Export, nitrogen cycle, sedimentation

Learning objectives:

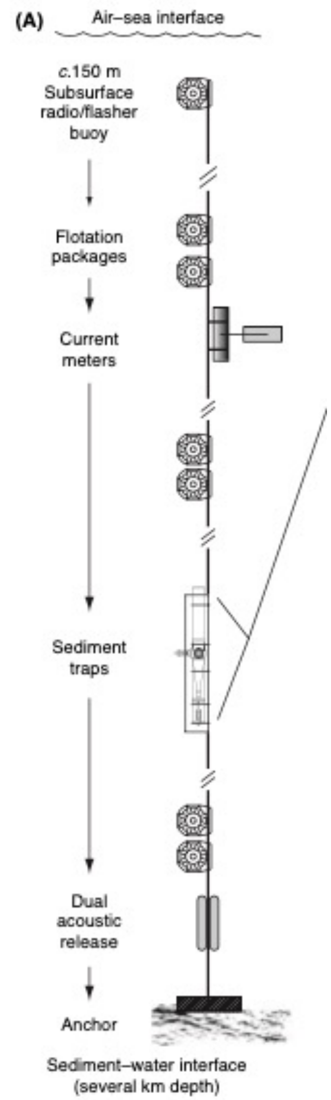
- Categorize different methods of estimating biological carbon export
- Describe the basics of the marine nitrogen cycle
- Discuss how patterns in export and water column chemistry are reflected in sediment distributions

Methods of estimating export

- Measurements of falling particles:
  - Sediment traps
  - ^{234}Th particle flux
  - Optical observations (backscatter, transmissivity, etc.)
- Mass balances
  - O_2, O_2/N_2, O_2/Ar, NO_3, DIC/Alk
- C isotopes
- Other:
  - Satellite algorithms, Global circulation models, inverse models

Falling particles

- Only capture particulate organic carbon (need to assume the contribution of dissolved fraction)
- Either directly capture particles (sediment traps), assume particle production (adsorption of ^{234}Th), or periodically observe particles (optical instruments)



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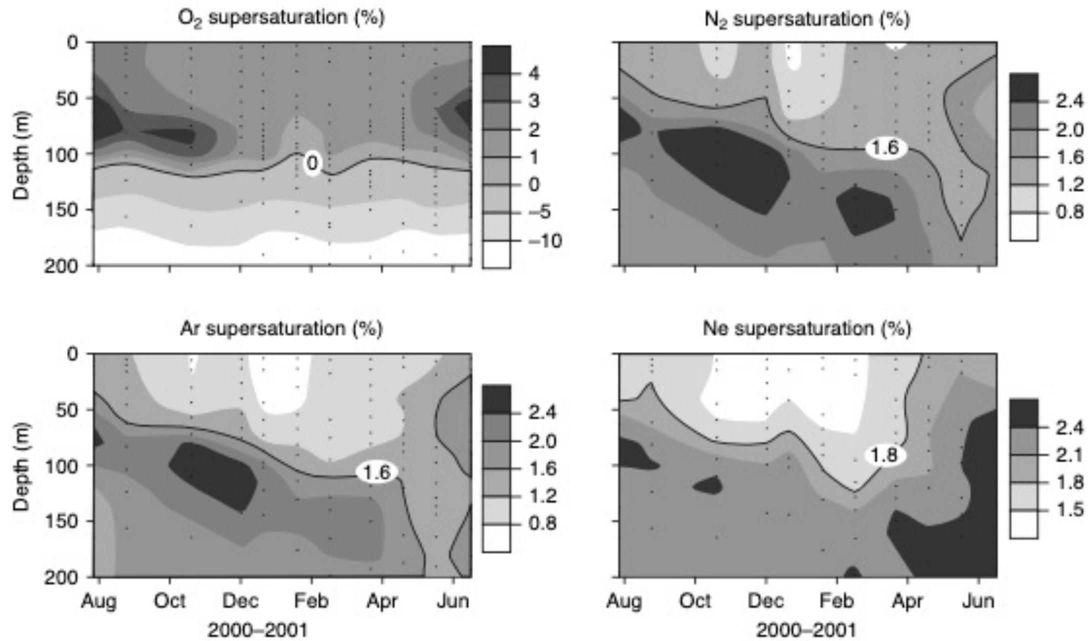
Mass Balances

- Use knowledge of photosynthesis/respiration stoichiometry and a measurable tracer
- Should include both POC/DOC fractions



Mass Balances

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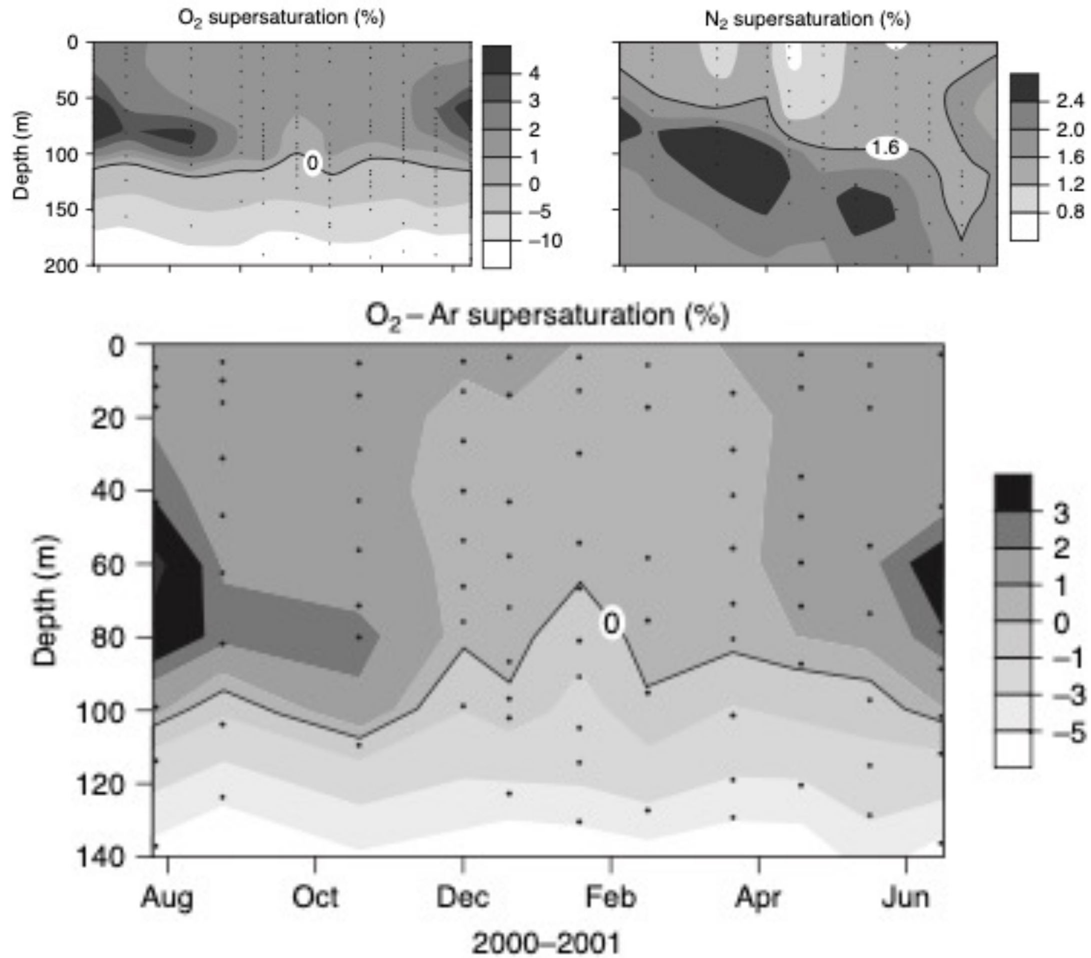
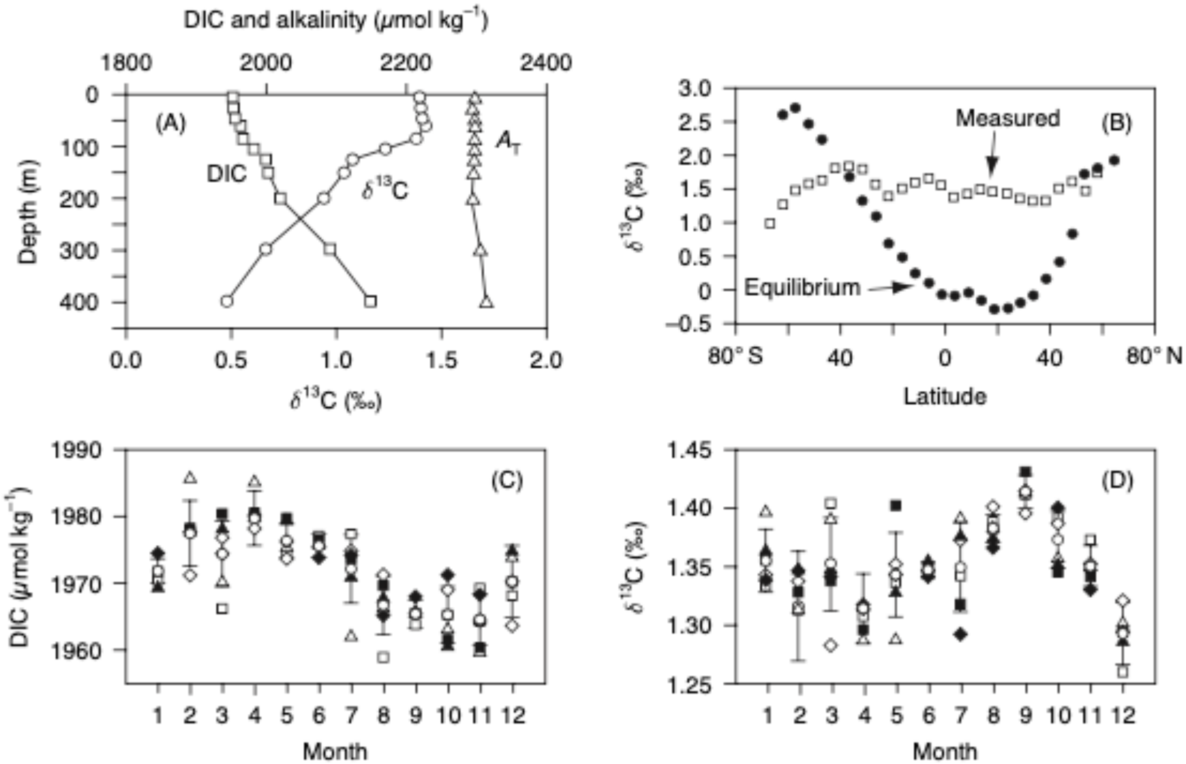


C isotopes

- DIC/DI^{13}C
- Photosynthesis preferentially takes up C^{12}, so DIC in the surface water is heavier
- Fractionation of -15 to -20 ‰



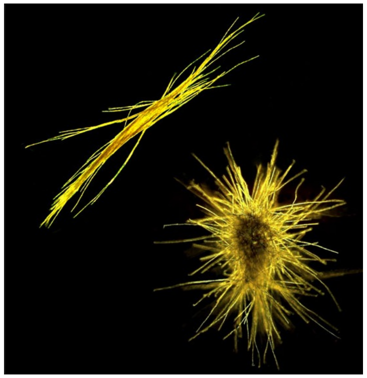
N sources and sinks

Main Ocean Source of N

- Nitrogen fixation:
  - Enzyme catalyzed reduction of N_2

$$N_2 + 8H^+ + 8e^- + 16\ ATP\ (energy) \rightarrow 2NH_3 + H_2 + 16\ ADP + 16\ P_i$$

- Mediated by a two protein (Fe and Fe-Mo) complex called nitrogenase
  - Inactivated when exposed to O_2



Trichodesmium

Main Ocean Sink of N

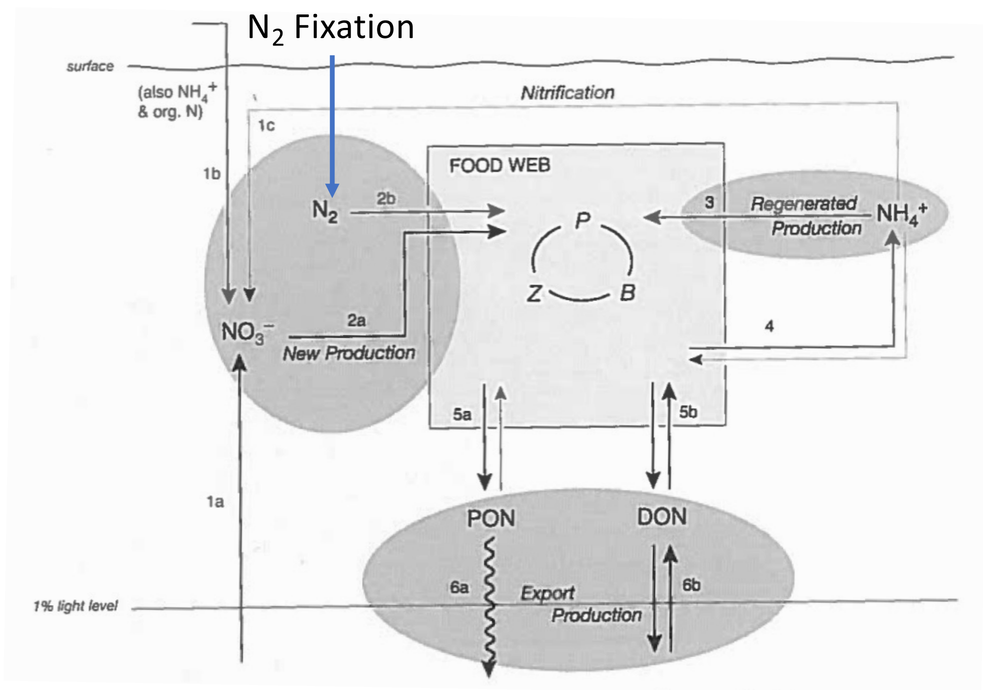
- Fixed Nitrogen (NO_3^-, NO_2^-, NH_4^+) is converted to N_2 in low oxygen zones of the ocean
- Two Pathways:
  - Denitrification (<2 to 10 mM O_2):

$$2NO_3^- + organic\ matter\ \rightarrow N_2$$

  - Anammox (<2 mM O_2)

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$$

Schematic of Upper Ocean Nitrogen Cycle



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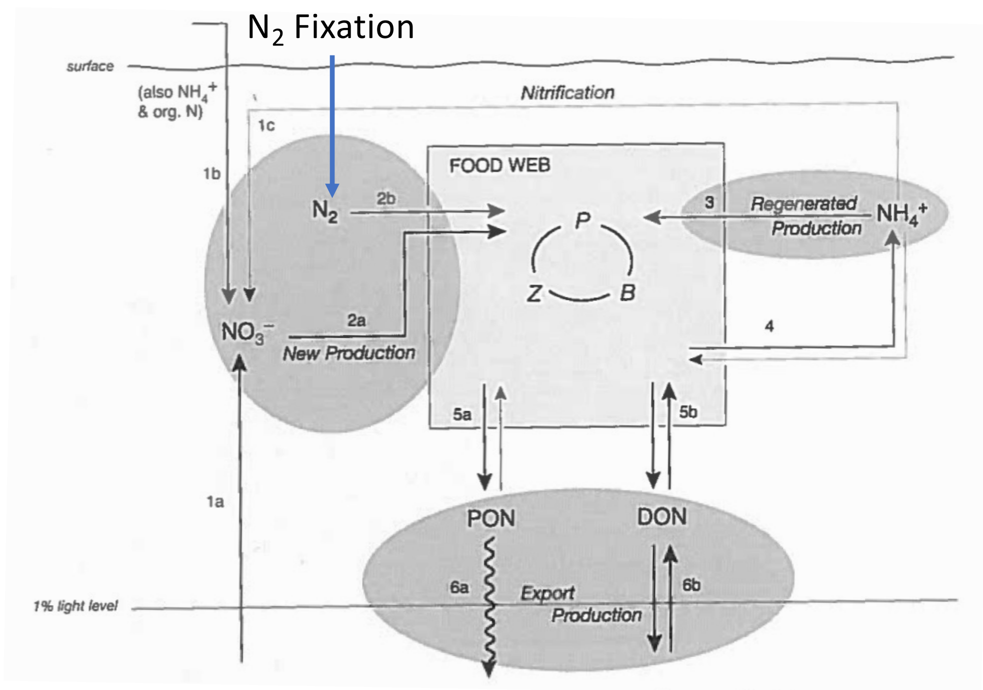
Sarmiento and Gruber, 2006, Ch. 4

Schematic of Upper Ocean Nitrogen Cycle



f-ratio = New production / NPP
e-ratio = export of organic matter (OM) / NPP.

ef-ratio = *f*-ratio and *e*-ratio are usually assumed equal to each other & thus referred to jointly as the *ef*-ratio

pe-ratio = export of particulate organic matter (POM)/NPP

Note: dissolved organic matter (DOM) contributes 20±10% to export

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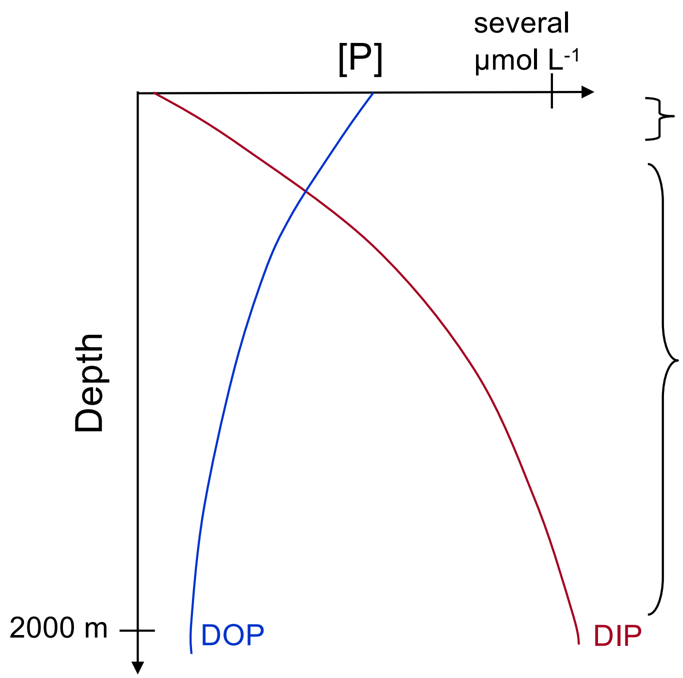
Sarmiento and Gruber, 2006, Ch. 4

Mid-Ocean Nutrient Profiles - Phosphorus

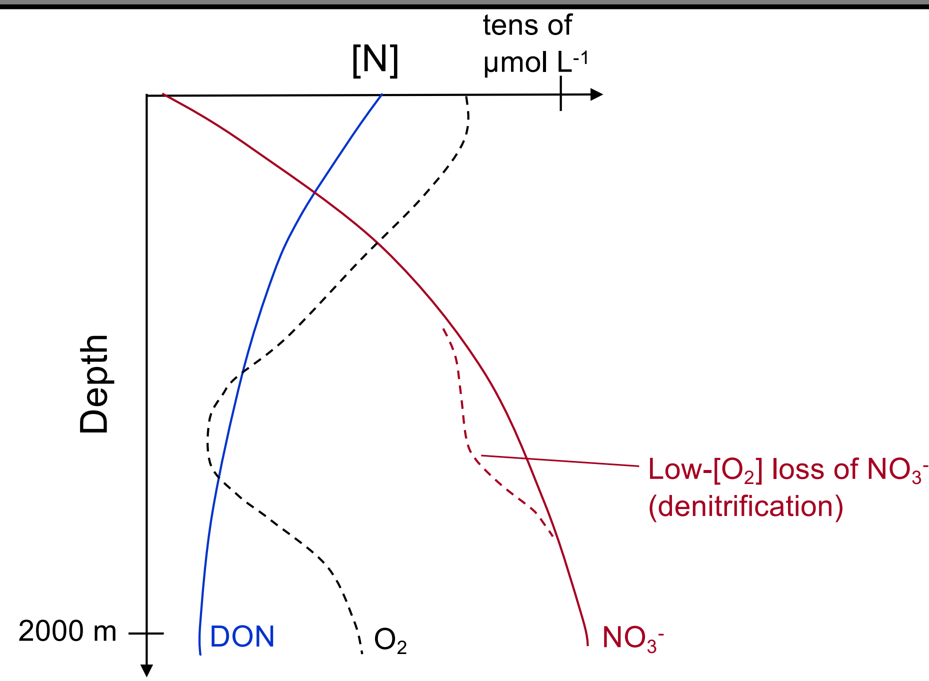
Main processes controlling vertical distribution of nutrients:



High consumption of inorganic nutrients; high production of organic nutrients

Slow release of inorganic nutrients due to decomposition of falling particles; slow utilization of organic nutrients

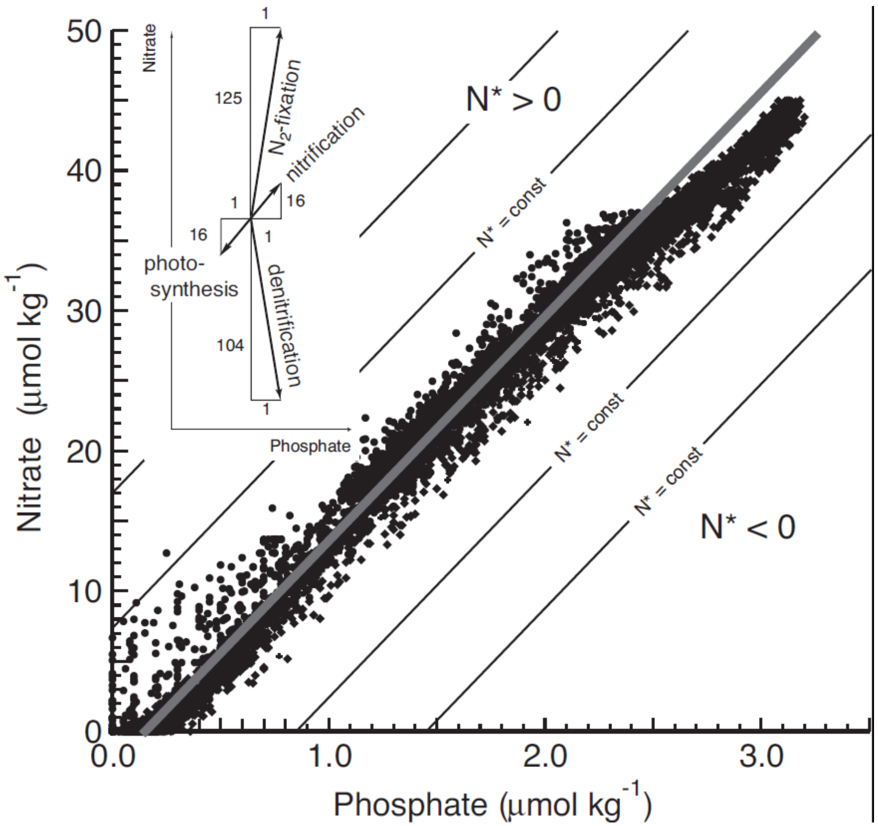
Mid-Ocean Nutrient Profiles - Nitrogen



Denitrification (nitrate reduction):

$2NO_3^- + CH_2O + 8H^+ + 6e^- \rightarrow N_2 + CO_2 + 5H_2O$

N* is a tracer for denitrification in the ocean



PO$_4$ versus Nitrate (WOCE data) from Sarmiento and Gruber (2006)

What is N*?

N* is defined as
N* = [NO_3] – 16 x [PO_4] +2.9

The solid line shows the linear equation with N:P =16

Values to the right have negative N* (denitrification) to the left have positive N* (nitrogen fixation)

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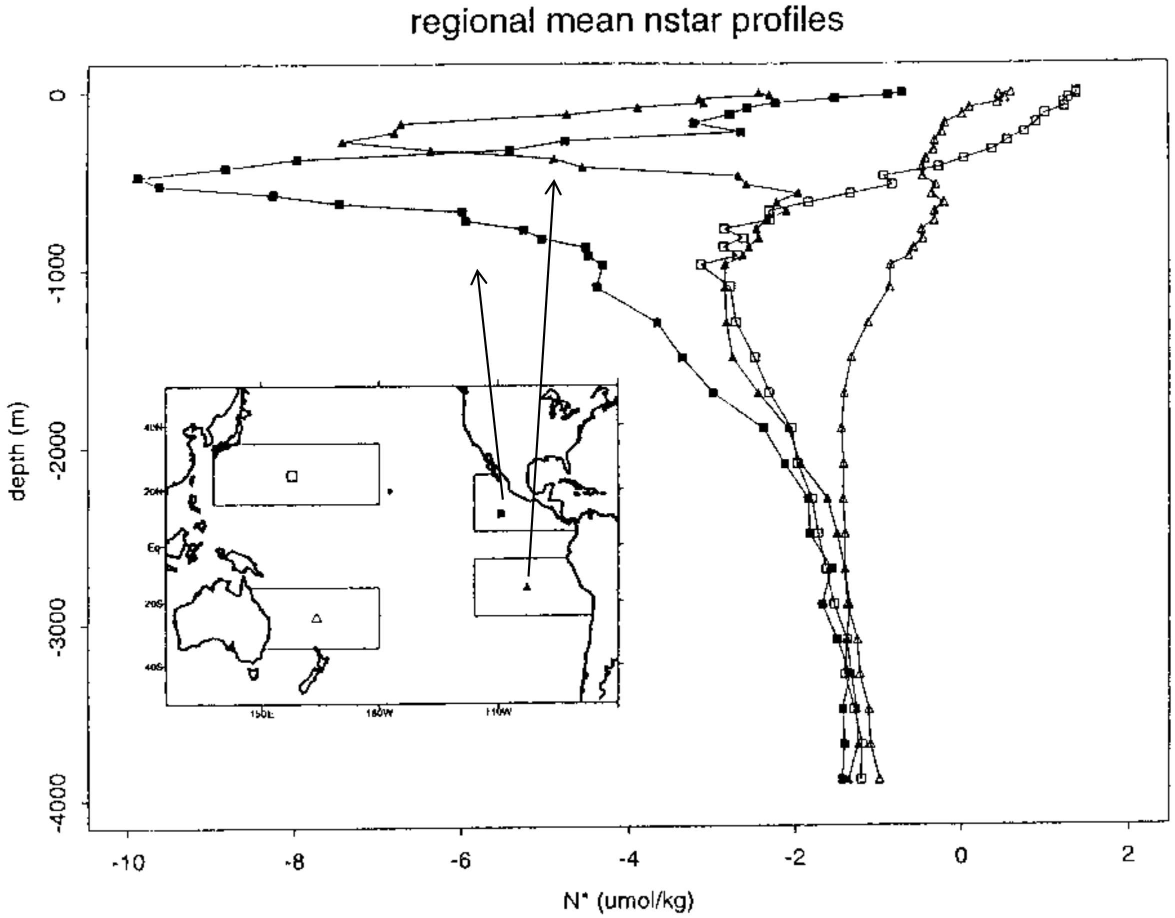
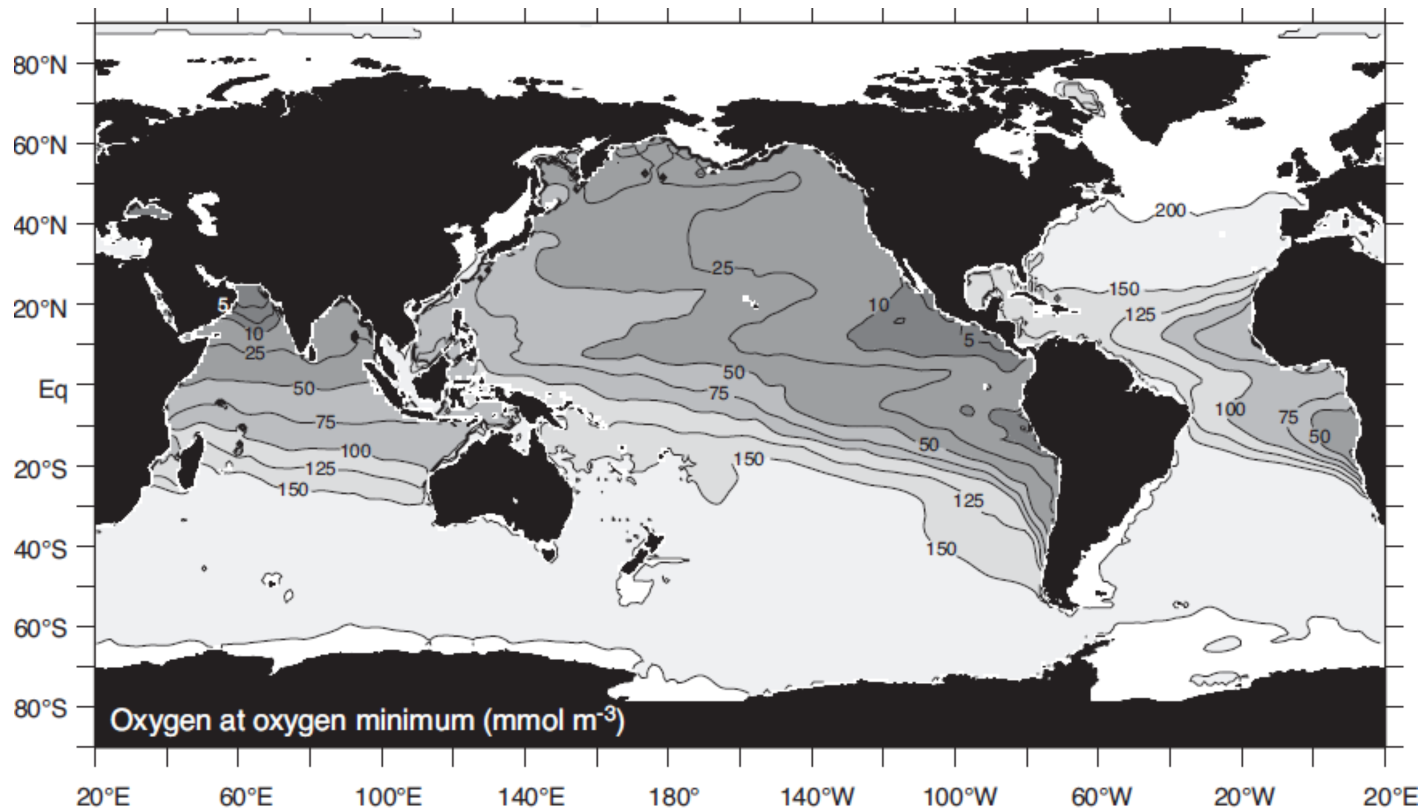


N* is defined as
N* = $[NO_3] - 16 \times [PO_4] + 2.9$

Global distribution of O_2 at the depth of the oxygen minimum



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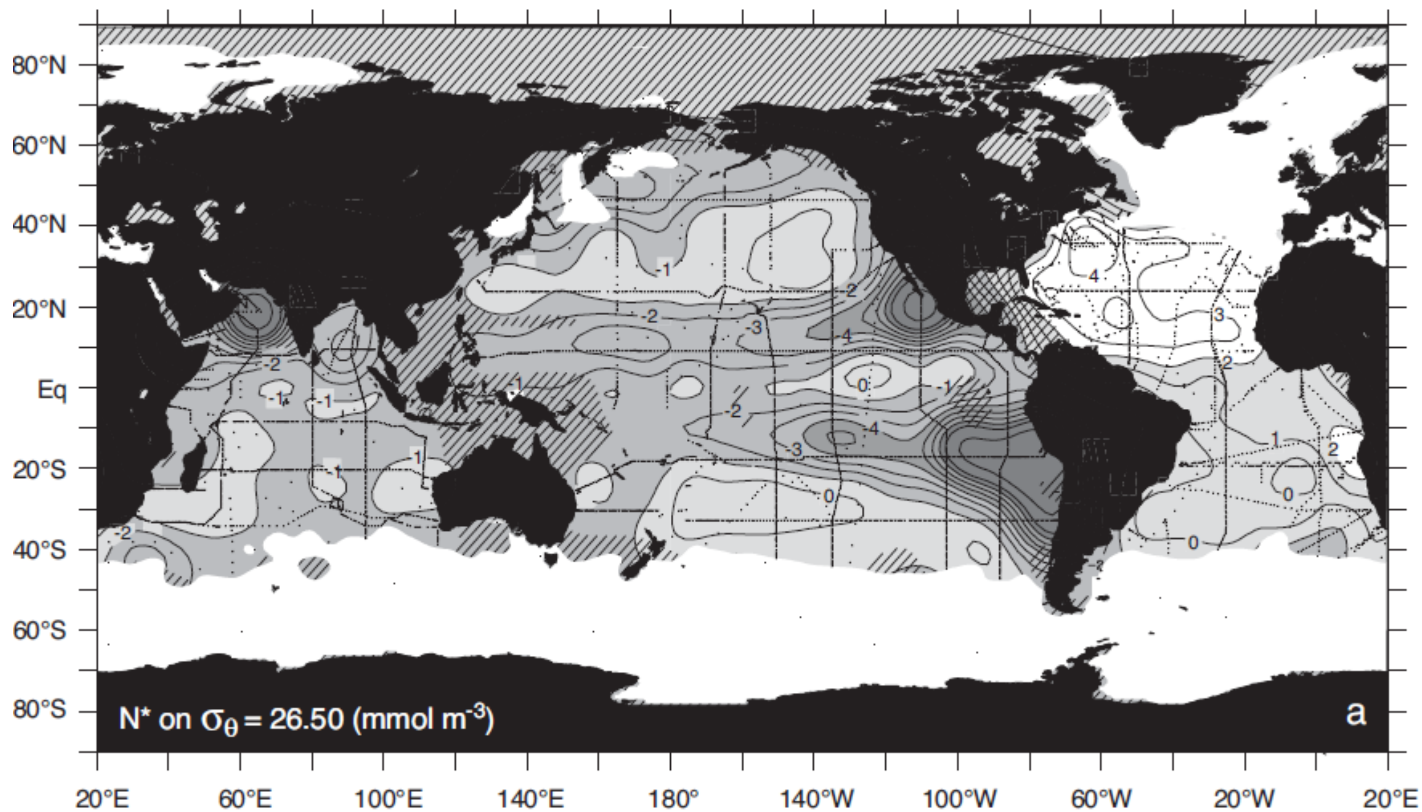
Gruber and Sarmiento, 2006

N* in the top of the thermocline



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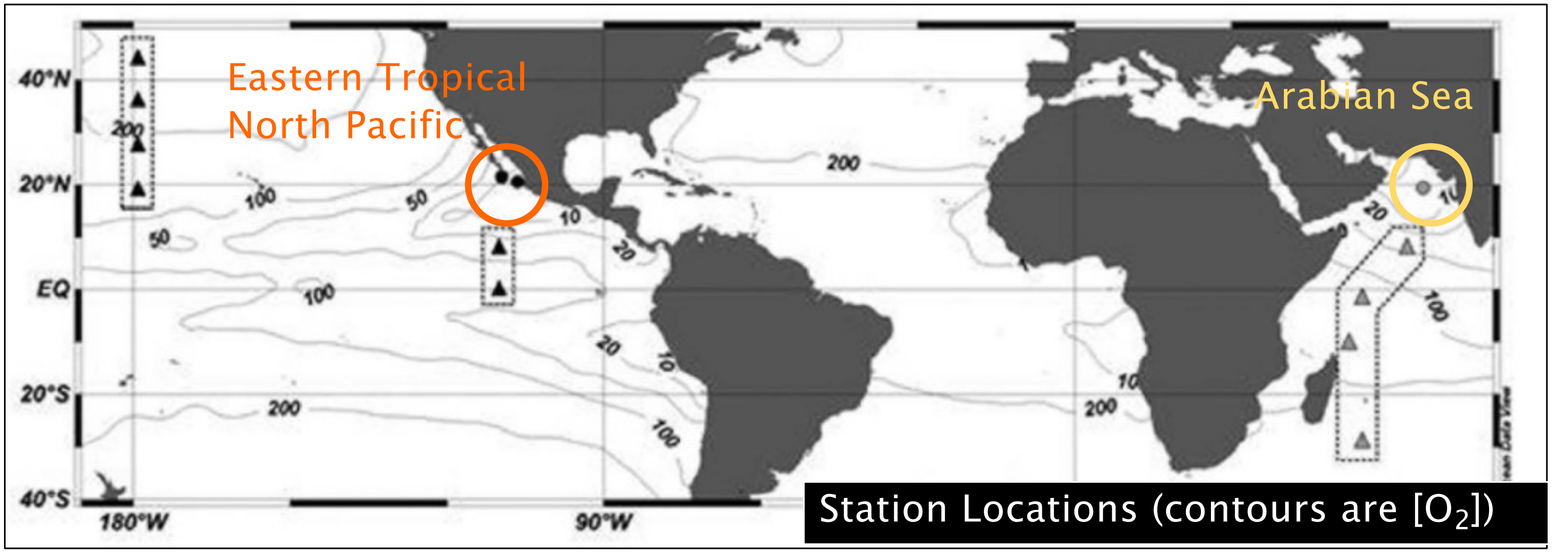
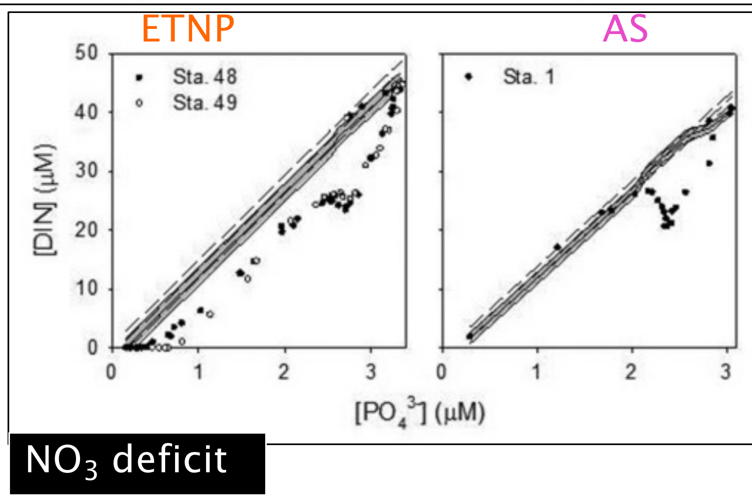
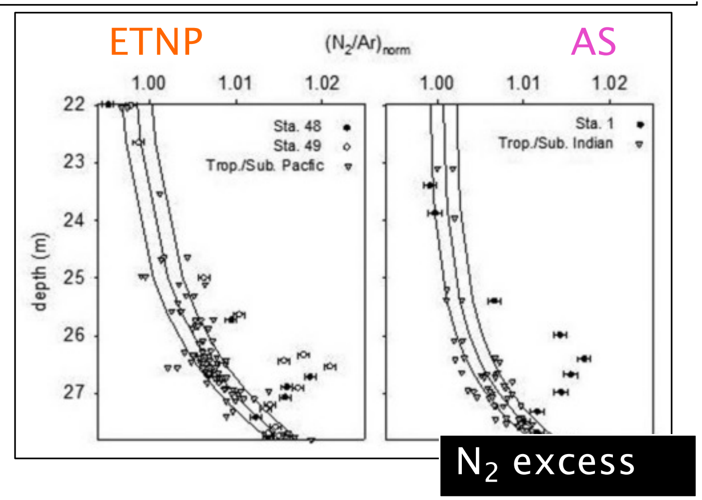
Gruber and Sarmiento, 2006

N_2/Ar ratio as a tracer for denitrification

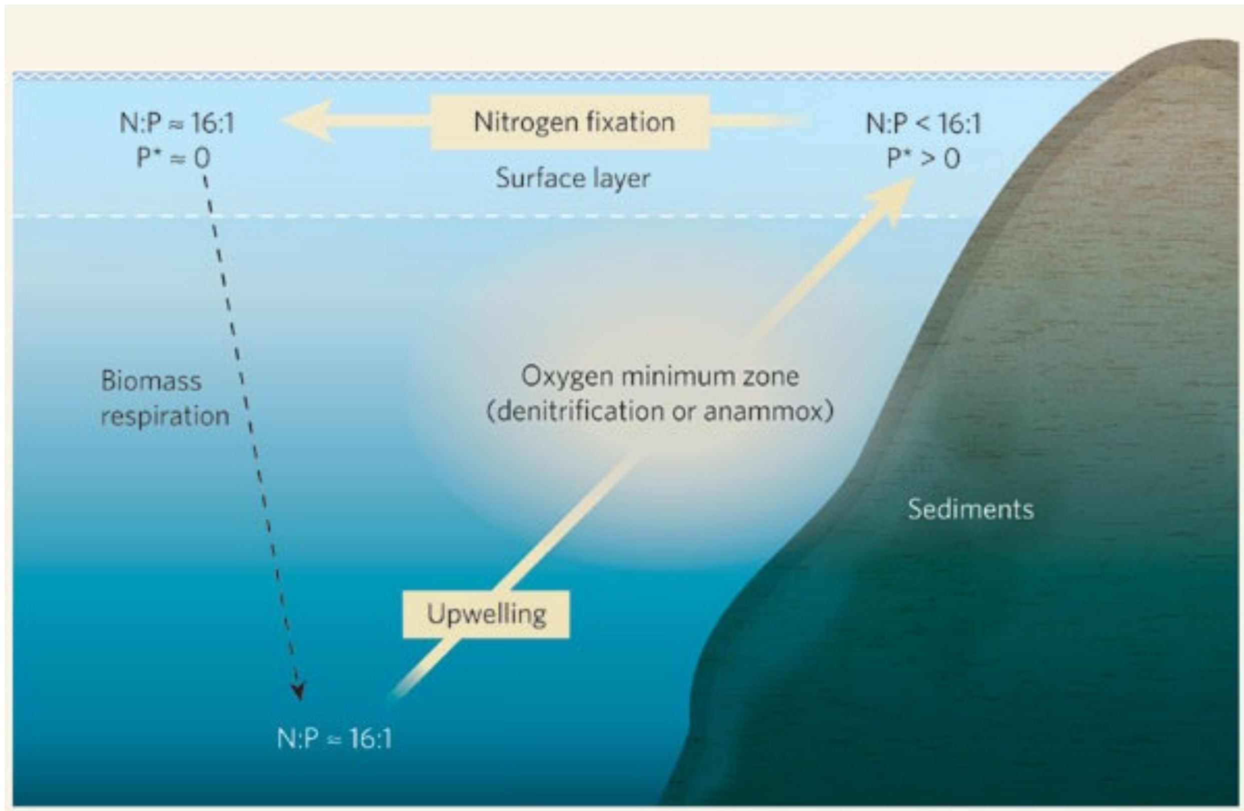
Chang et al (2012) GBC, 26







Coupling of N sources and sinks (Deutsch et al, 2007, Nature, 445, 163)



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Capone and Knapp (2007) Nature, 445, 159

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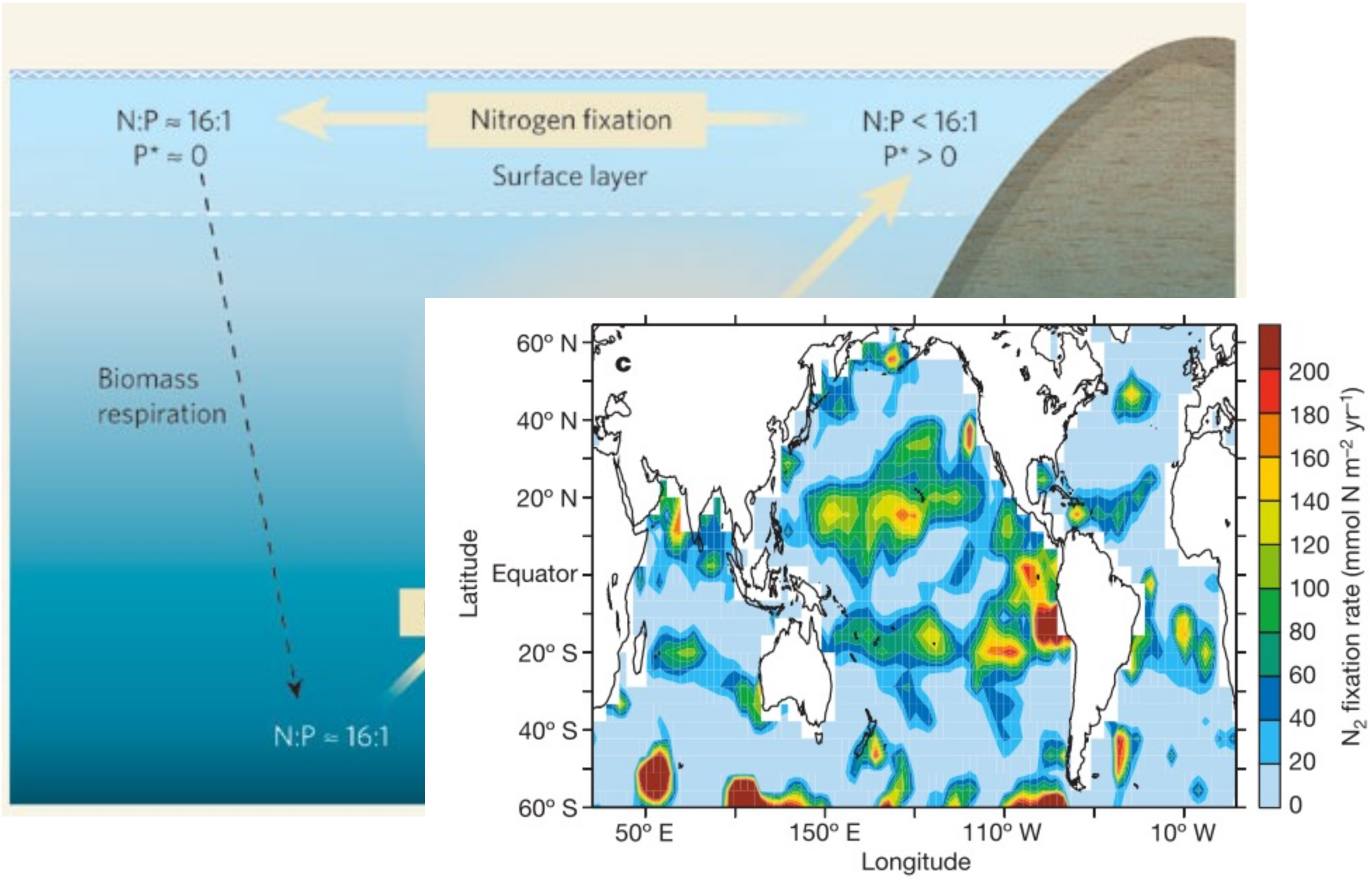

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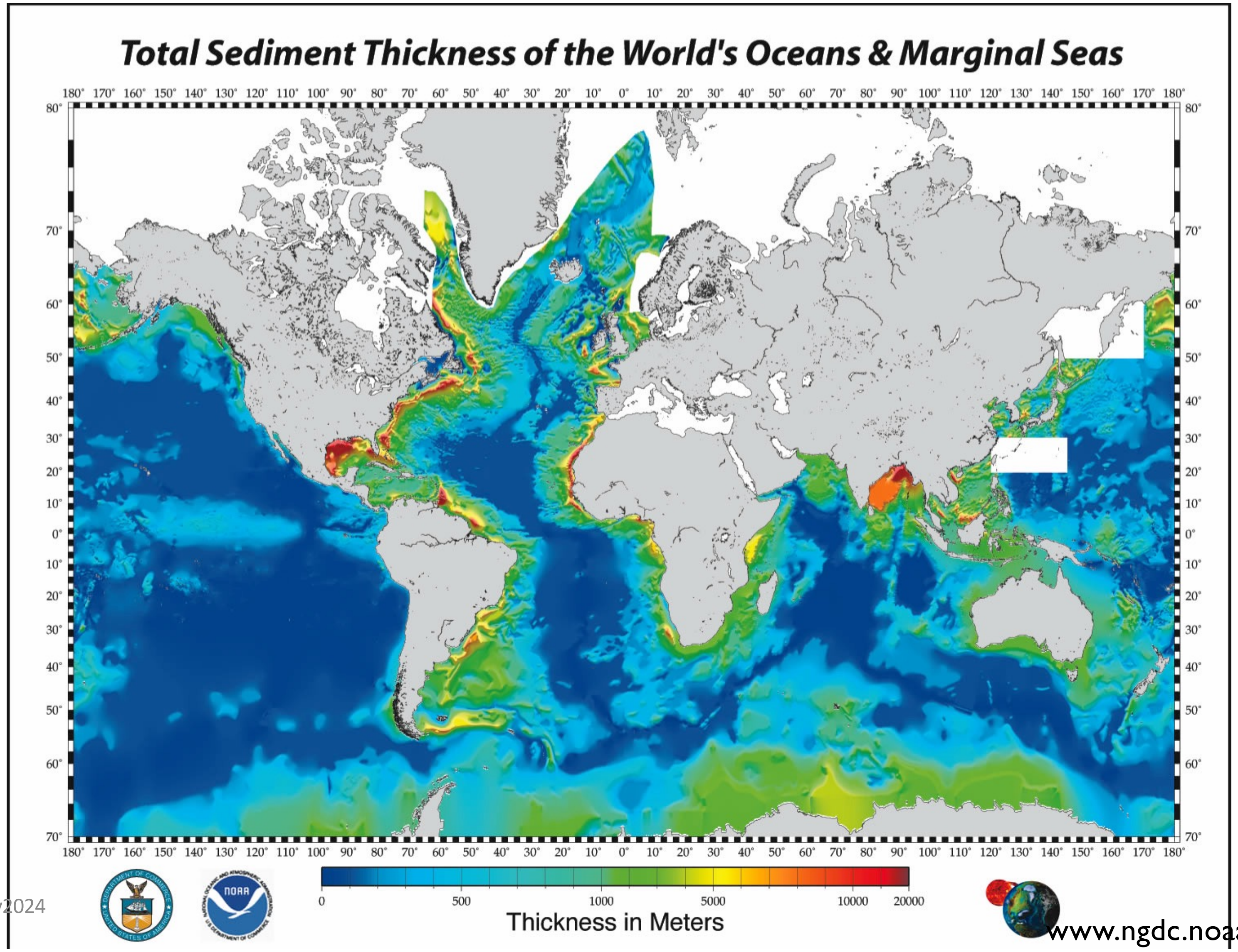
Capone and Knapp (2007) Nature, 445, 159

Chemical Composition of Biological Particulate Material

Hard Parts - Shells

Name	Mineral	Size (um)
Coccoliths	$CaCO_3$ Calcite	5
Diatoms	SiO_2 Opal	10-15
Silicoflagellates	SiO_2 Opal	30
Foraminifera	$CaCO_3$ Calcite and Aragonite	~100
Radiolaria	SiO_2 Opal	~100
Pteropods	$CaCO_3$ Aragonite	~1000
Acantharia	$SrSO_4$ Celestite	~100



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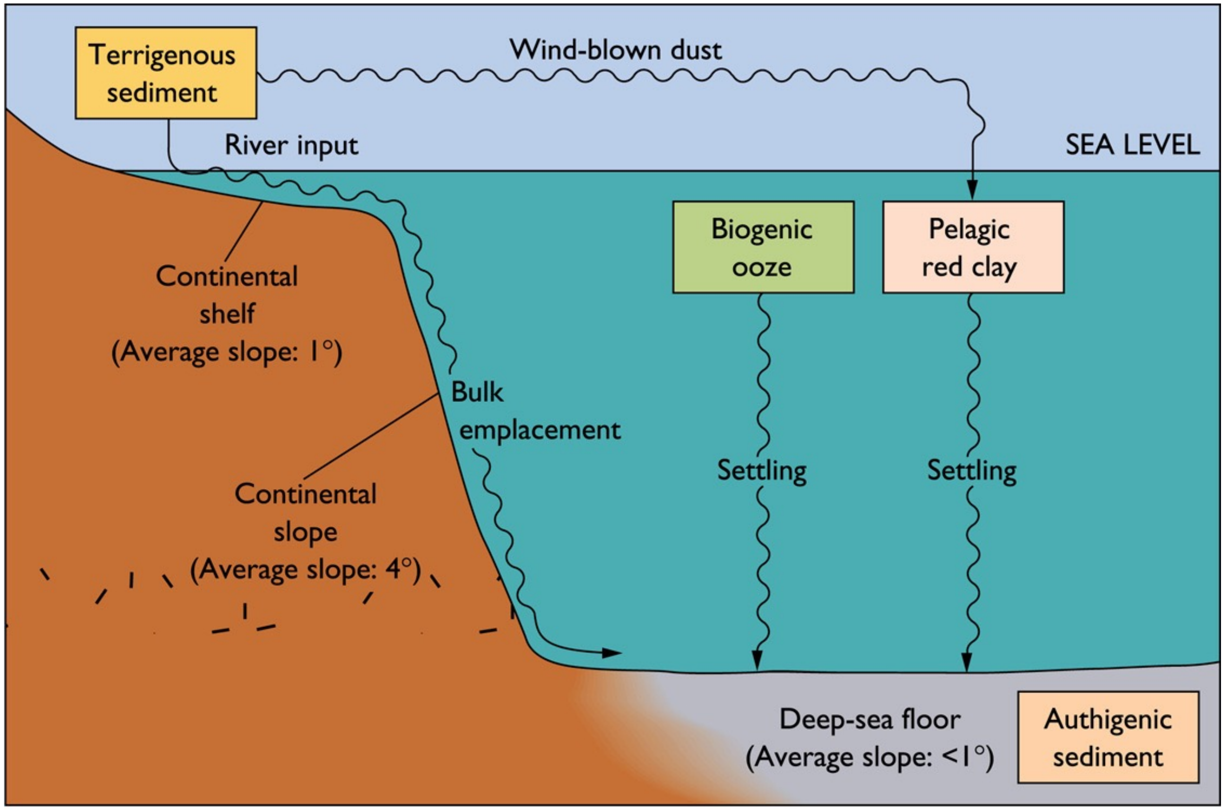
www.ngdc.noaa.gov/mgg/sedthick/sedthick.html

Deep Sea Sedimentation



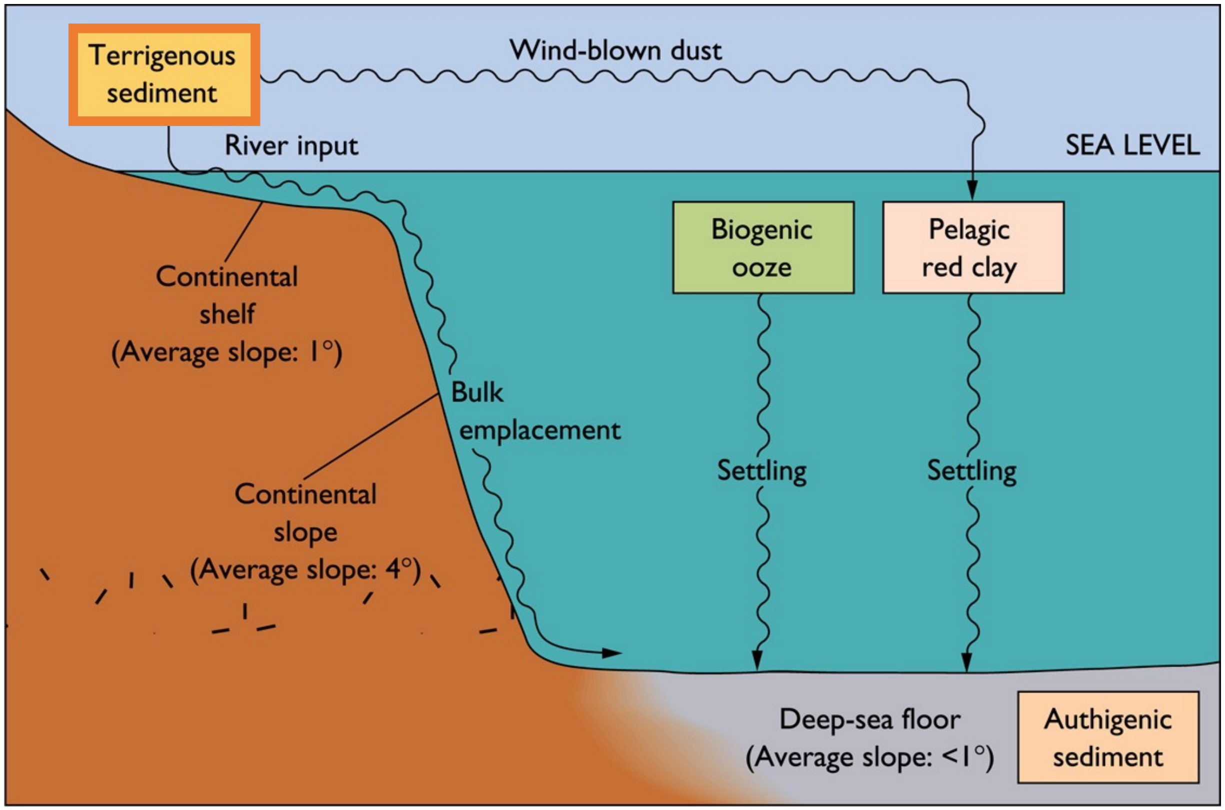
Major Sediment Types:

Detrital: non-living; from land

Authigenic: created in situ by precipitation in water (also known as hydrogenous)

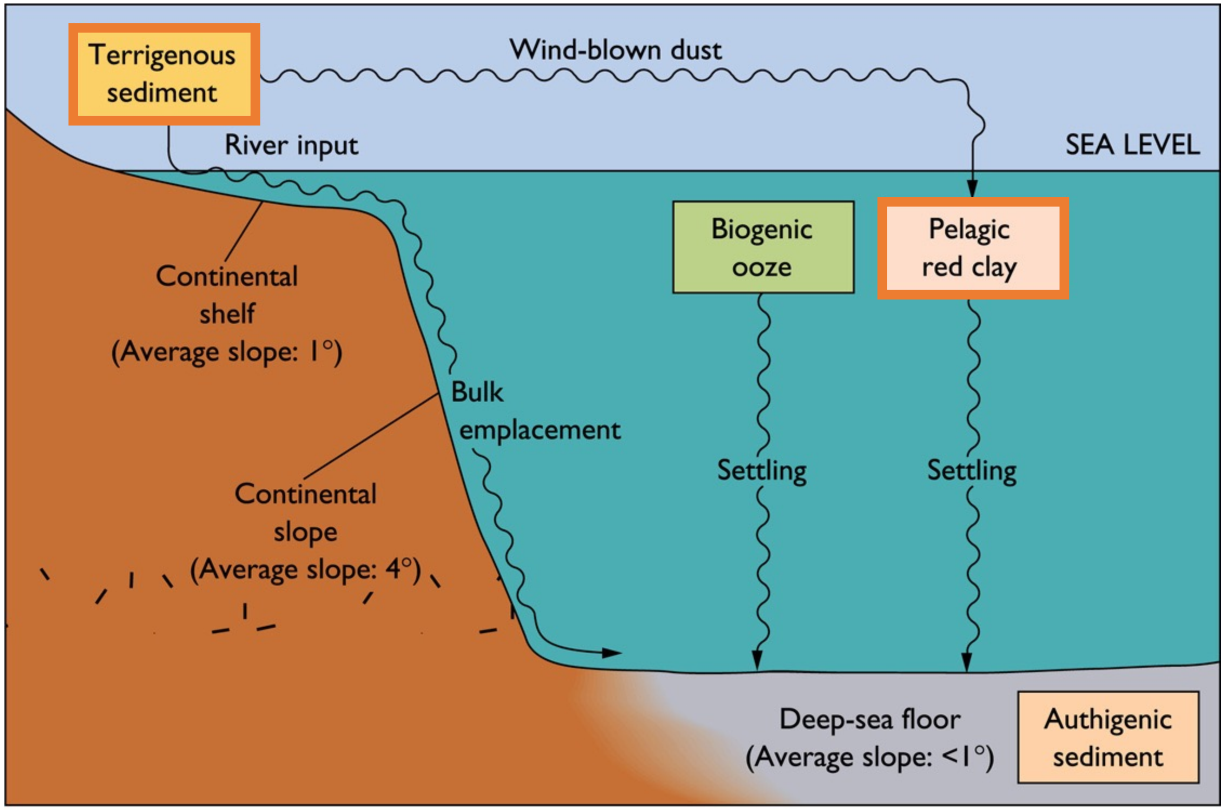
Biogenic: formed by marine organisms

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

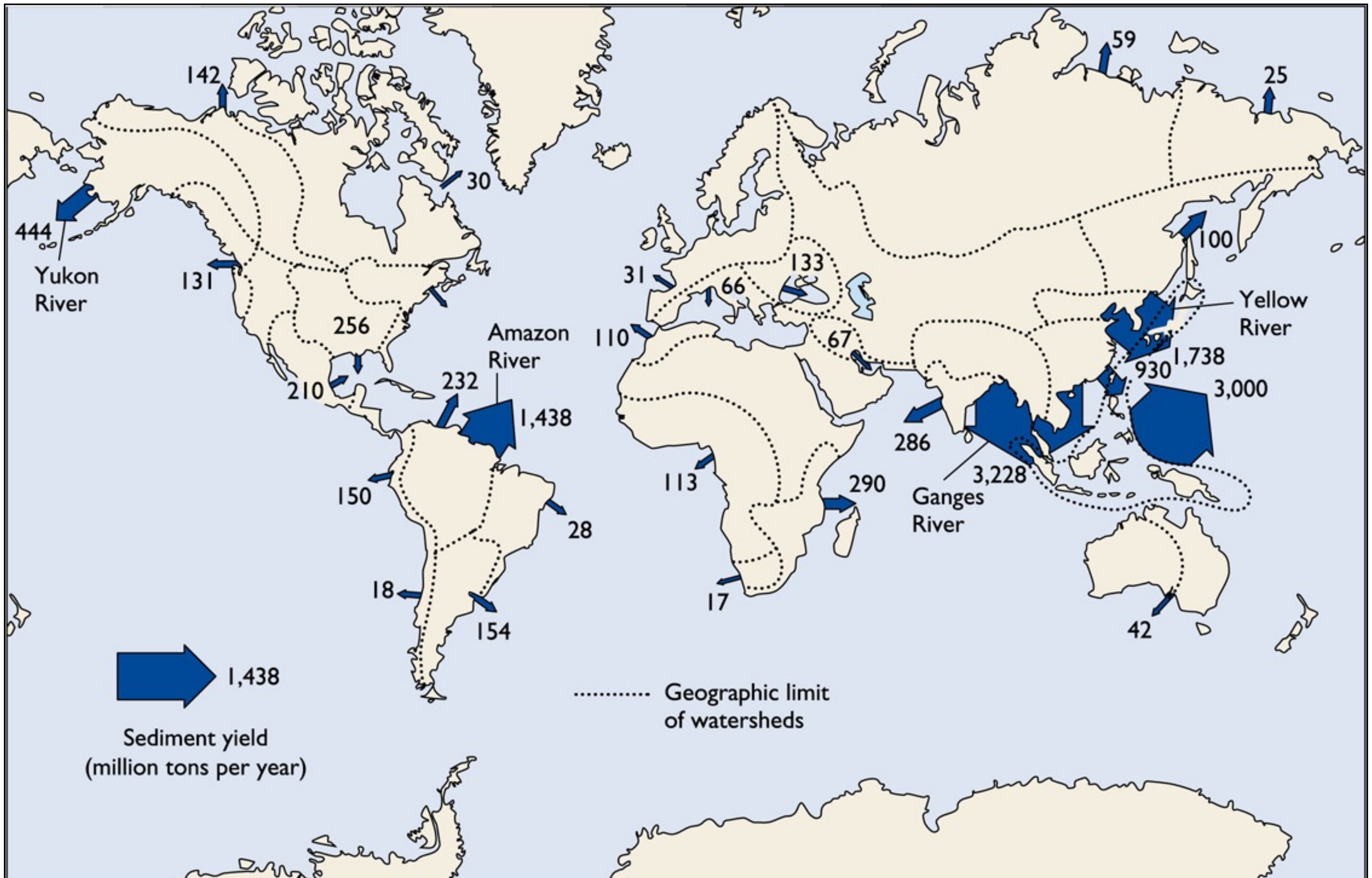
Detrital Sediments – red clay



- ***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

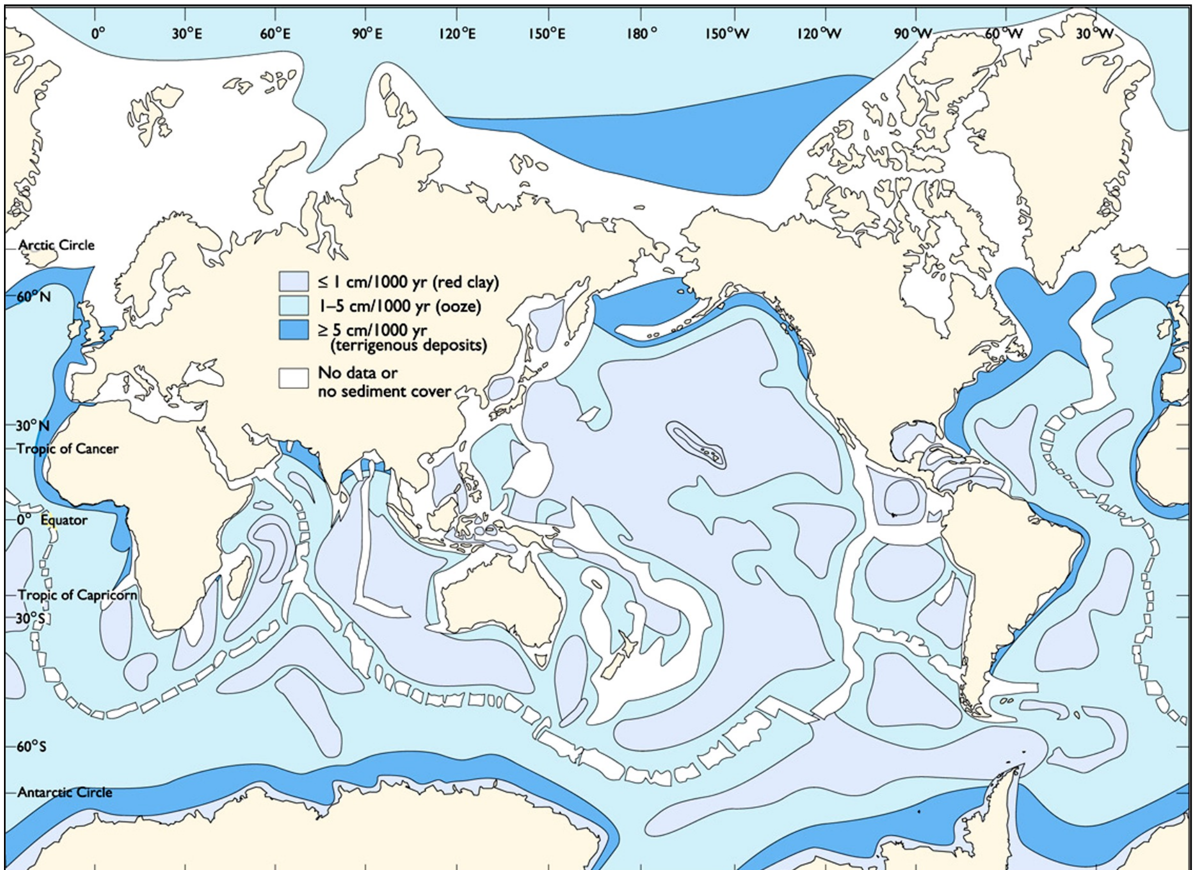
Riverine Sediment Inputs



(b) RIVER INPUT OF SILT TO OCEANS

Pinet 2006

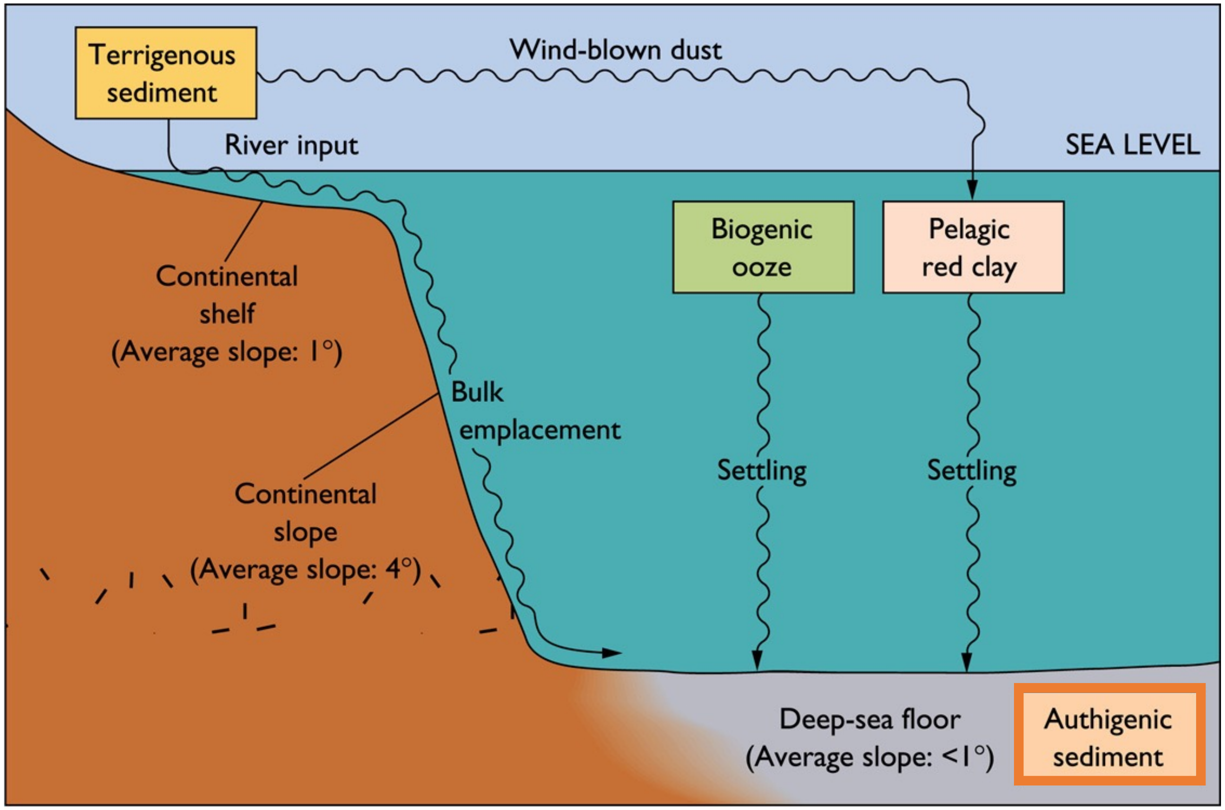
Sediment Deposition Rates



(b) SEDIMENTATION RATES

Pinet 2006

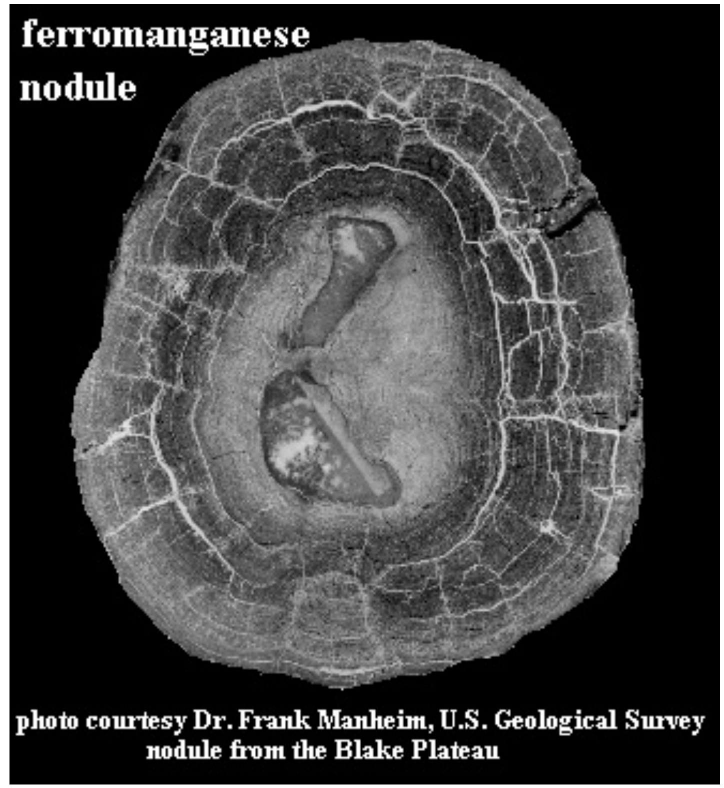
Authigenic Sediments



- Formed by crystallization within sediment or water column (also referred to as hydrogenous sediments)
- 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

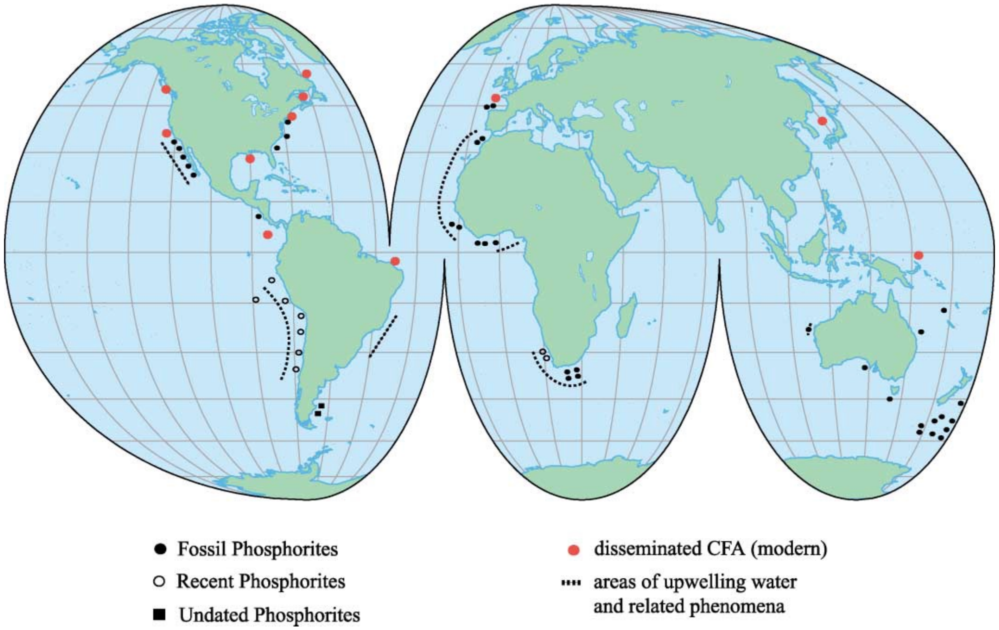
- Ferromanganese nodules
  - Deep-sea deposits
  - Concentric layers of metallic compounds
  - Precipitated by a combination of bacteria, foraminifera, and inorganic chemical reactions
  - Important commercial interest; contain precious metals



Major Authigenic Sediments

- 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
  - Major component to global P cycling

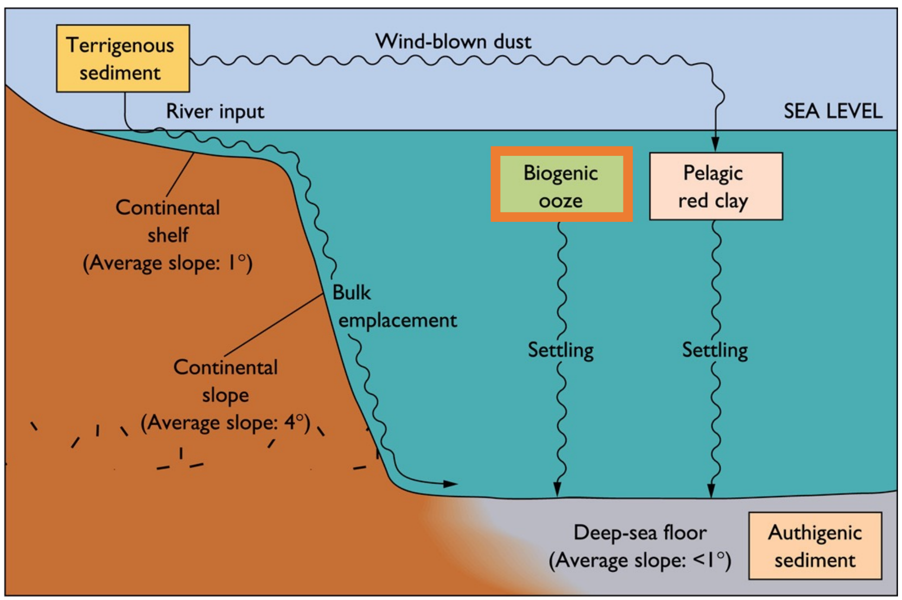
Distribution of disseminated CFA, recent and fossil phosphorites, and their relationship to upwelling areas



Ruttenberg (2003)

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 %



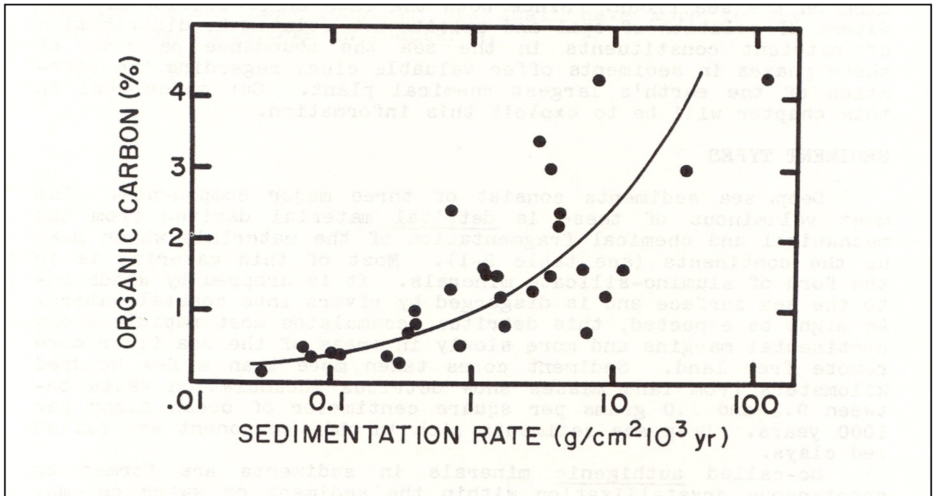


Figure 2-1. Organic carbon content of marine sediments as a function of bulk sediment accumulation rate. Results summarized by Ross Heath and his colleagues (531).

Composition of Biogenic Sediments

- Biogenic oozes are fine-grained sediments -- at least 30% is shells of micro-organisms
- Classified by their composition:
  - Calcareous oozes consist of the CaCO3 shells of:
    - Foraminifera (animals, protozoa)
    - Pteropods (planktonic gastropods)
    - Coccoliths (algae)
    - Ostracods (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

Composition of Biogenic Sediments

- Biogenic oozes are fine-grained sediments -- at least 30% is shells of micro-organisms
- Classified by their composition:
  - Calcareous oozes consist of $CaCO_3$ shells
  - ***Siliceous oozes*** consist of the shells of:
    - **Radiolarians** (protozoa)
    - **Diatoms** (algae)

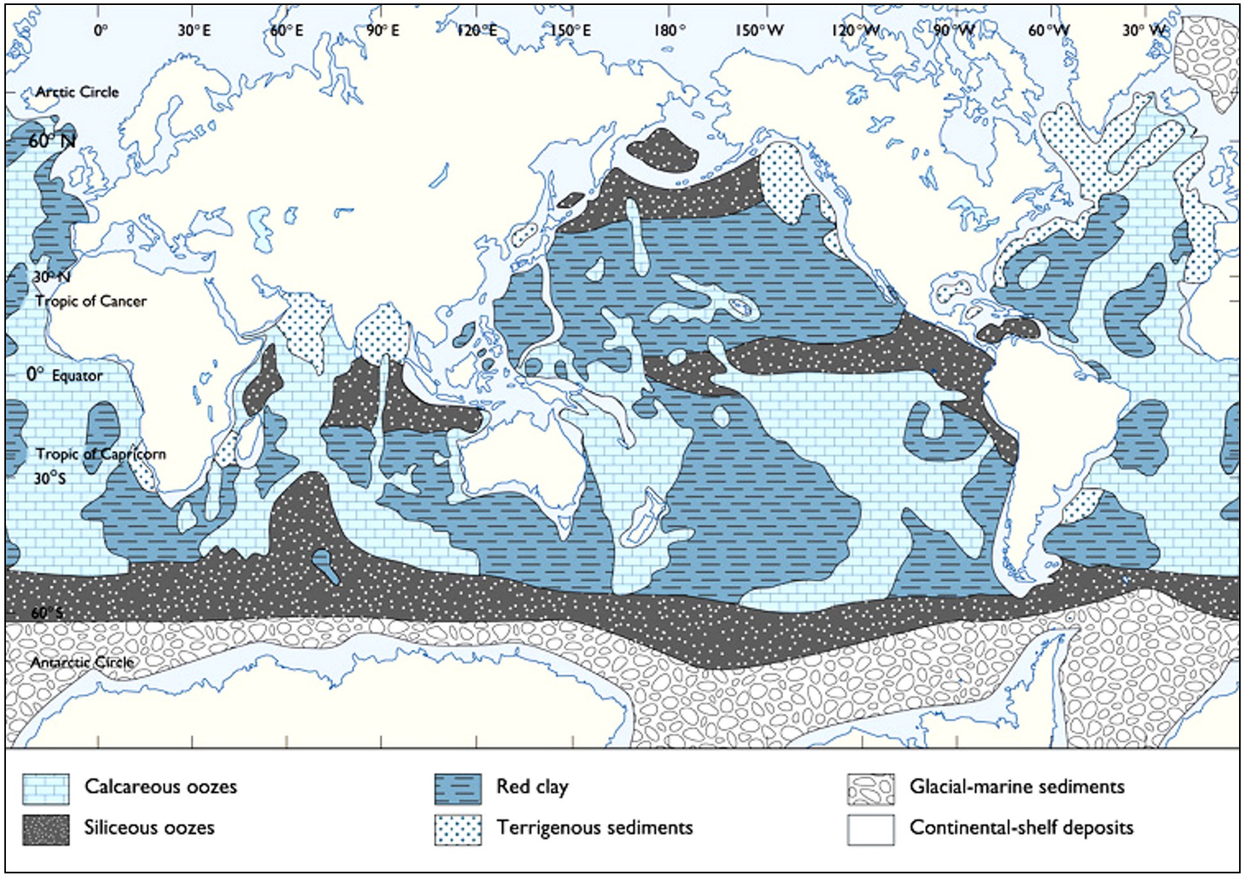
  - Diatoms are common in cold water (Antarctica)
  - Radiolaria are common near the equator
  - Siliceous oozes account for about 14% of deep-sea sediment
  - Distribution of ***opal*** ($SiO_2 \cdot nH_2O$) in deep-sea sediments is closely related to pattern of productivity in overlying water…

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?

Deep-Sea Sediment Distribution



Seawater Si Removal by Phytoplankton

Dominated by Upwelling Regions:

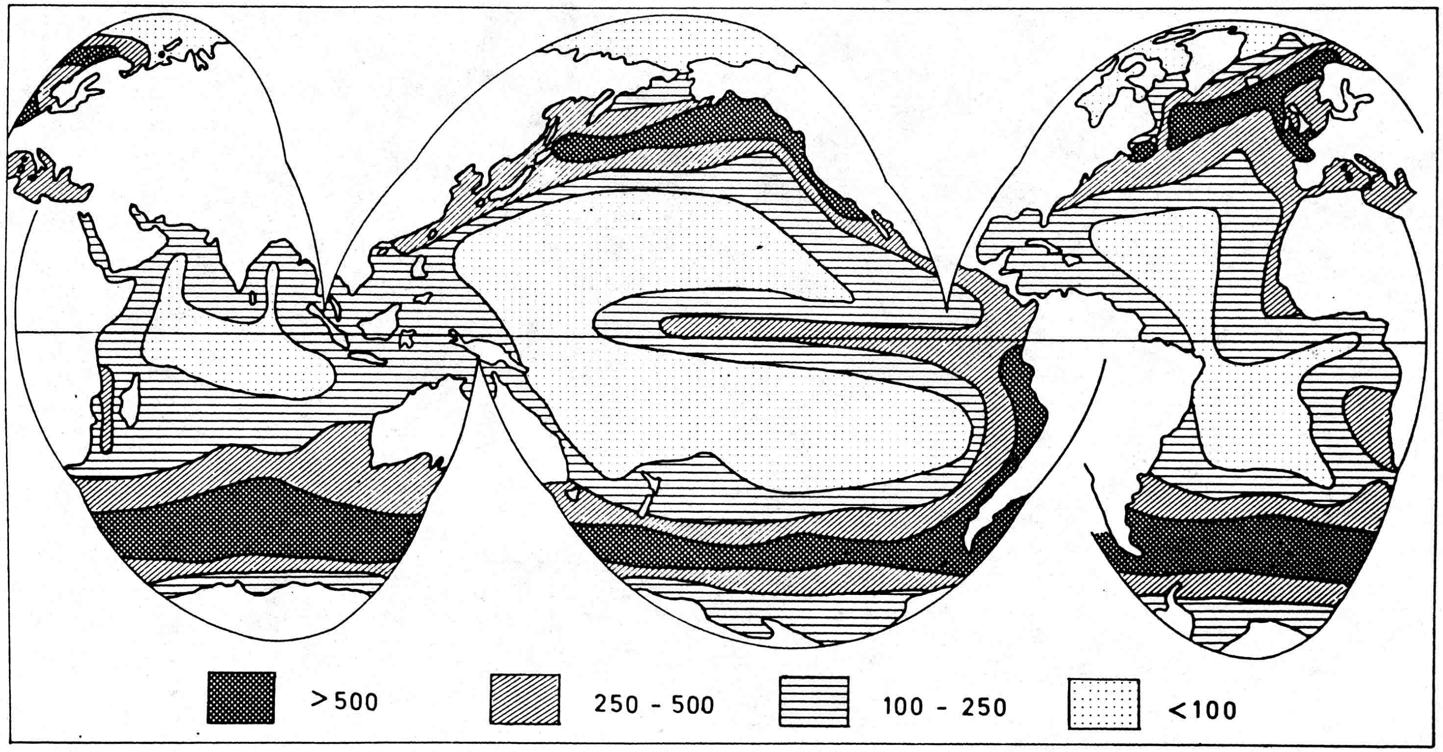


Fig. 2. Regional variation in the rate of extraction of dissolved silicon (g SiO_2 m^{-2} $year^{-1}$) by phytoplankton in near-surface waters. Modified from Lisitzin *et al.* (1967).

Distribution of Opal in Marine Sediments

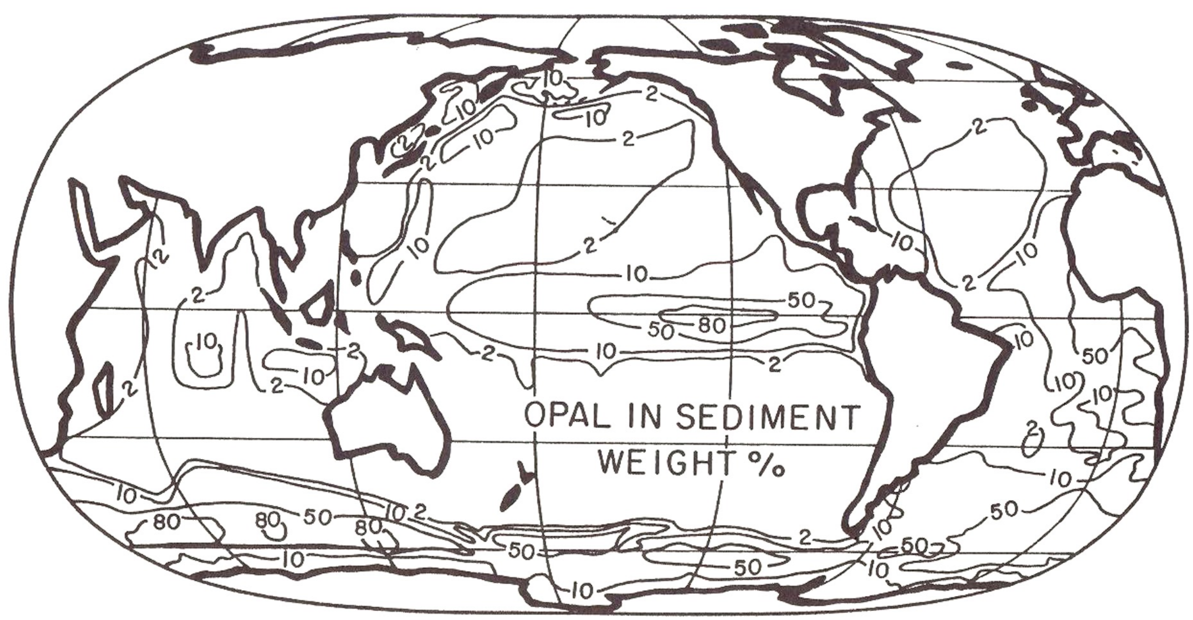
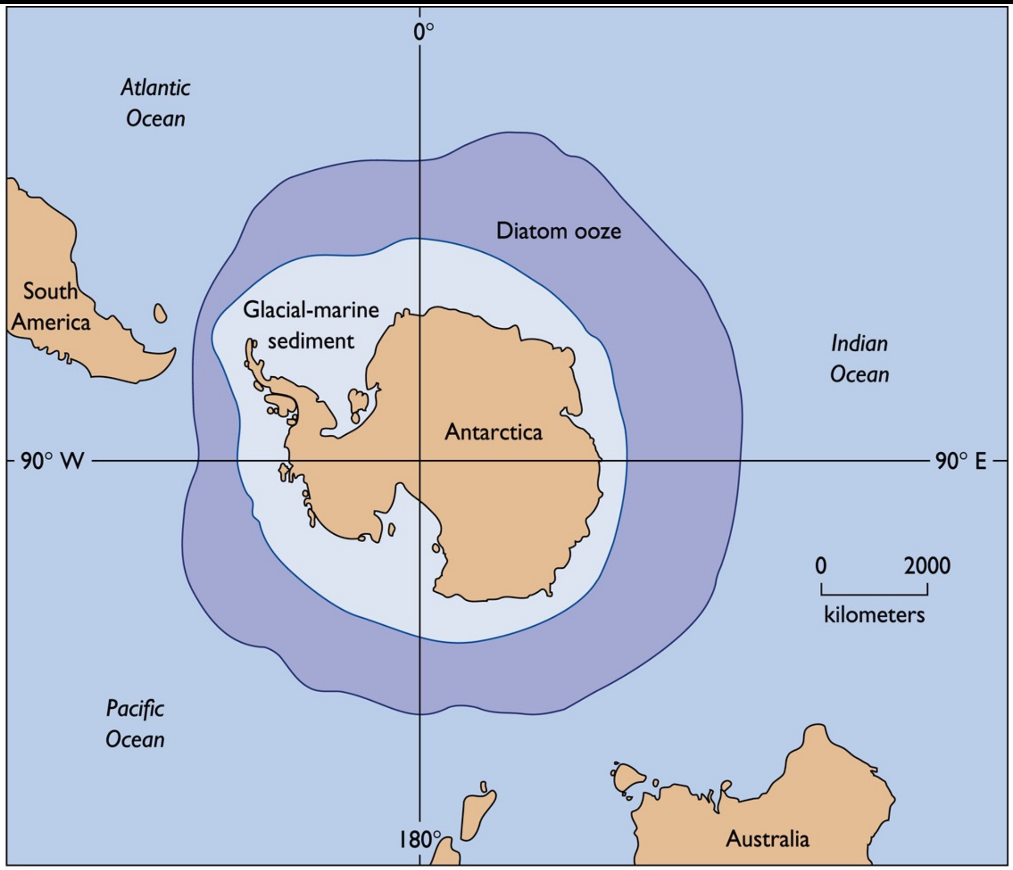


Figure 2-2. The distribution of opal in marine sediments. Prepared by Ross Heath of Oregon State University. It must be kept in mind that, since this map shows the proportion of opal in the sediment, the patterns depend on the rate of accumulation of the non-opal components of the sediment as well as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

Opal sediments around the Southern Ocean



(b) DEEP-SEA DEPOSITS AROUND ANTARCTICA

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 sediments
- 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 TCO_2 (more acidic) deep water

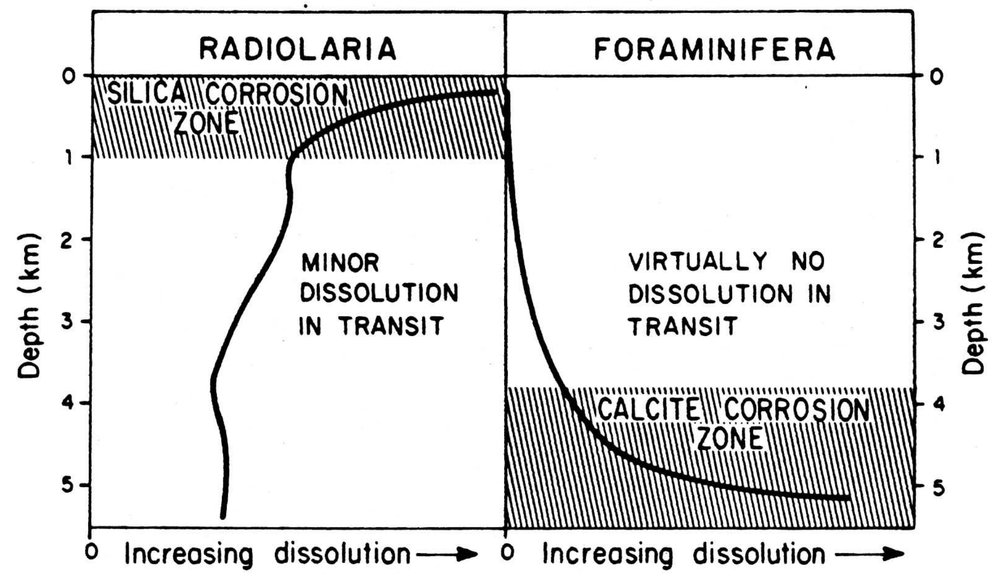


FIG. 29.17. Corrosion zones for siliceous and calcareous particles, based on field experiments in the North Pacific near 19° N, 169° W (Berger, 1967, 1968b). Boundaries have been drawn at depth of maximum rate change, they are not the same as facies boundaries in the ocean.

Berger, 1976

Exam – Feb. 6, 2024

- Take home – 1:30pm Tuesday to 1:30pm Wednesday
  - My goal is **NOT** for you to spend 24 hours straight on this, but ideally to give you time to think / take your time if you want it
- Available through Laulima
- I will be available the first 1.25 hours of the exam (either in person or via zoom), then e-mail otherwise
- Open book, open notes. Please don't discuss with others. Please don't search online (can't see it being very helpful) unless it's for something like the Universal Gas Constant.
- Review session this Thursday during class – come with questions or I will just go through highlights