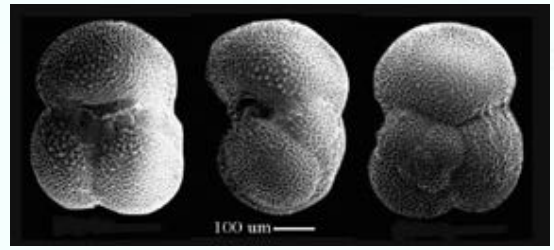
Radiolarians (protozoa)

Diatoms (algae)

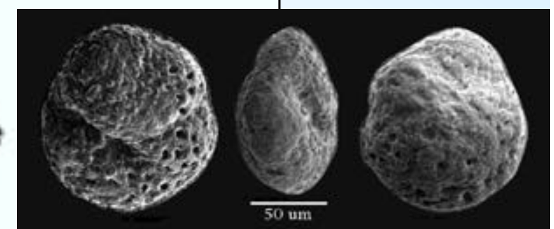
- Diatoms are common in cold water (Antarctica)
- Radiolaria are common near the equator
- Siliceous oozes account for about 14% of deep-sea sediment
- Distribution of ***opal*** ($SiO_2 \cdot nH_2O$) in deep-sea sediments is closely related to pattern of productivity in overlying water…

Primary Organisms Contributing to Deep-Sea Biogenic Sediments

A. CALCAREOUS



1. Forams
   a. Protozoans (Class Sarcodina)
   b. Both planktonic and benthonic forms
   c. Planktonic
      1. Calcite
      2. Generally 50-400 microns; up to 1 mm
      3. Generally 0-200 m depth (photic zone) because most have zooxanthellae
      4. Evolved in Jurassic; presently 30 species
      5. Nonmotile
      6. Distribution limited by food; sensitive markers of water mass

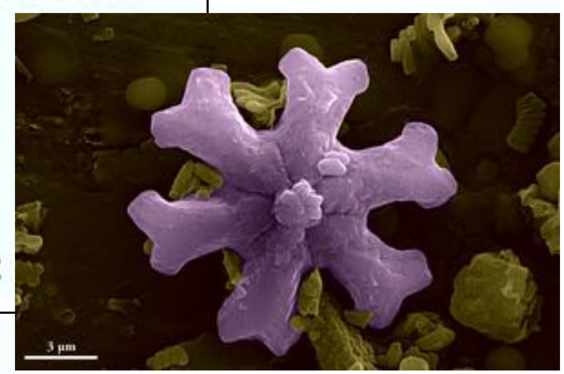


   d. Benthonic
      1. Calcite; a few aragonite, Mg-calcite, siliceous, and agglutinated forms
      2. 20-300 microns; up to 16 mm
      3. All depths; important only in nearshore
      4. Evolved in Cambrian
      5. Live at or near the sediment surface; both mobile and sessile forms
      6. Good indicators of bottom water characteristics (temperature, etc.) so depth zonations are important
   e. Important in paleooceanography
      1. High diversity
      2. Present in all marine environments (marginal basins, deep sea, surface ocean, all latitudes)

2. Pteropods
   a. Gastropods
   b. Planktonic
   c. Aragonite ($CaCO_3$ - more soluble than calcite)
   d. Generally 0.3-10 mm
   e. Generally upper few 100 m
   f. Evolved in Eocene, but most important in Quaternary so of limited biostratigraphic use
   g. Mobile (have gastropod foot) so can select environment
   h. Distinct water mass preferences - tropics and subtropics
   i. Pteropod oozes found only in semi-isolated marginal seas because of limited preservation of aragonitic test

3. Nannofossils
   a. Coccolithophorida
      1. Single-celled algae
      2. Mostly planktonic
      3. Calcite surface cells (coccoliths) surround body (coccosphere)
      4. Coccospheres - 2-50 microns; rare in sediments; contain 10-150 coccoliths
      5. Coccoliths - <1-10 microns; usually disc-shaped; important in sediments
      6. Limited to photic zone
      7. Evolved in early Jurassic; especially important in Cretaceous
      8. T range: 0-34 C; S range: 15-40 % ; a few fresh water varieties
      9. Very important in sediments

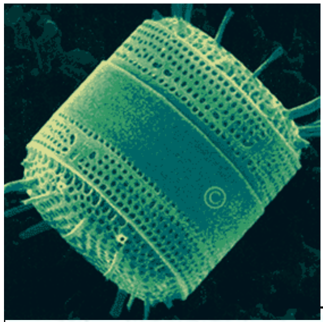
   b. Discoasters
      1. Star-shaped; calcite
      2. 6-25 microns
      3. Warm surface waters
      4. Late Paleocene to Plio/Pleistocene boundary; now extinct

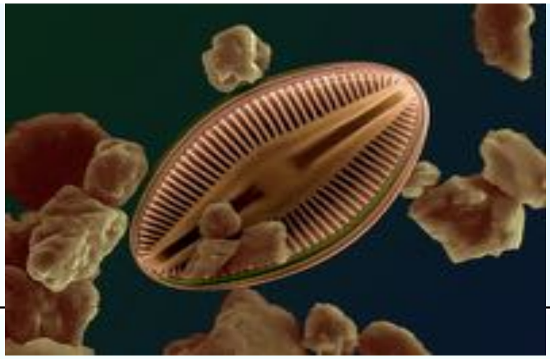


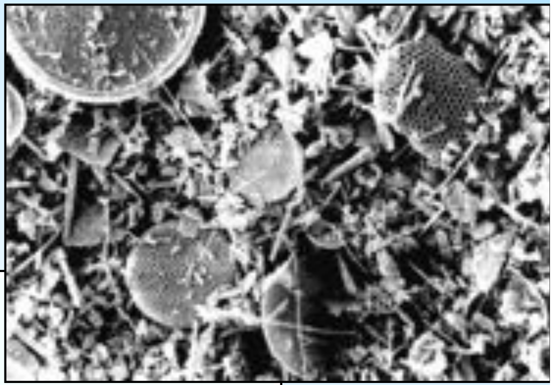
4. Ostracods
   a. Crustaceans
   b. Mostly benthonic (planktonic are chitinous, not preserved)
   c. Bivalve carapace of chitinous-rich calcite
   d. 0.5-2 mm
   e. All depths
   f. Plentiful since Ordovician
   g. Wide salinity tolerance as a group; sensitive to water mass so good tracers for bottom waters
   h. Volumetrically unimportant

B. SILICEOUS

1. Radiolaria
   a. Protozoans
   b. All planktonic; marine
   c. 3 major groups
      1. Acantharia - $SrSO_4$ tests
      2. Tripylea - siliceous/organic tests
      3. Polycistina - opaline silica tests ($SiO_2.4H_2O$); important in sediments; 2 morphologies: spherical (Spumellaria) and cap or helmet shaped (Nasselaria)
   d. 50-400 microns
   e. Generally near surface (50-200 m), although some as deep as 2000 m
   f. Evolved in Cambrian
   g. Most diverse of marine microfossils
   h. High densities in upwelling regions

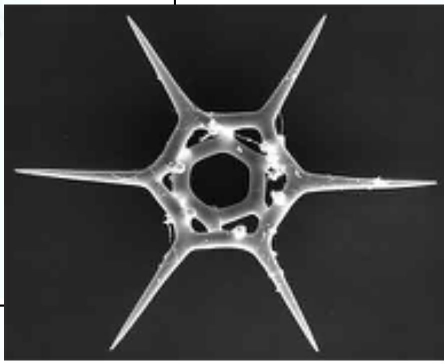






2. Diatoms
   a. Solitary or colonial algae
   b. Both planktonic and benthonic forms
   c. Highly diverse - marine, fresh water, and wet soil environments
   d. Opaline silica
   e. 2 microns to 2 mm, mostly 10 -100 microns
   f. Limited to photic zone
   g. Naked forms (no test) evolved in Jurassic; centric forms (mostly planktonic) evolved in Cretaceous; pennate forms (mostly benthonic) evolved in late Paleocene
   h. Especially important in sediments under regions of high productivity and at high latitudes
   i. 70-90 % of suspended opaline silica is in diatoms

3. Silicoflagellates
   a. Single celled algae/protozoa (characteristics of both)
   b. Planktonic
   c. Internal skeleton of hollow tubes of opaline silica - not well preserved
   d. 10-100 microns
   e. Photic zone; mobile (have flagellum)
   f. Evolved in mid-Cretaceous
   g. Slow evolution so not useful biostratigraphically



The Paradoxes of Biogenic Sediments

- Opal (SiO_2) and calcite ($CaCO_3$) generated by organisms in the sea account for ~50% of sediment accumulation on seafloor
- Geographic distribution of sediment is not uniform
- Some areas of nearly pure opal, some of nearly pure carbonates…
- Other areas nearly devoid of biogenic sediment…

WHY?

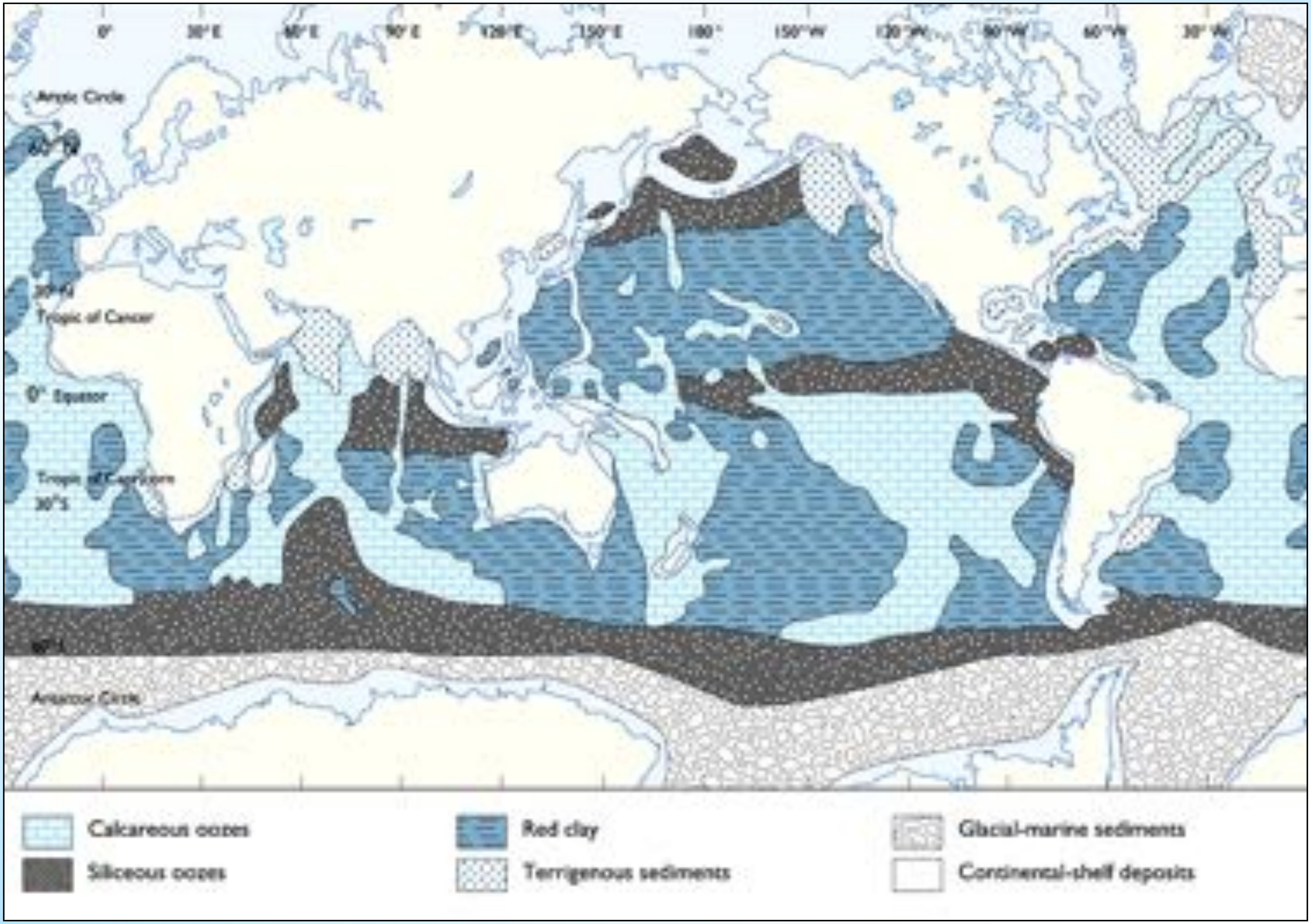
II. Controls on Type of Sediment

If influx of terrigenous sediment is low and the water is warm, carbonate sediments will dominate

If influx of terrigenous sediment is low and the water is cold, siliceous sediments **can** dominate

The distribution of sediments in the deep ocean varies greatly, but is strongly controlled by corrosion of carbonates in deep waters

Deep-Sea Sediment Distribution



Seawater Si Removal by Phytoplankton

Dominated by Upwelling Regions:

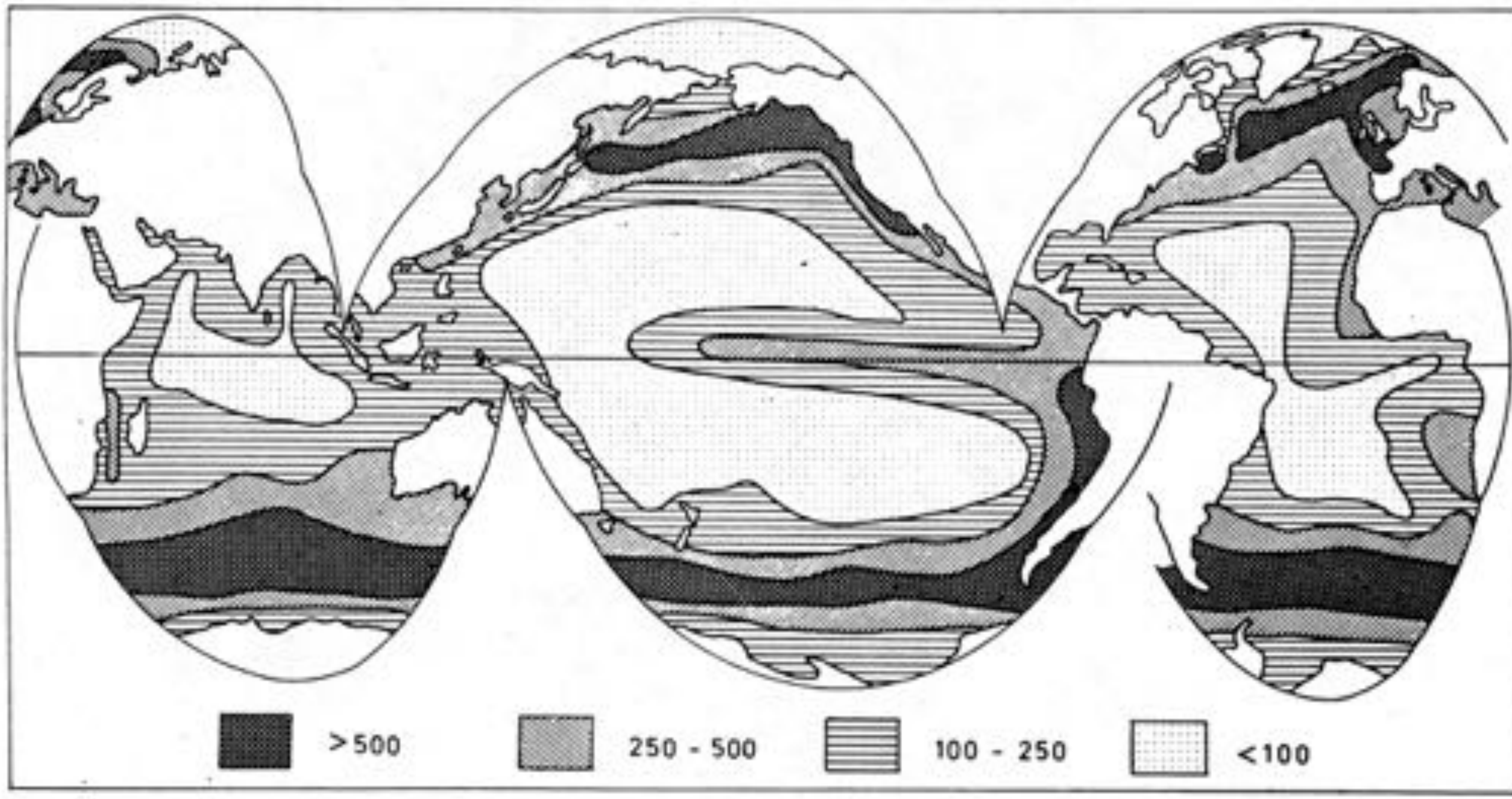


Fig. 2. Regional variation in the rate of extraction of dissolved silicon (g SiO_2 m^{-2} $year^{-1}$) by phytoplankton in near-surface waters. Modified from Lisitzin *et al.* (1967).

Distribution of Opal in Marine Sediments

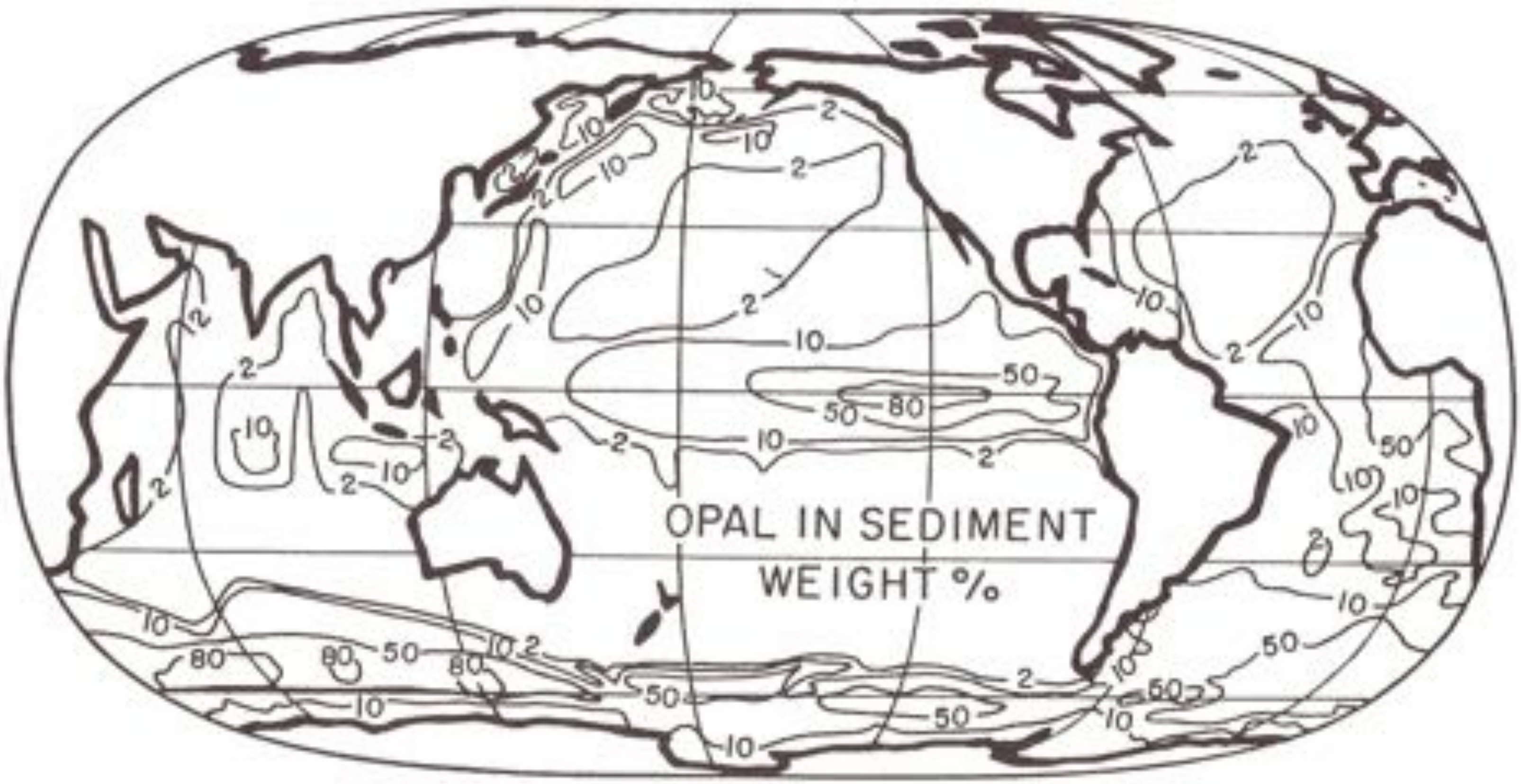
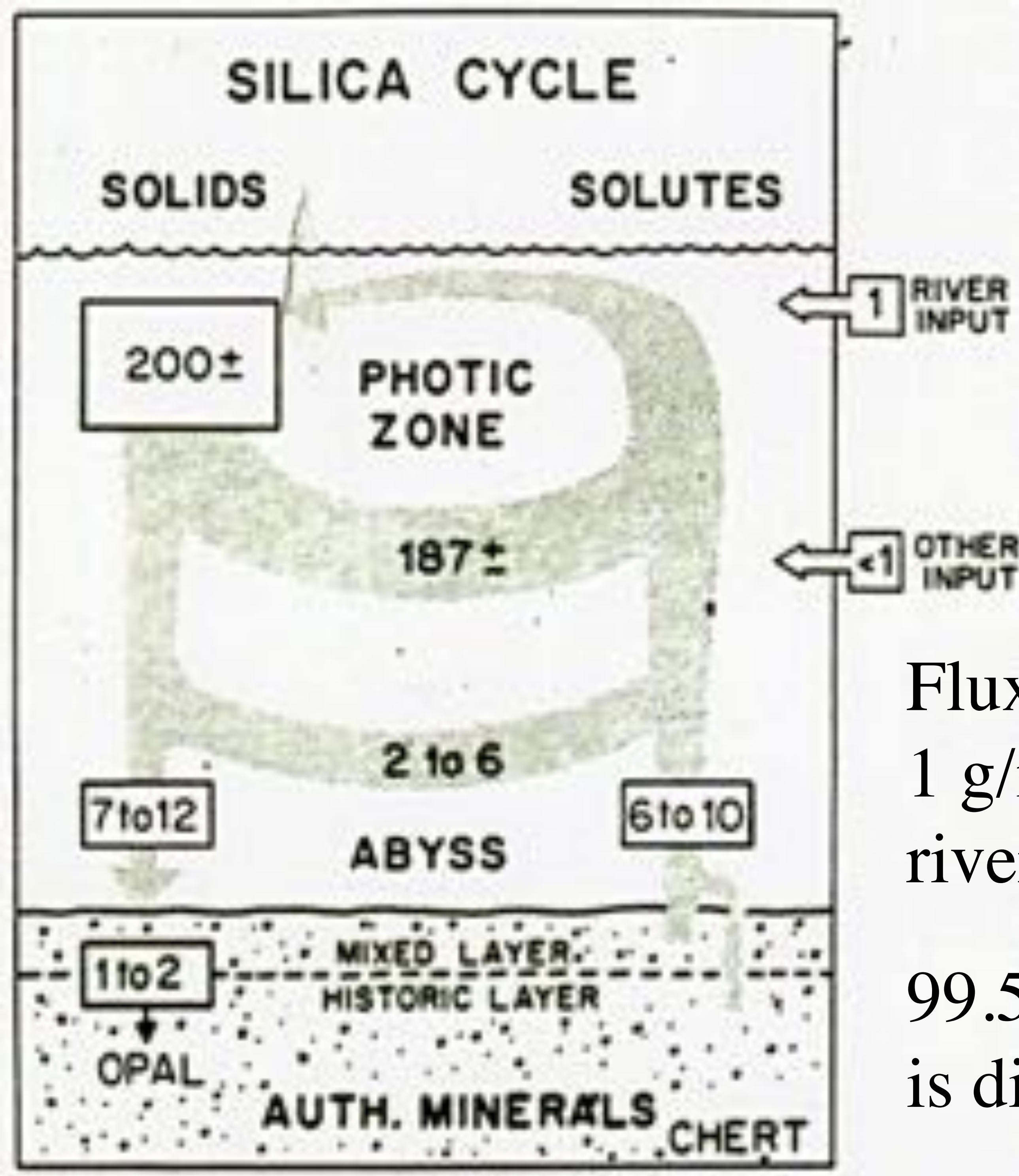


Figure 2-2. The distribution of opal in marine sediments. Prepared by Ross Heath of Oregon State University. It must be kept in mind that, since this map shows the proportion of opal in the sediment, the patterns depend on the rate of accumulation of the non-opal components of the sediment as well as that for opal.



River input is 4×10^{14}g/yr

Production is 200 $g/m^2/yr$

Flux into sediment is 1 $g/m^2/yr$ to balance river input

99.5% of production is dissolved

Distribution of Carbonates in Marine Sediments

- Calcite production is widespread and relatively uniform in surface waters
- Si is not needed for growth of calcareous organisms
- Yet large areas of world do not have calcareous seds
- Calcite-rich zones are found on ridge crests and other topographic highs

Controls on Biogenic Sediment Distribution

- Production rates (siliceous and carbonaceous)
- Preservation during transport and deposition
  - Settling velocity
  - Sedimentation rate
  - Solubility
- Dilution by non-biogenic material

Settling Velocities of Biogenic Particles

Settling velocity is proportional to size:

Typical settling rates of empty shells

Ranked from slow to fast. All figures are approximations. Within each group rates vary within a factor of at least 2 or 3, depending on the thickness of the shell and the morphology.*

	Size	m day^{-1}
Coccolithophores		
Solitary	~10 μm	0·3–13
Aggregate	up to 1 mm	10–6000
Diatoms		
Skeletonema	~20 μm	~1 (max. 7)
Coscinodiscus	70 μm	15
Ditylum	60 μm	7
Ethmodiscus	1 mm	500
Radiolarians		
Various Forms	30–60 μm	50
	60–120 μm	100–200
	240 μm	500
Foraminifera		
Various Forms	62–125 μm	250
	125–177 μm	500
	177–250 μm	1000
	> 250 μm	2000
Pteropods	mm range	1000–2000
Faecal Pellets		
Euphausid	n.d.	100–1000
Unspecified	120 × 50 to 200 × 100 μm	100–300
Copepod	100 × 45 to 200 × 45 μm	100–200

Effect of Settling Rate on Preservation

- The range of settling velocities observed for biogenic particles in the ocean is very large
- This has a significant effect on the degree of particle dissolution
- The longer particles spend in the water column, the more they can “react” with seawater
- Opal (amorphous silica) and calcite, however, display VERY different dissolution behavior in the oceans…

Corrosion Zones for Biogenic Particles

- Silica dissolves **more** in warmer, higher pH surface water

- Calcite dissolves in colder, higher ΣCO_2 (more acidic) deep water

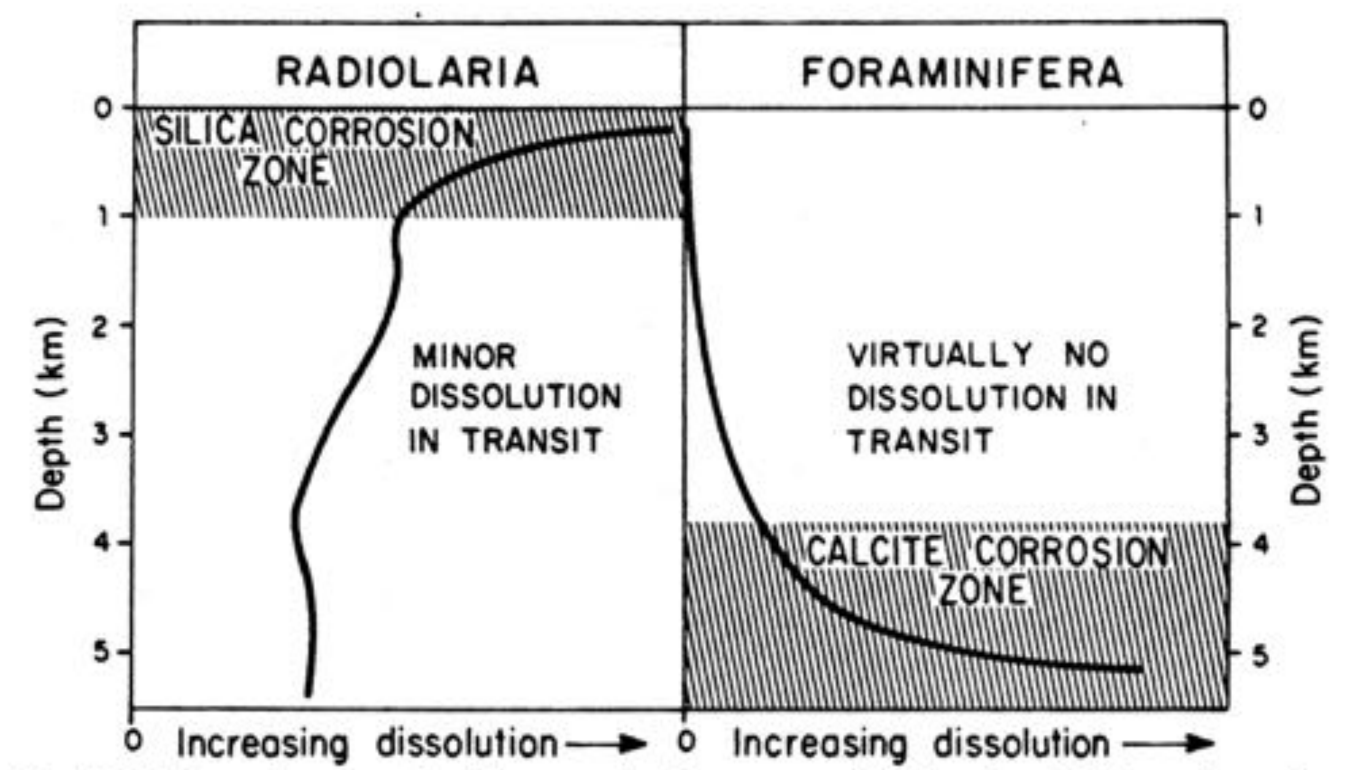
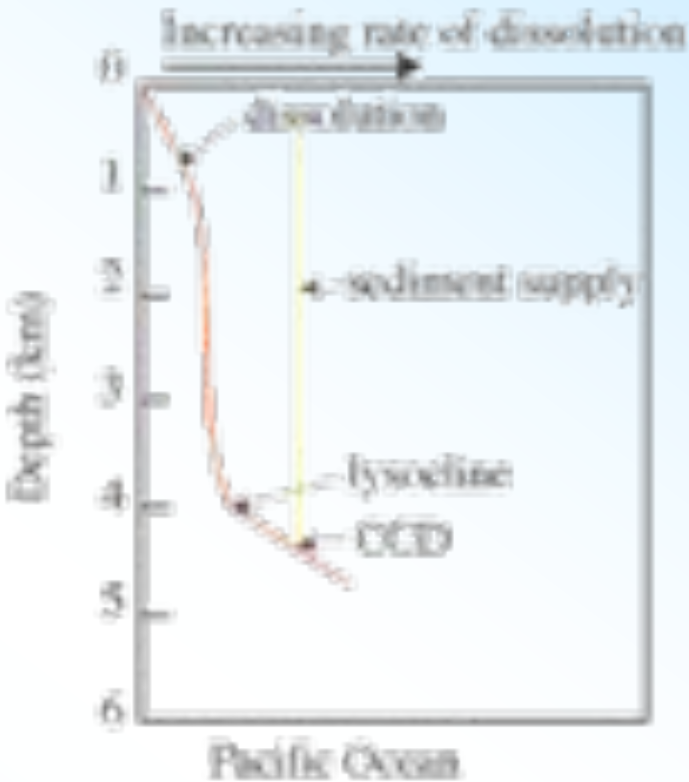


FIG. 29.17. Corrosion zones for siliceous and calcareous particles, based on field experiments in the North Pacific near 19° N, 169° W (Berger, 1967, 1968b). Boundaries have been drawn at depth of maximum rate change, they are not the same as facies boundaries in the ocean.

Berger, 1976

Calcite Compensation Depth

- Lysocline is point where dissolution increases markedly
- CCD is point where rate of calcite supply is matched by rate of dissolution



Calcite Dissolution

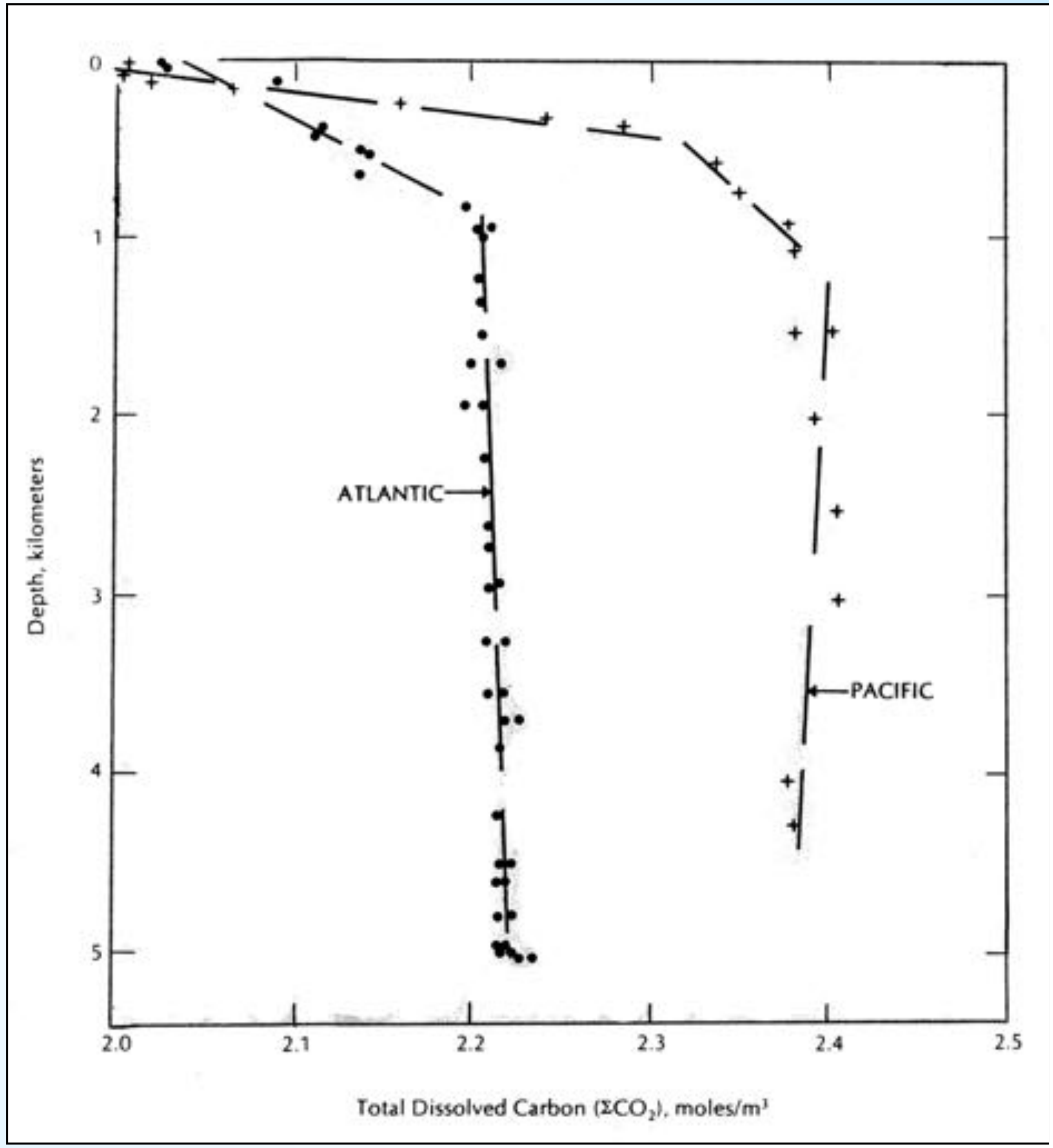
- Remineralization of organic matter in the water column produces CO_2 that reacts with CO_3^{-2}

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

$$CO_2 + CO_3^{-2} + H_2O \rightarrow 2HCO_3^{-}$$

- Higher ΣCO_2 at depth
- Lower CO_3^{-2} at depth

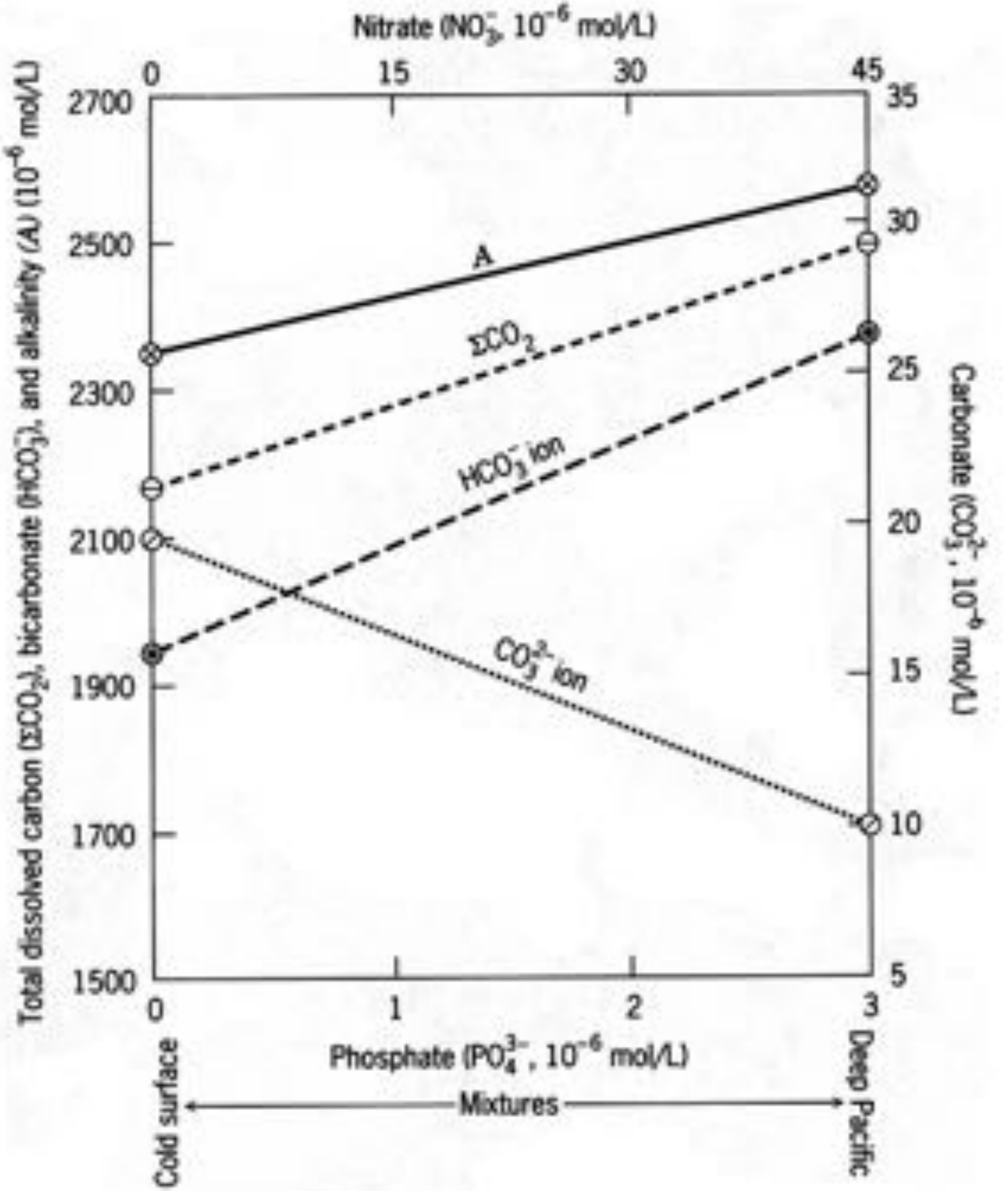
- In the deep ocean, the decrease in $[CO_3^{-2}]$ from this reaction has a marked effect on $CaCO_3$ solubility



Two endmembers:

- Cold surface seawater
- Pacific Deep Water

Alkalinity increase due to release of Ca^{2+}



Saturation State of SW

- The saturation state of SW with respect to calcite (and aragonite, Mg-rich calcite, etc.) determines whether these phases will dissolve or not

- Define the *saturation state of SW with respect to calcite* ($CaCO_3$) as:

Assumes $\{CaCO_3\} = 1$

The denominator is also known as K_{sp}, the "solubility product"

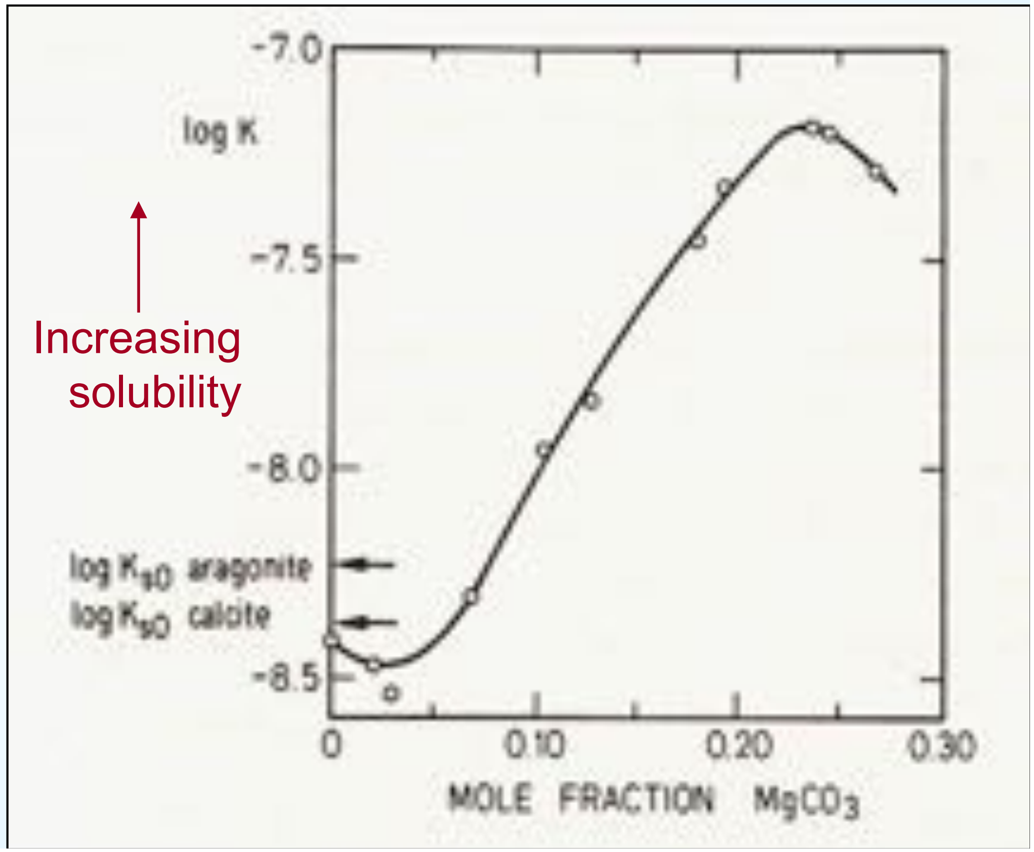
- Depth at which $\Omega = 1$ is called the ***saturation horizon***

Solubility of Mixed Carbonates

A variety of mixed carbonates, $Ca_{(1-x)}Mg_{(x)}CO_3$:

$x = 0$	Calcite or aragonite
$x < 0.04$	Low Mg-calcite
$0.04 < x < 0.20$	High Mg-calcite
$x = 0.5$	Dolomite
$x = 1$	Magnesite

Solubility of Mg-calcite increases with increased Mg content

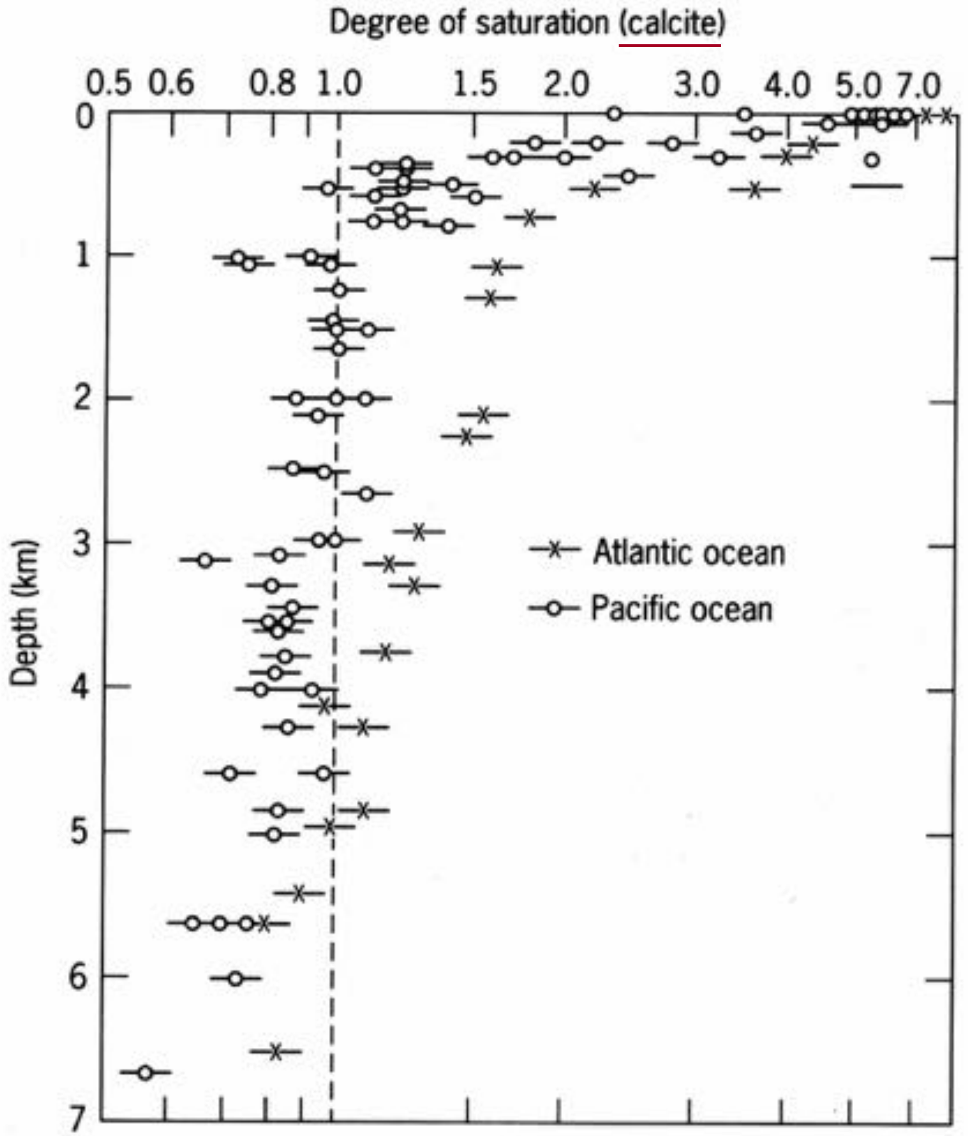


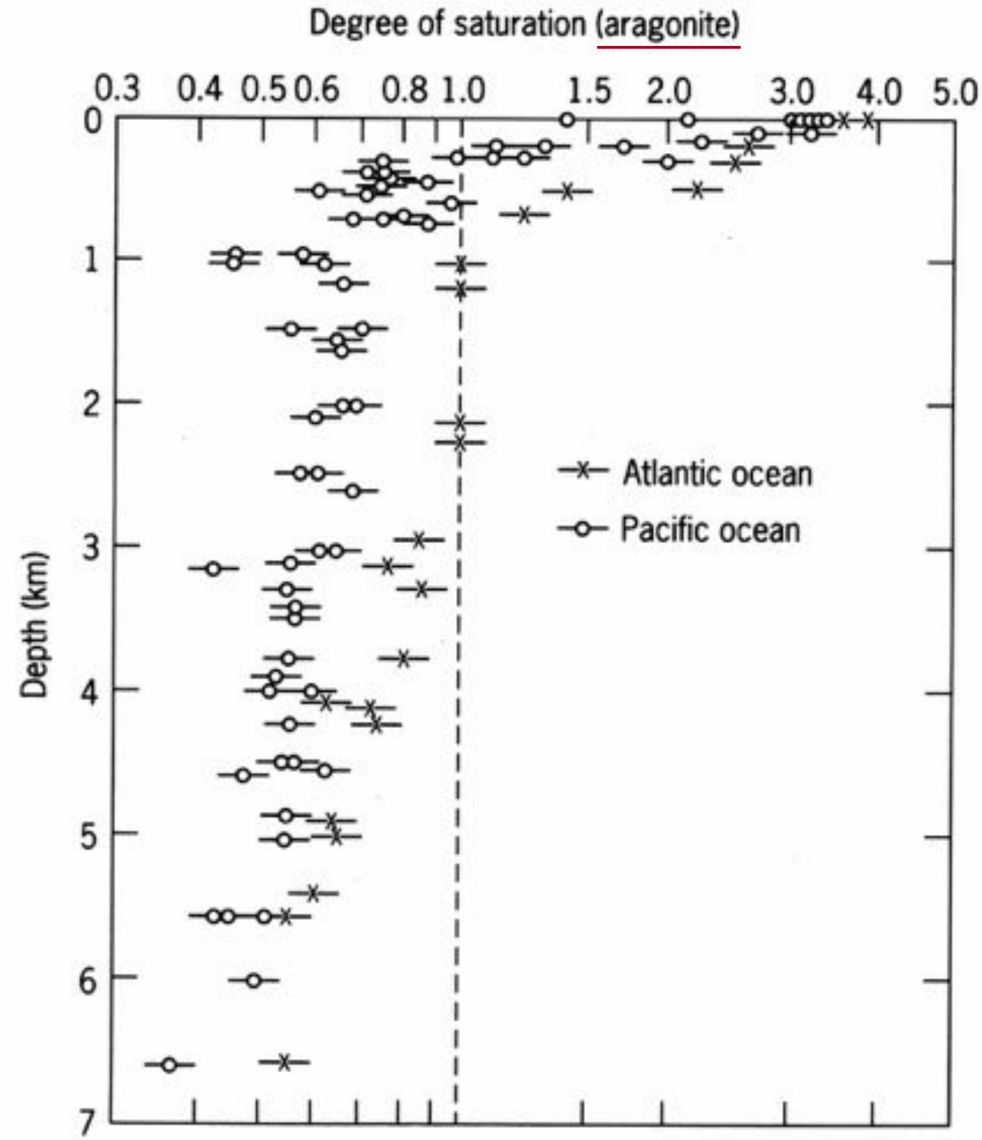
$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$

$K = \{Ca^{2+}\} \{CO_3^{2-}\} / 1$

Higher K means $CaCO_3$ dissolves with higher activities of Ca^{2+} and CO_3^{2-}

$\therefore$ $CaCO_3$ is more soluble





- The upper ocean is supersaturated wrt both calcite and aragonite
- Aragonite is more soluble than calcite in SW
- Saturation horizon is deeper in Atlantic than in Pacific

Some Definitions

- ***Saturation Horizon*** is where "Ω" = 1

- ***Lysocline*** is where dissolution effects first appear in carbonate grains
  - Since degree of saturation decreases with depth, dissolution rates should increase with depth… (Libes has this wrong)

- ***Carbonate Compensation Depth (CCD)*** is where the depositional rate of carbonate is equal to the dissolution rate (i.e., no net accumulation)

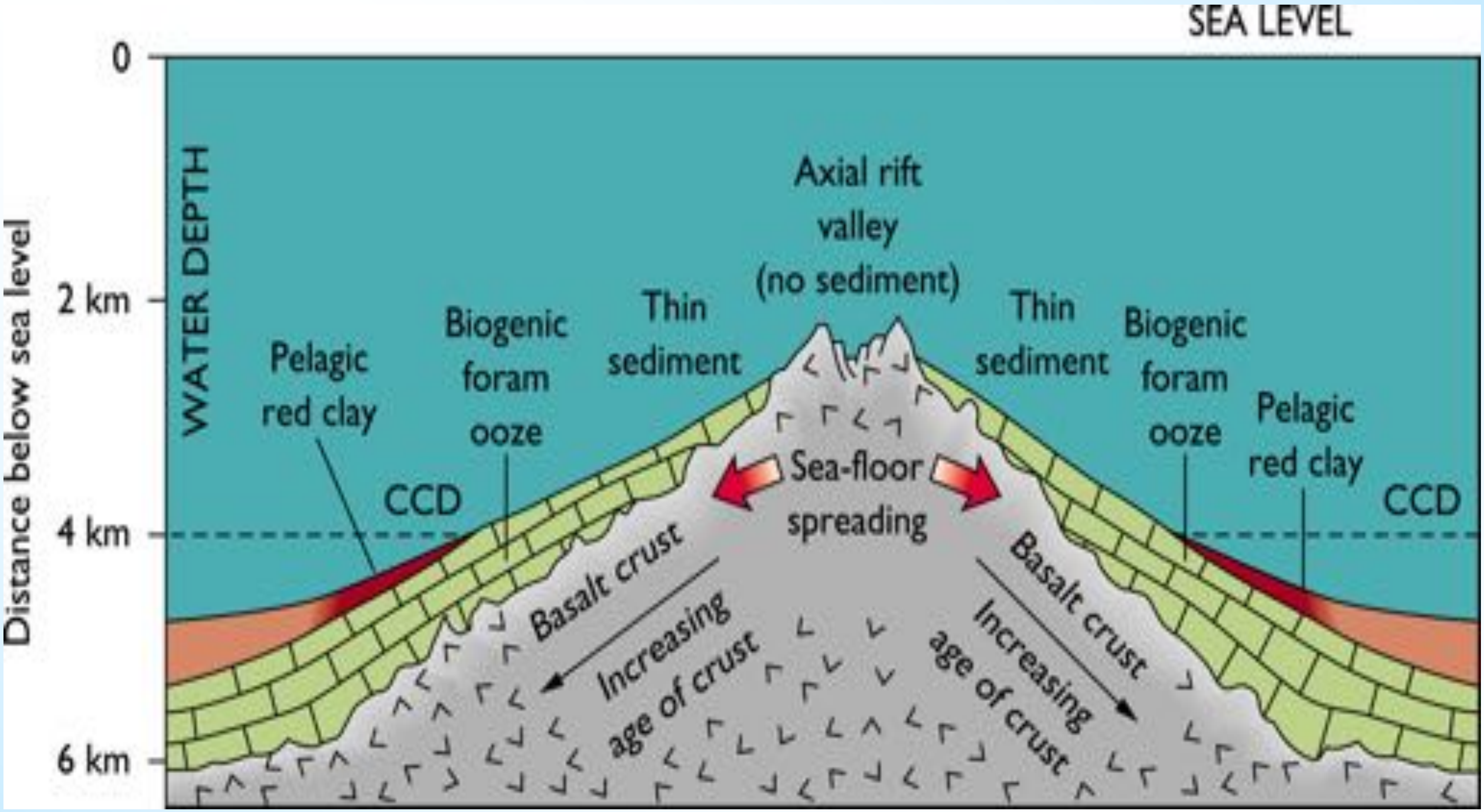
- The lysocline occurs above the CCD, but is at or below the saturation horizon because of
  - Kinetic effects
  - Protection by organic matter on particulates
  - Inhibitory effect of dissolved species like phosphate which have mid-depth maxima

- No calcite should persist below ~4500 m in Atlantic and ~3500 m in Pacific
- No aragonite should persist in either ocean below ~1000 m
- However, carbonate sediments occur well below these depths (*i.e.*, the CCD is deeper than the saturation horizon) --- WHY?

Kinetic Considerations

- $CaCO_3$ should not be preserved in sediments below the saturation horizon
- Yet, calcareous shells do persist… Why?
- Main factor: slow dissolution rates relative to rates of sinking (in water) and burial (in sediment)
- Likelihood of dissolution of a shell depends on factors that control sinking rate and dissolution
- Both influenced by the **size, density and shape** of a shell
- Dissolution is also controlled by **organic coatings** and effects of **trace ions** on shell surfaces

Deep Sea Sediments - Overview



Compare with figures: “Sediment Deposition Rates”
“Deep-Sea Sediment Distribution”

What Controls the Distribution of Various Kinds of Seafloor Sediments?

The answer is "the 3 D's":

1) Delivery: Without delivery of sediments into the ocean, they will of course never be found there.
2) Dilution: Many different types of sediment particles reach the seafloor. If too much of one type reaches a given place, or the rate of dilution is very high, the other types will become unimportant.
3) Destruction: Certain chemical, physical, and biological processes destroy sedimentary particles, removing them from the seafloor sediment.

Distribution Summary of the Principal Types of Sediment on the Seafloor

Thick terrigenous layers in aprons around continents;
Biogenic in equatorial band & along western continental boundaries…WHY?
Authigenic and eolian sediments across vast areas of deep ocean floor covered by sediments of ~100s meters
Volcanic tephra within 1000km of islands arcs and volcanic belts
Thin sediment at active spreading centers

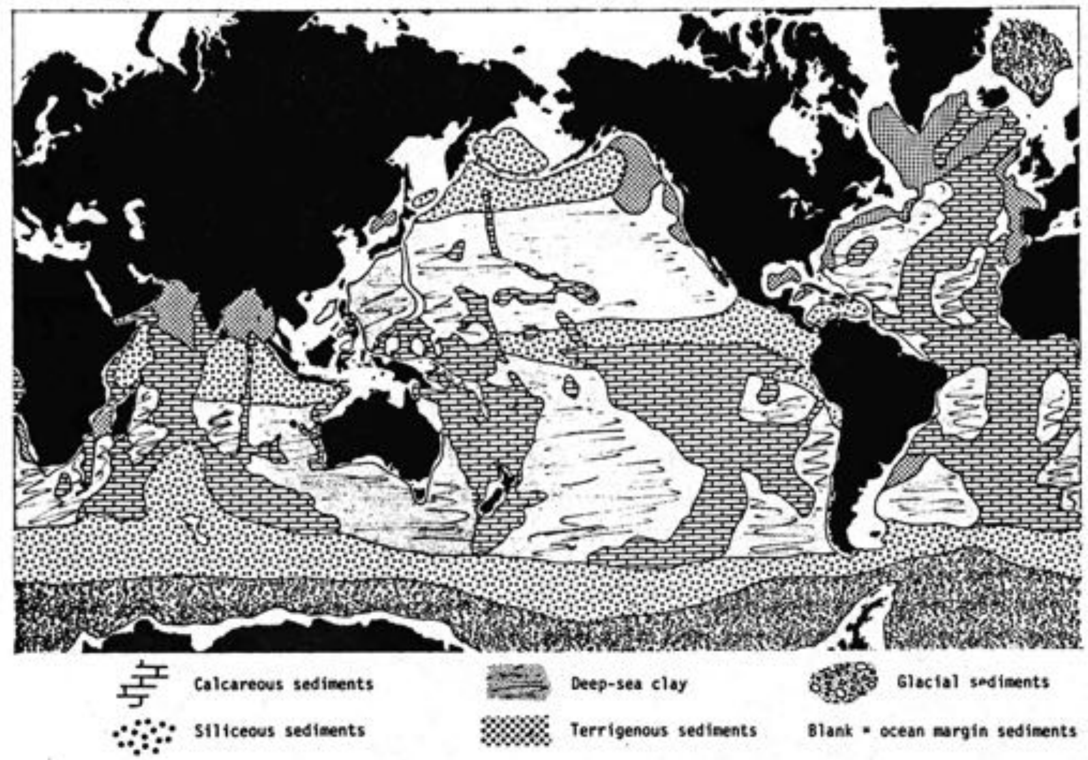


FIG. 24.7. Distribution of the principal types of sediment on the floors of the oceans. (Based on data from many sources.)

Davis & Gorsline, 1976