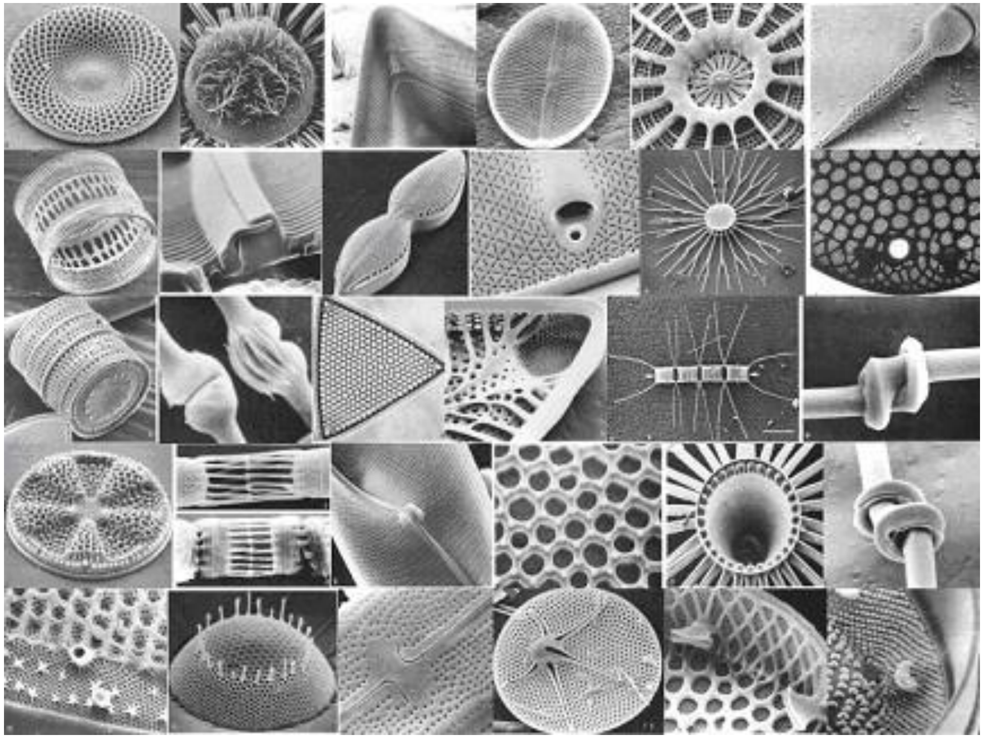
The Oceanic Biogeochemical Cycle of Si

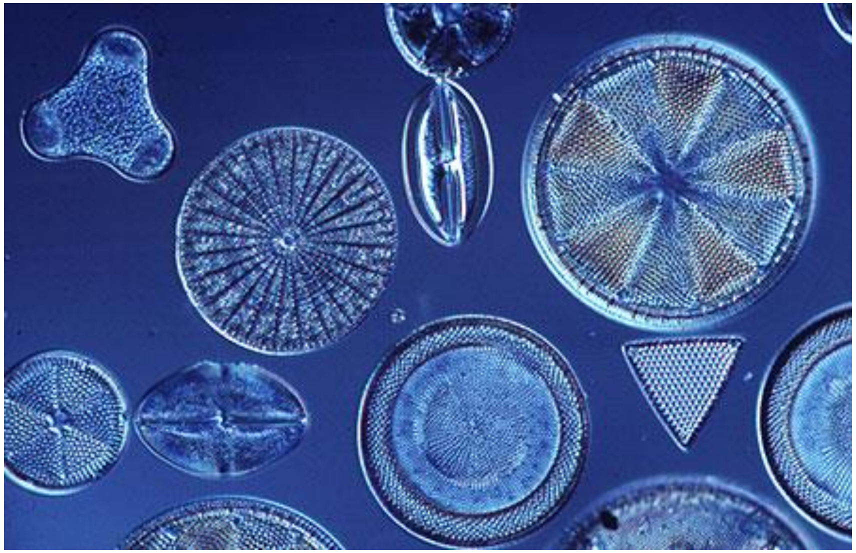
Silicon

- Major nutrient: for selected organisms (e.g. diatoms, radiolarians, sponges)

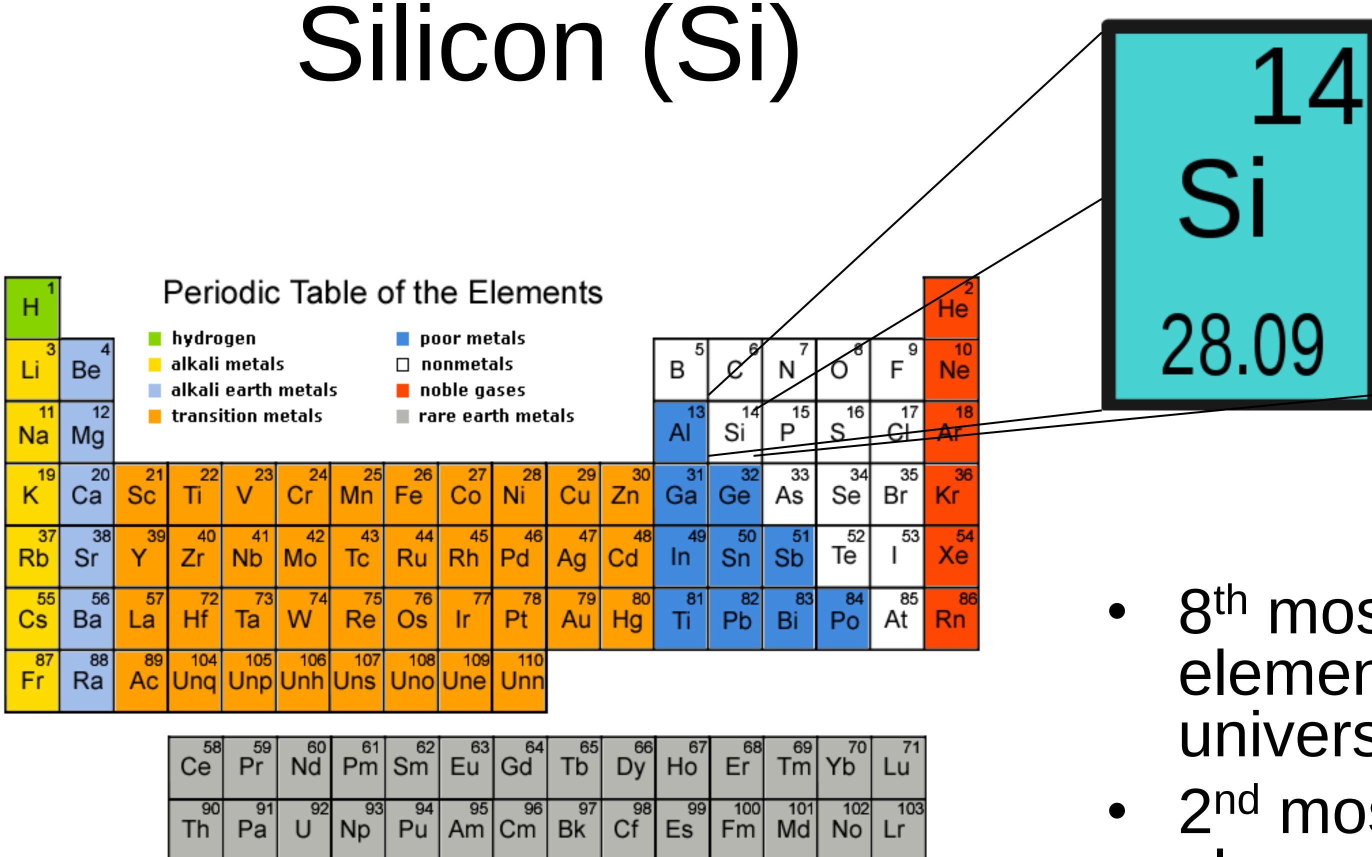
- Diatoms can account for up to 40 % of marine primary production)

- Plays an important role in the ‚biological pump‘





Silicon (Si)



- 8th most abundant element in the universe
- 2nd most abundant element in the earth's crust

Silicon

On land:

- Silicate minerals (combined with cations e.g. Fe, Mg, Ca)
- Quartz (pure SiO_2, stable crystalline)

In Ocean:

Suspended or particulate material

- From weathering of rocks: quartz, feldspar, clay minerals
- Framework silicate minerals are thermodynamically very stable, therefore, on biological time scales their dissolution in the ocean is very slow
- Biogenic silica: amorphous (non-crystalline) SiO_2 (opal) from plankton

Dissolved

- mainly from dissolution of amorphous silica
- SiO_2 (s) + 2 H_2O $\rightarrow$ $Si(OH)_4$ (aq)
- Silicic acid (often referred to as silicate)
- Not known if there are dissolved organic forms (likely negligible)

Silicate minerals

Quartz
SiO_2

Olivine
$(Mg,Fe)_2SiO_4$

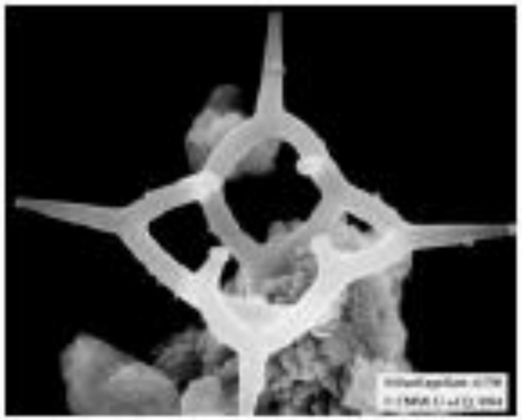
- Most of the Si in nature is found in silicate minerals

Kaolin
$Al_2Si_2O_5(OH)_4$.

Opal

- Biogenic silica = amorphous opaline silica = opal
- $SiO_2 \cdot n\ H_2O$

Silicate (silicic acid) is used by several important groups



Silicoflagellates

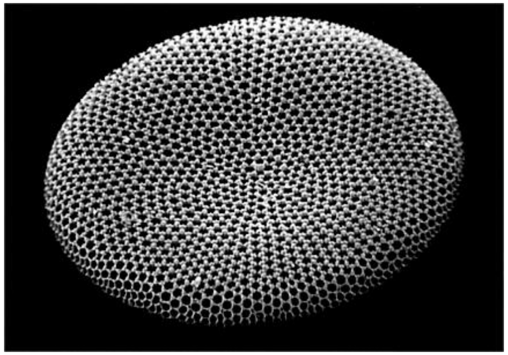
Radiolarians

Glass sponges

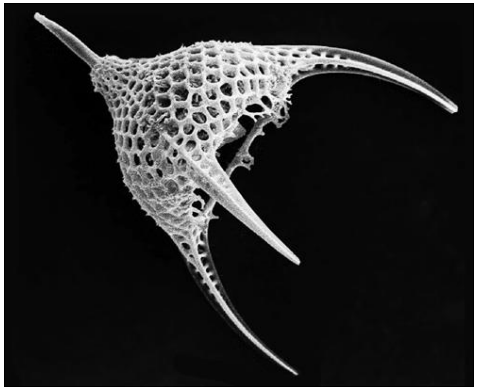
Diatoms

Si: an essential nutrient

Horsetail
(*Equisetum sp.*)



Diatoms



Radiolarians

Bamboo

Sponges

Silicoflagellates

Silicic acid or ‚Silicate'

1st dissociation

$H_4SiO_4 \rightarrow H^+ + Si(OH)_3O^-$

For NaCl (0.6M; 25 C) $pK_{si}^* = 9.47$

Therefore $\frac{[H_3SiO_4^-]\,[H^+]}{[H_4SiO_4]} = 3.9 \times 10^{-10}$

at pH of 8.2, only about 5% of silicic acid is ionized

2nd dissociation

$pK^{2*} = 12.6$

$H_3SiO_4^{2-} \rightarrow H_2SiO_4^{2-} + H^+$

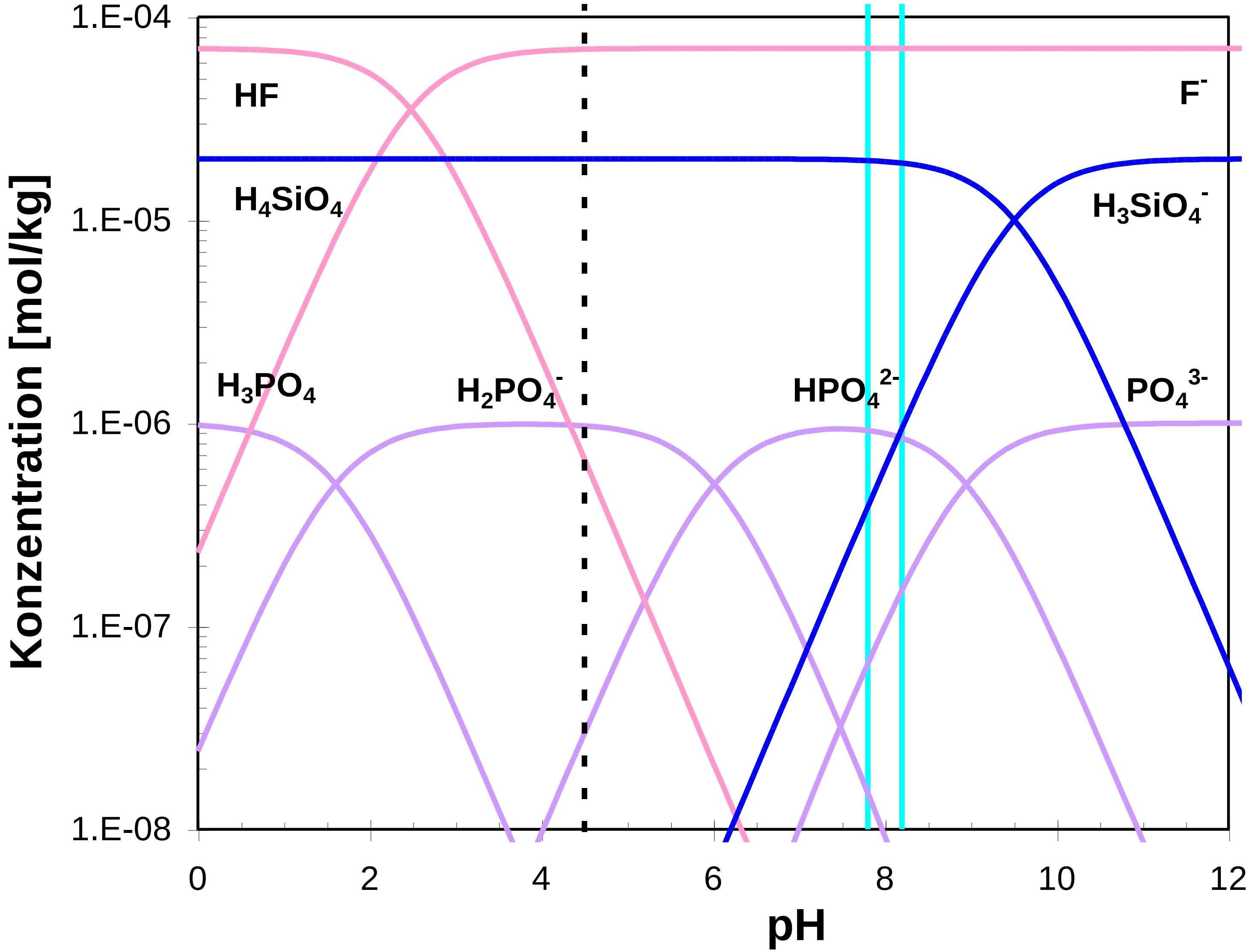
Therefore

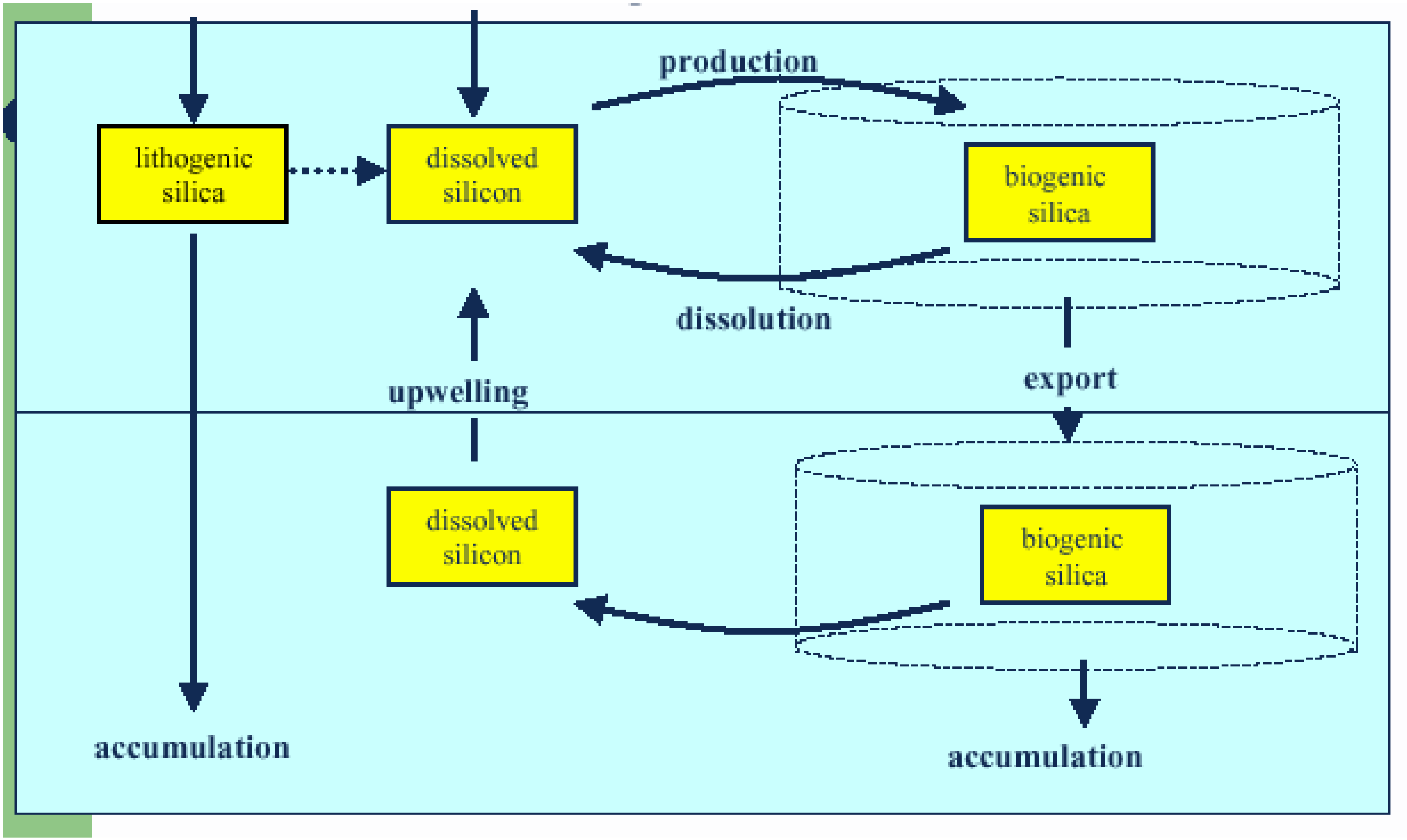
$$\frac{[H_2SiO_4^{2-}][H^+]}{[H_3SiO_4^-]} = 2.5 \times 10^{-13}$$

at pH of 8.2, this silica species is completely negligible.

Dissolved silicate concentration range in the ocean: 0-200 μmol kg^{-1}

Inorganic Speciation




production
lithogenic silica
dissolved silicon
biogenic silica
dissolution
upwelling
export
dissolved silicon
biogenic silica
accumulation
accumulation

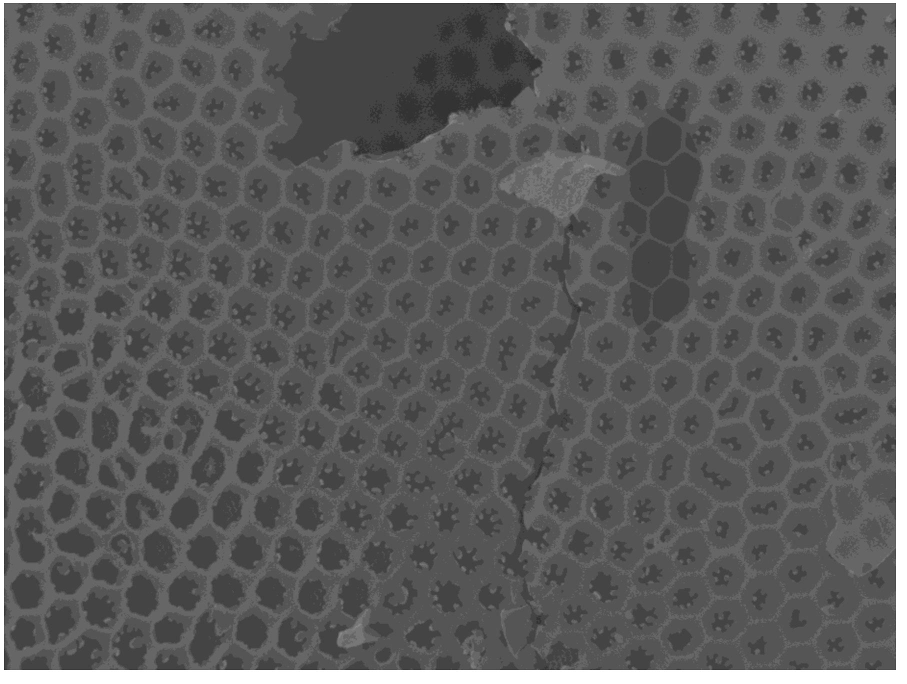
Biogenic silica production

- Biogenic silica production ranges between 2 and 90 mmol m^{-2} . d^{-1} (200-280 Tmol Si yr^{-1})
- Without resupply of silicic acid to the surface ocean, the photic zone would be depleted in less than 100 days!!
- Where does the resupply come from?

Dissolved silica inputs

- Reactive Si (Si that can be utilised by organisms) enters the ocean from rivers, Aeolian dust and hydrothermal sources.
- Inputs of reactive Si to the ocean only account for about 6 Tmol Si yr^{-1}.

Biogenic silica recycling

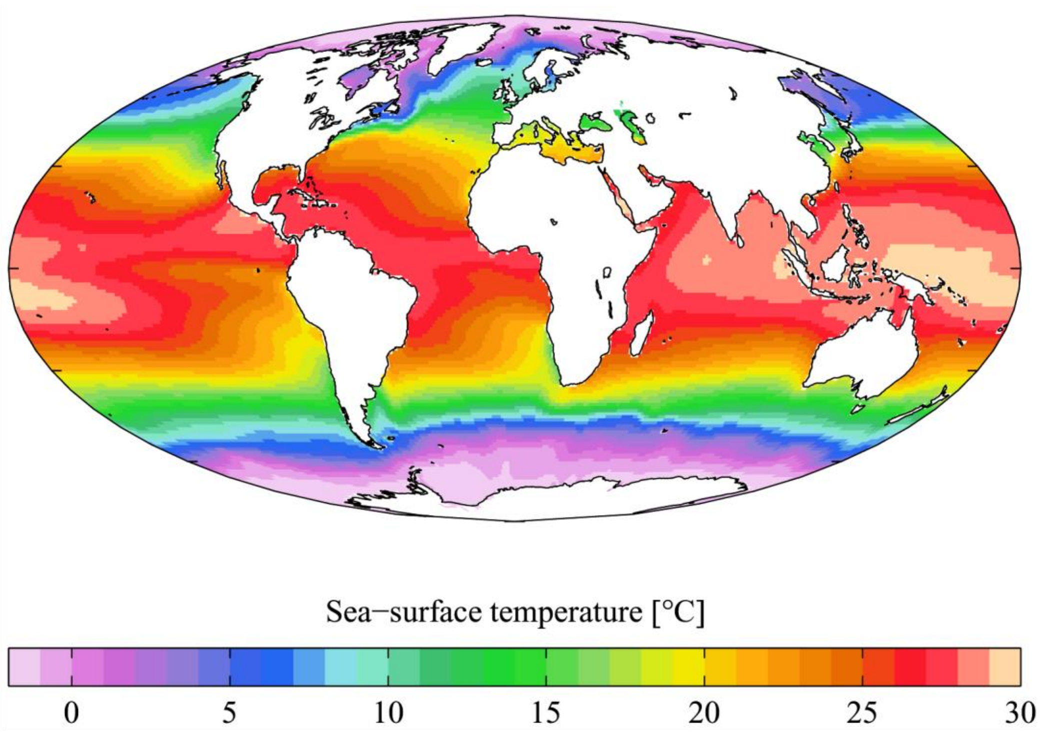


- Unlike crystalline silicate minerals, biogenic silica is very unstable in seawater and dissolves relatively fast.

Dissolution efficiency

- Environmental parameters
  Temperature and Pressure
- Intrinsic properties of the frustules
  Silicification (thickness, surface area)
- Ecosystem processes
  bacterial activity
  grazing and faecal pellet formation
  aggregation

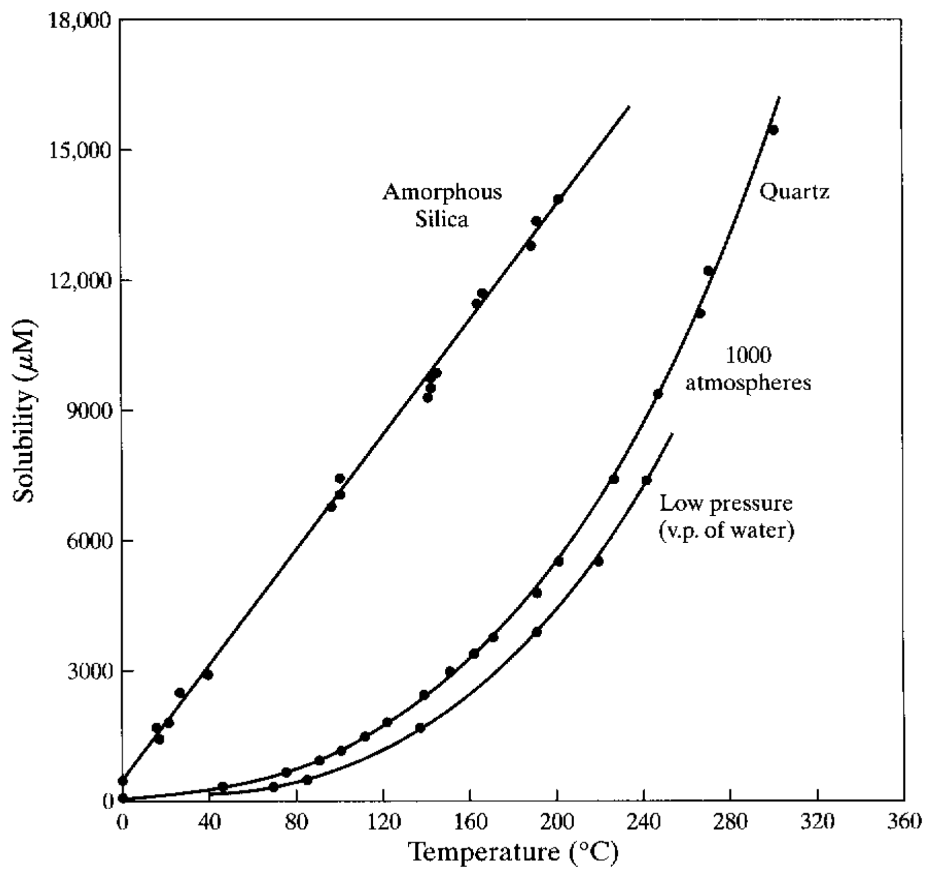
Temperature

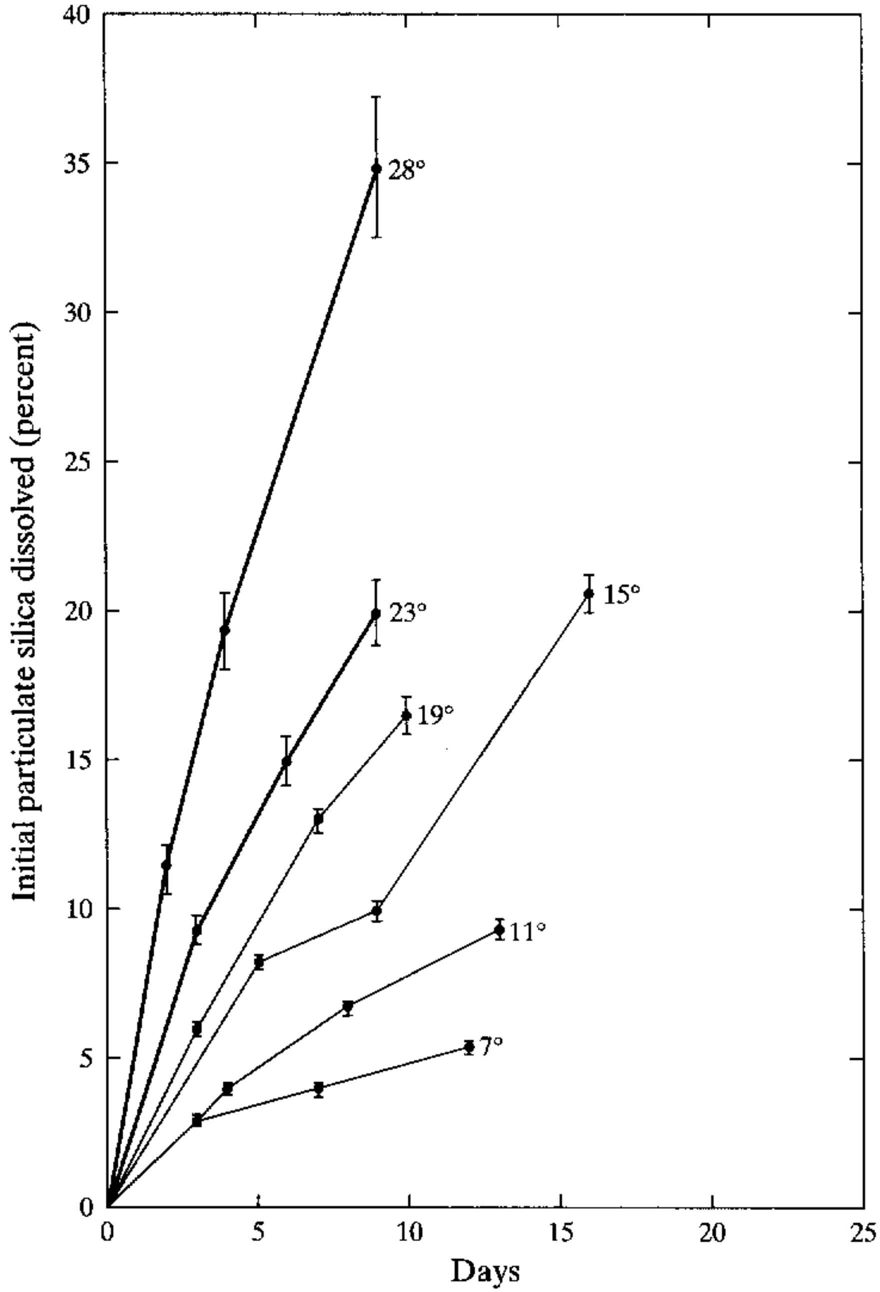


Dissolution rates of biogenic silica can be more than 10 times slower in polar than equatorial waters

Temperature

- Higher T can enhance the bacterial degradation of the protective organic layer which encases diatom frustules.
- Higher T enhances diatom growth rates leading to less silicified frustules.


18,000
15,000
12,000
9000
6000
3000
0
0
40
80
120
160
200
240
280
320
360
Solubility (μM)
Temperature (°C)
Amorphous Silica
Quartz
1000 atmospheres
Low pressure (v.p. of water)


40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
Initial particulate silica dissolved (percent)
Days
28°
23°
19°
15°
11°
7°

Solubility and Dissolution of Silica

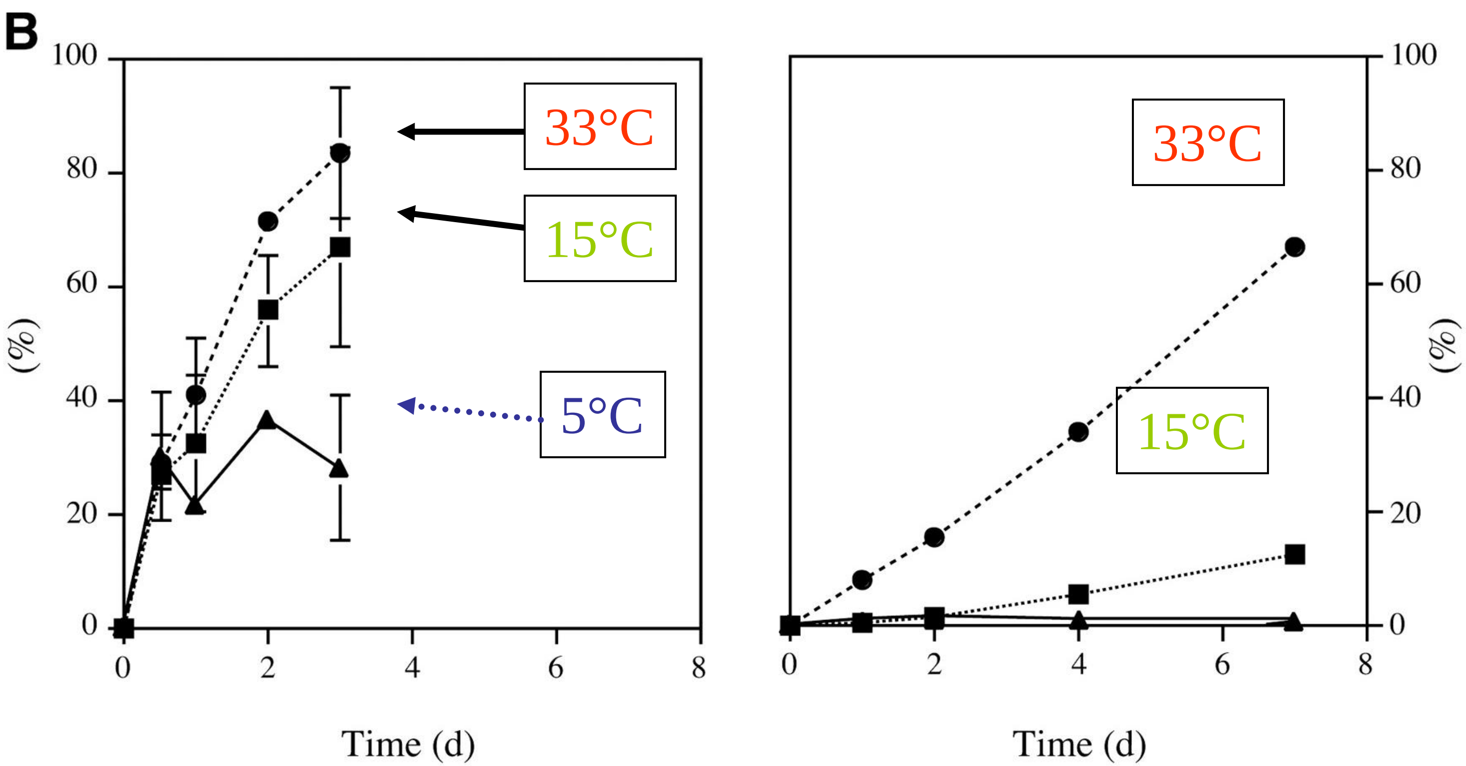
- Quartz solubility: 100 μmol kg^{-1} (25°C), 50 μmol kg^{-1} (5°C)
  Deep oceans are SUPERsaturated
  Quartz does not precipitate (kinetic barriers)

- Amorphous silicate (opal) solubility: 1800 μmol kg^{-1} (25°C)
  Solubility of ‚real' diatom shells: 1600 μmol kg^{-1} (25°C)
  900 μmol kg^{-1} (3°C)
  Surface and Deep oceans are UNDERsaturated,
  BUT organisms precipitate opal within the oceans,
  once formed, opal tends to dissolve
  dissolution rate is: temperature dependent
  slightly pressure dependent
  surprisingly slow

Warming can directly affect the ocean's biological carbon pump in complex ways (Bidle et al, 2002)

POC utilization

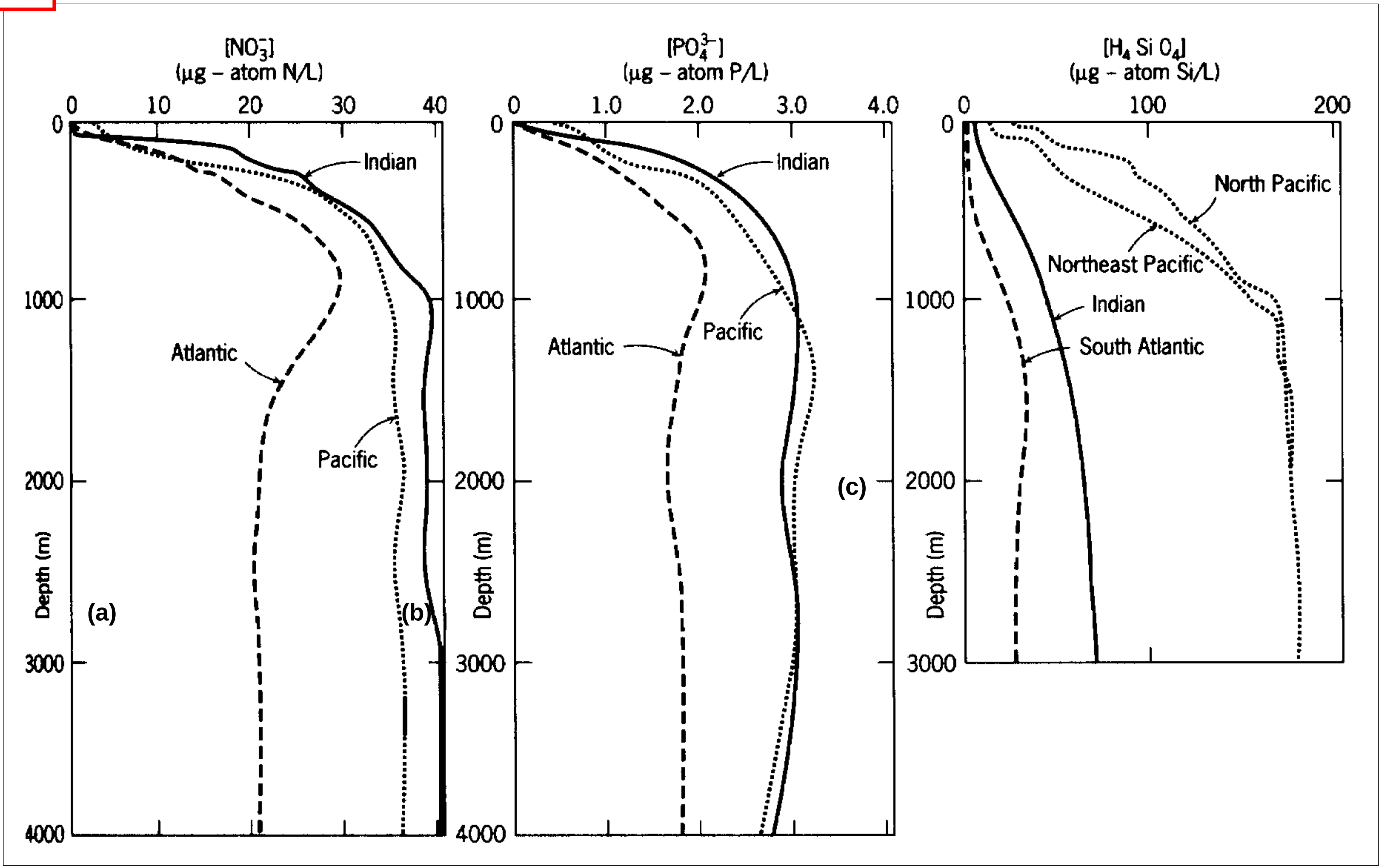
biogenic silica dissolution



Laboratory experiments

Natural bacterial assemblages and diatom detritus

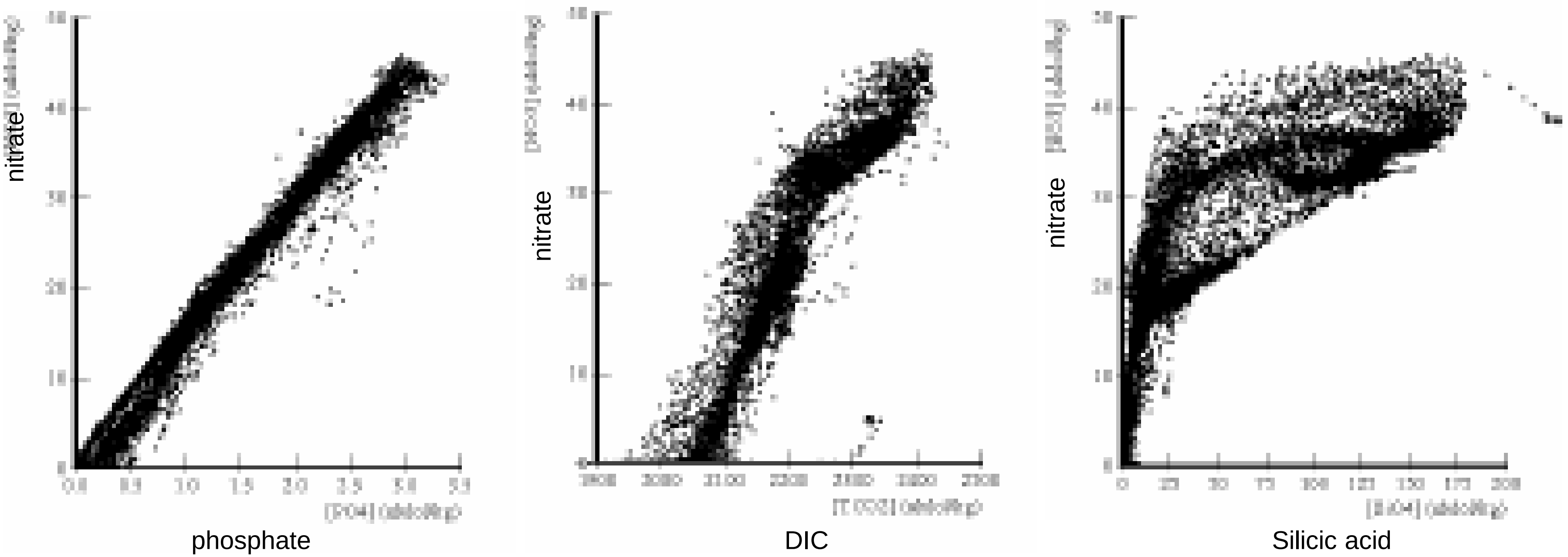
Importance of organic coatings on opal surface / diatom tests



For the deep ocean basins (ATLantic, INDian, PACific):

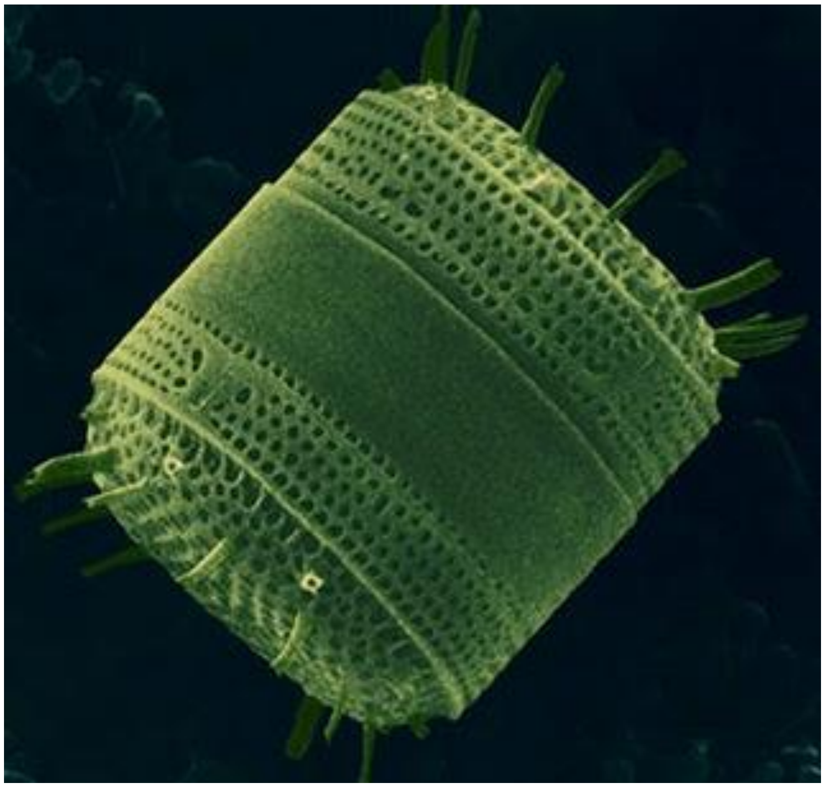
$[nutrients]_{ATL} < [nutrients]_{IND} < [nutrients]_{PAC}$

Nutrient:Nutrient Scatterplots



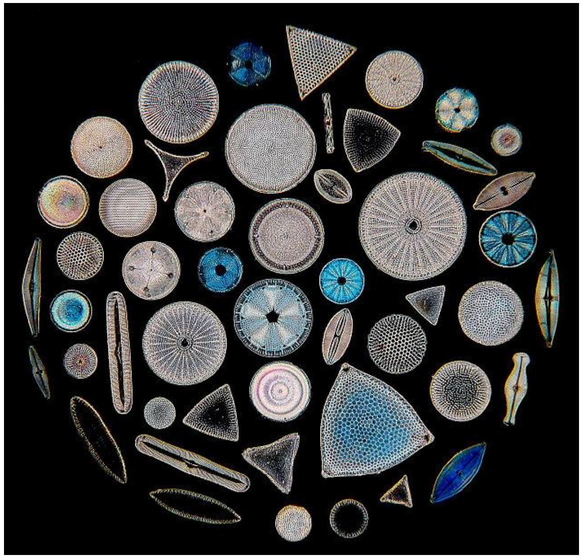
[GEOSECS data]

Diatoms



- Diatoms are one of the most predominant phytoplankton groups in the ocean
- Unicellular organisms
- Diatom cells are encased within a silica wall called frustule

Diatoms:



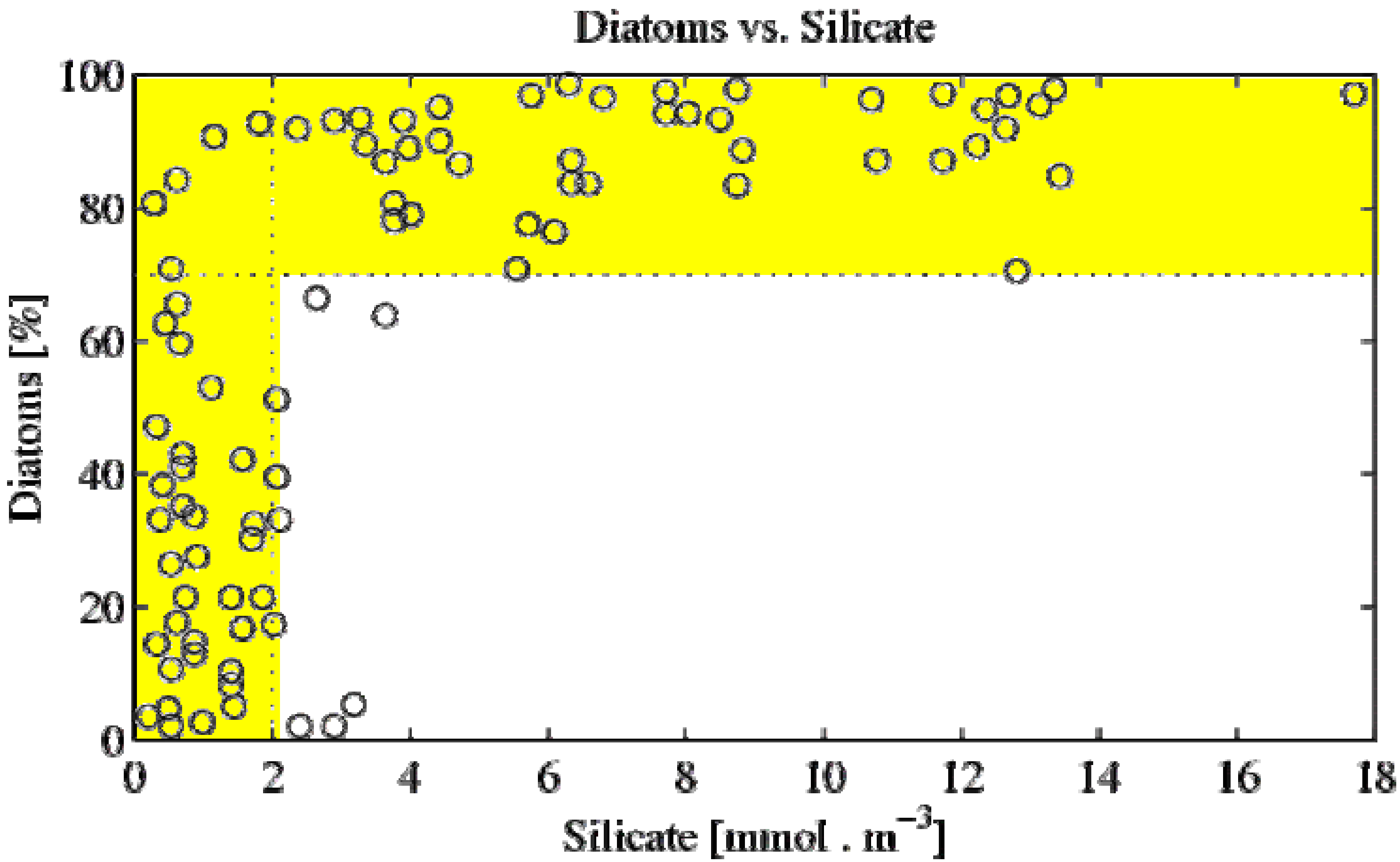
- About 10,000 recognised species
- Extremely efficient primary producers
- Account for 35-50% of oceanic primary production
- Responsible for up to 90% of organic carbon export
- [H_4SiO_4] >2μM: diatoms outcompete non-siliceous algae

Differences between Diatoms and Others

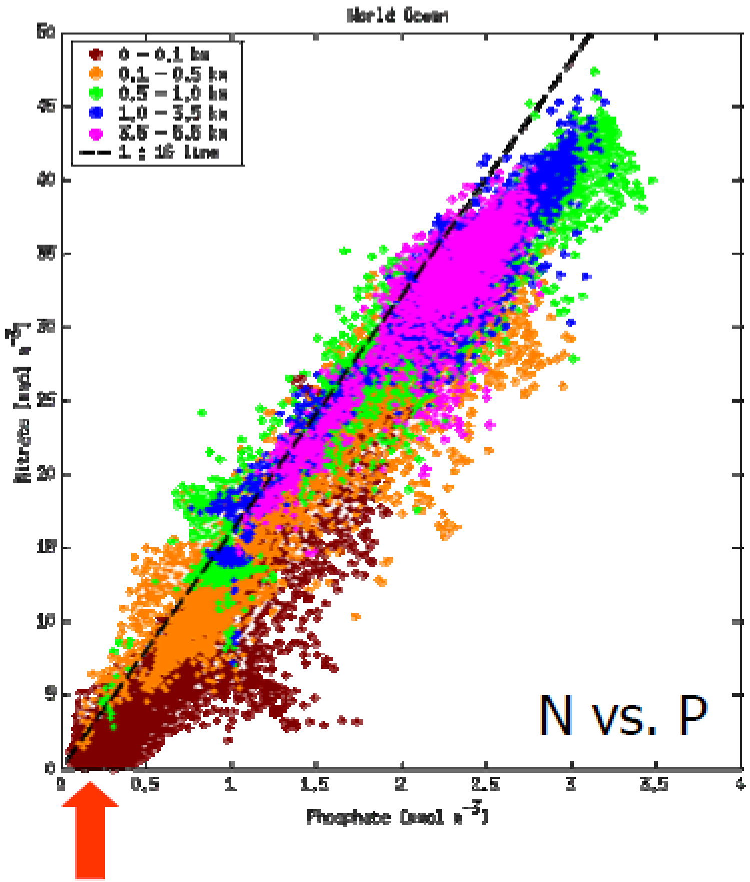
1. Diatoms have faster maximum growth rate.

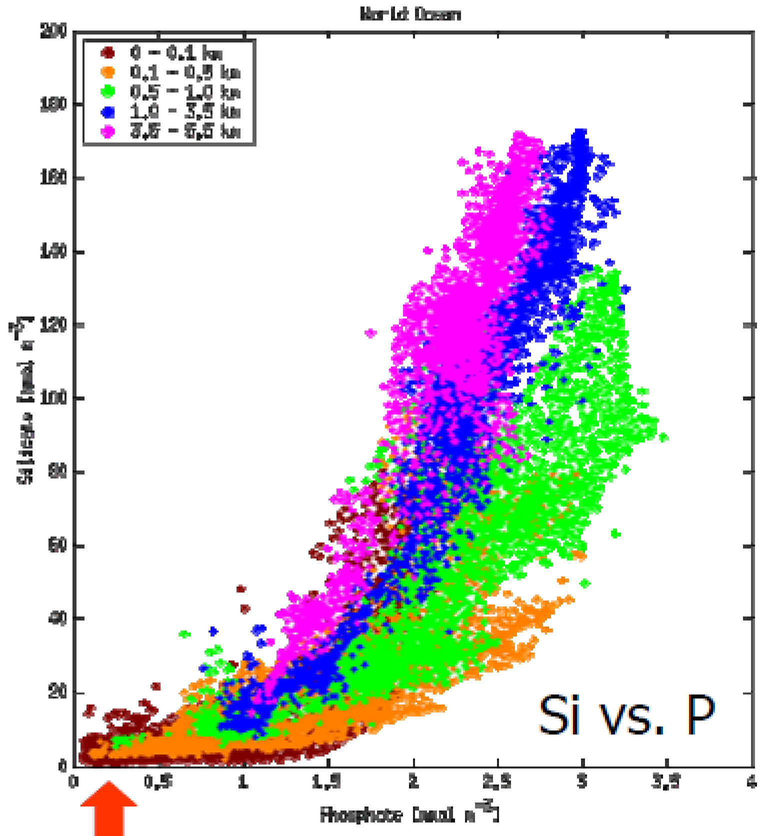
2. Diatoms are limited by silicic acid if scarce.

Diatoms tend to dominate ecosystems whenever silicate is abundant



Egge & Aksnes (1992) *MEPS* **83** : 281-289

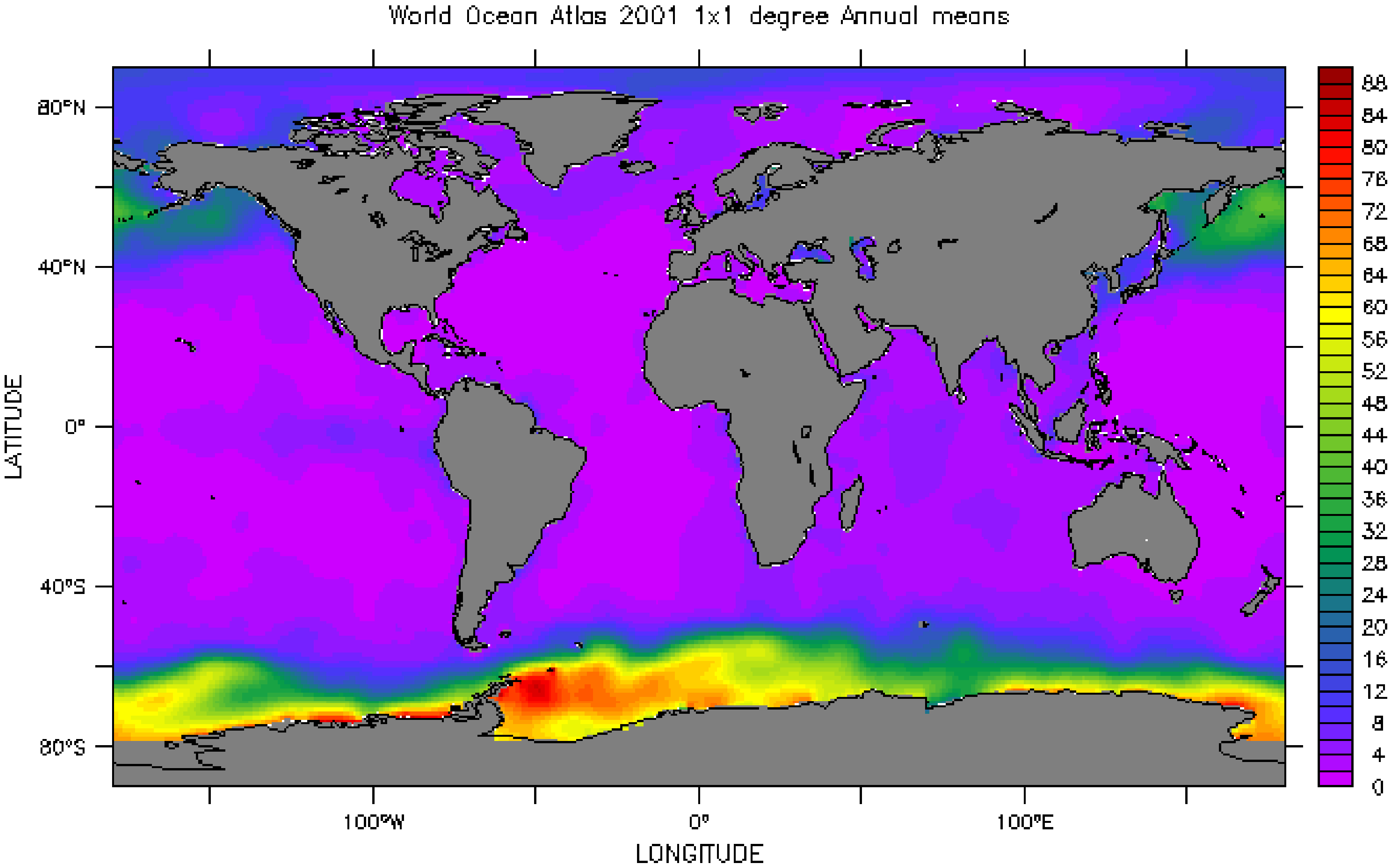




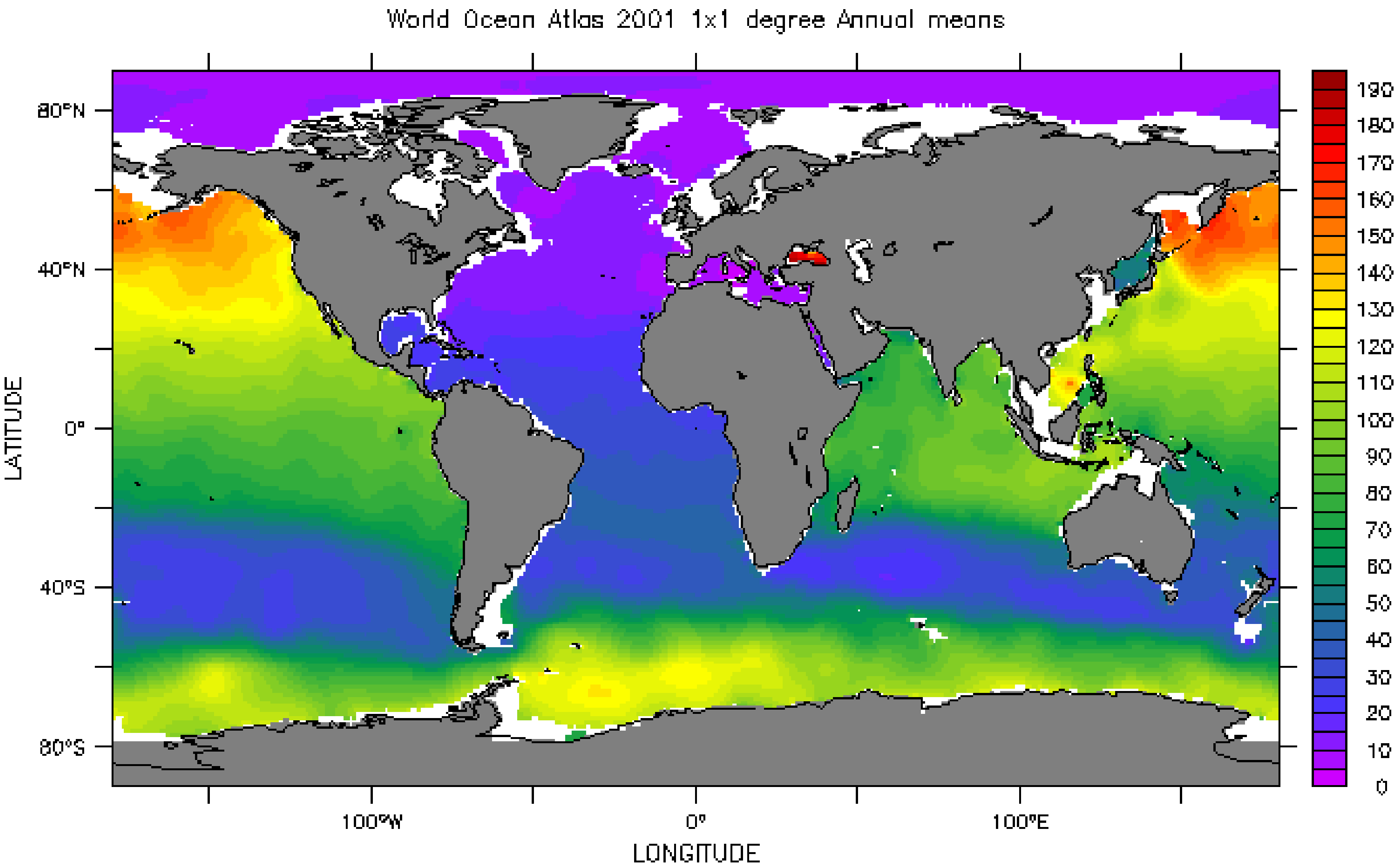
Conkright *et al.* (1994) NOAA atlas

Silicic acid gets depleted before phosphate (and nitrate)

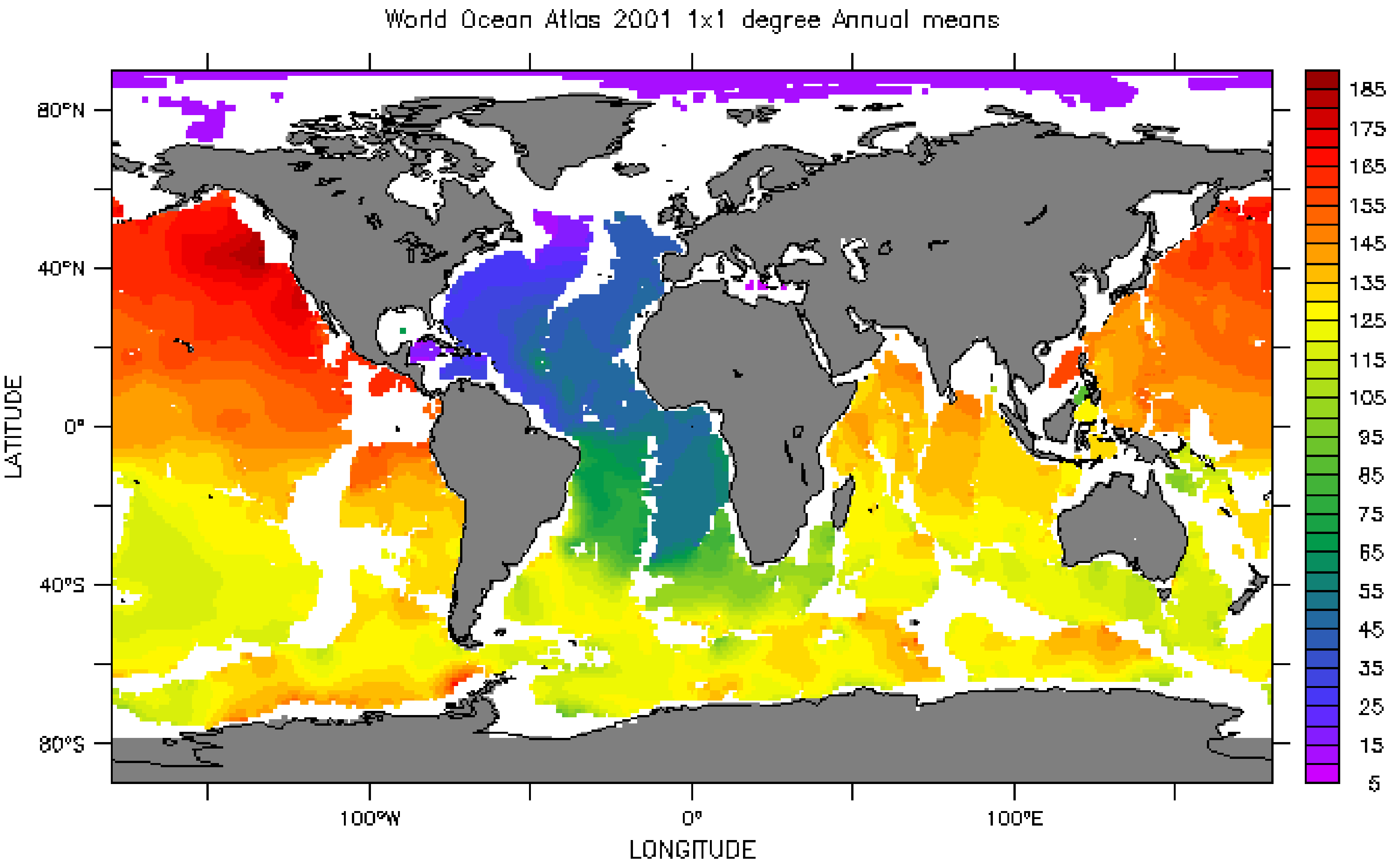
Surface dissolved silicate (annual mean)



Dissolved Silicate at 1000 m (annual mean)



Dissolved Silicate at 4000 m (annual mean)



Factors affecting opal accumulation in sediments

Rain rate of opal

overlying productivity (and silicate supply)

Degree of preservation during sinking and shallow/surface sediments

concentration in underlying waters; temperature

type of particles (wall thickness; sinking rate)

Accumulation of other sediments

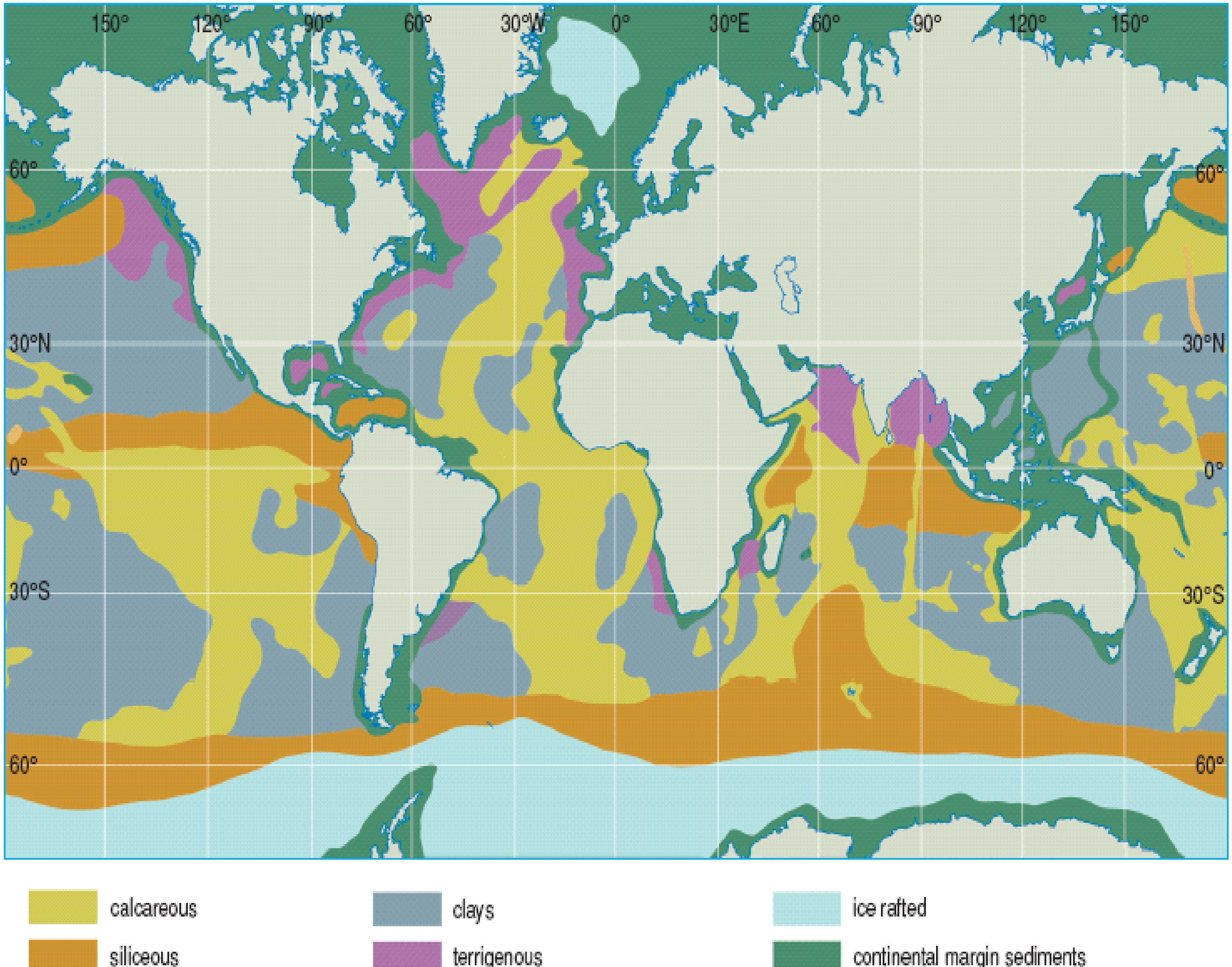
rapid burial ? (dilutes but preserves)

Production / supply

Dissolution

Dilution

(by other sediment types)



Distribution of upwelling regions

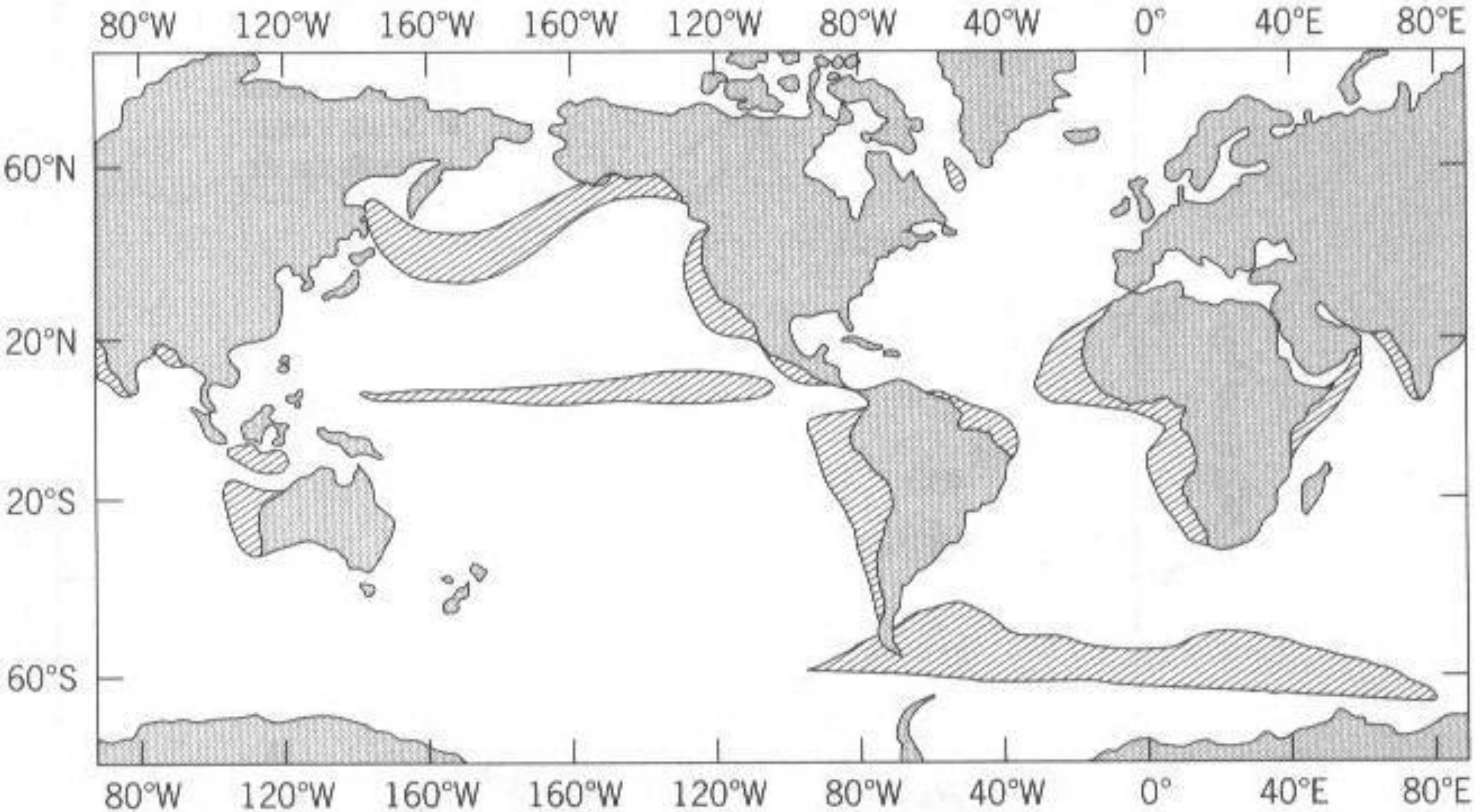
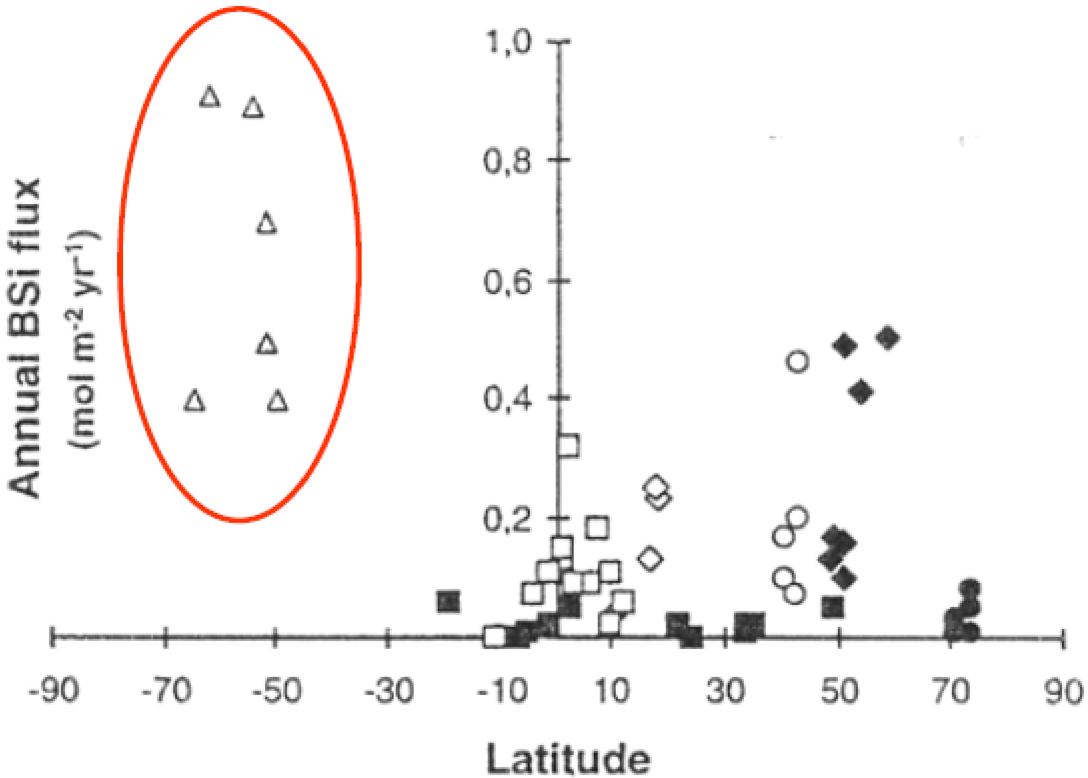


FIGURE 16.3. **General world areas of upwelling driven by Ekman transport.**

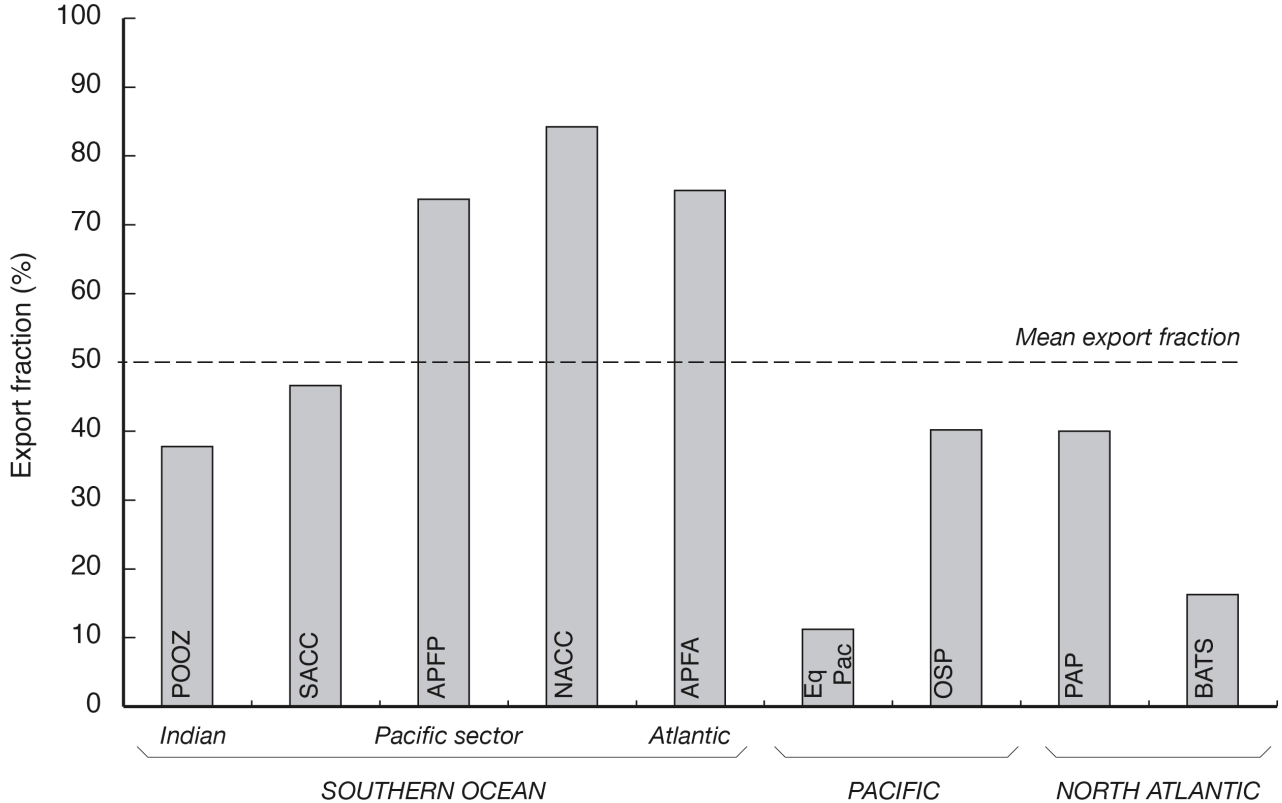
High Silica Burial in the Southern Ocean



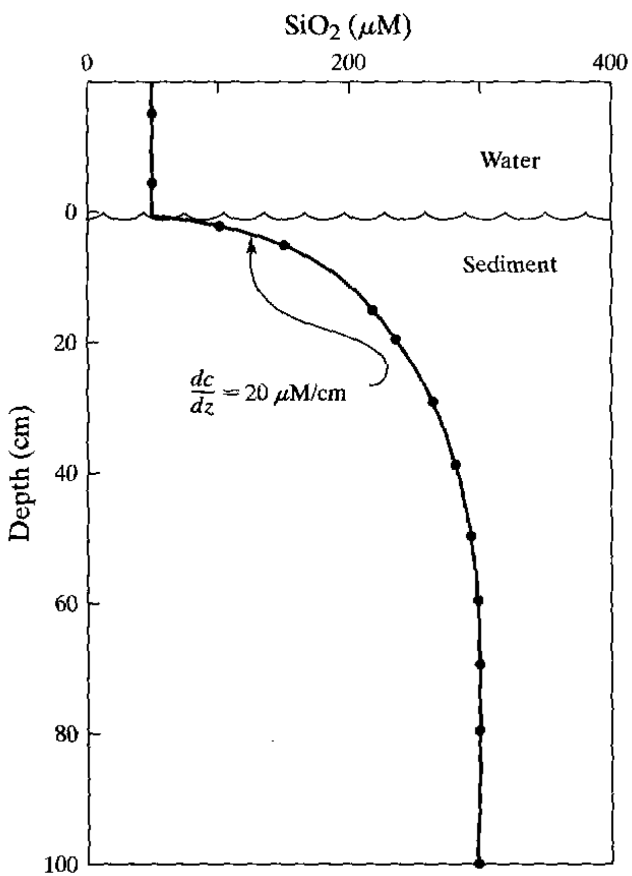
Triangles are from sediment traps in the Southern Ocean

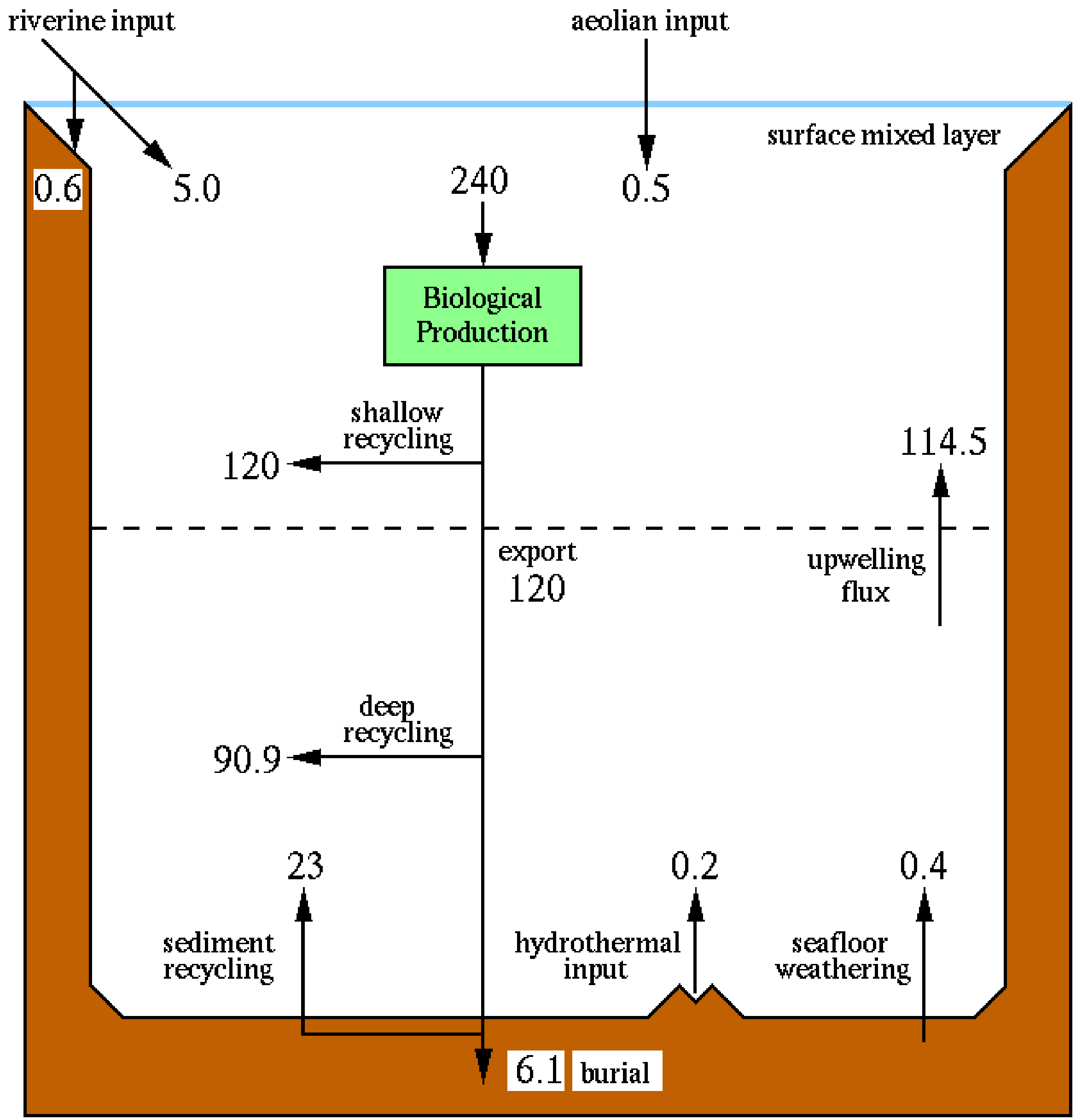
O Rageuneau et al (2000) A review of the silica cycle in the modern ocean, *Global and Planetary Change*, **26**: 317-365.

Dissolution and export



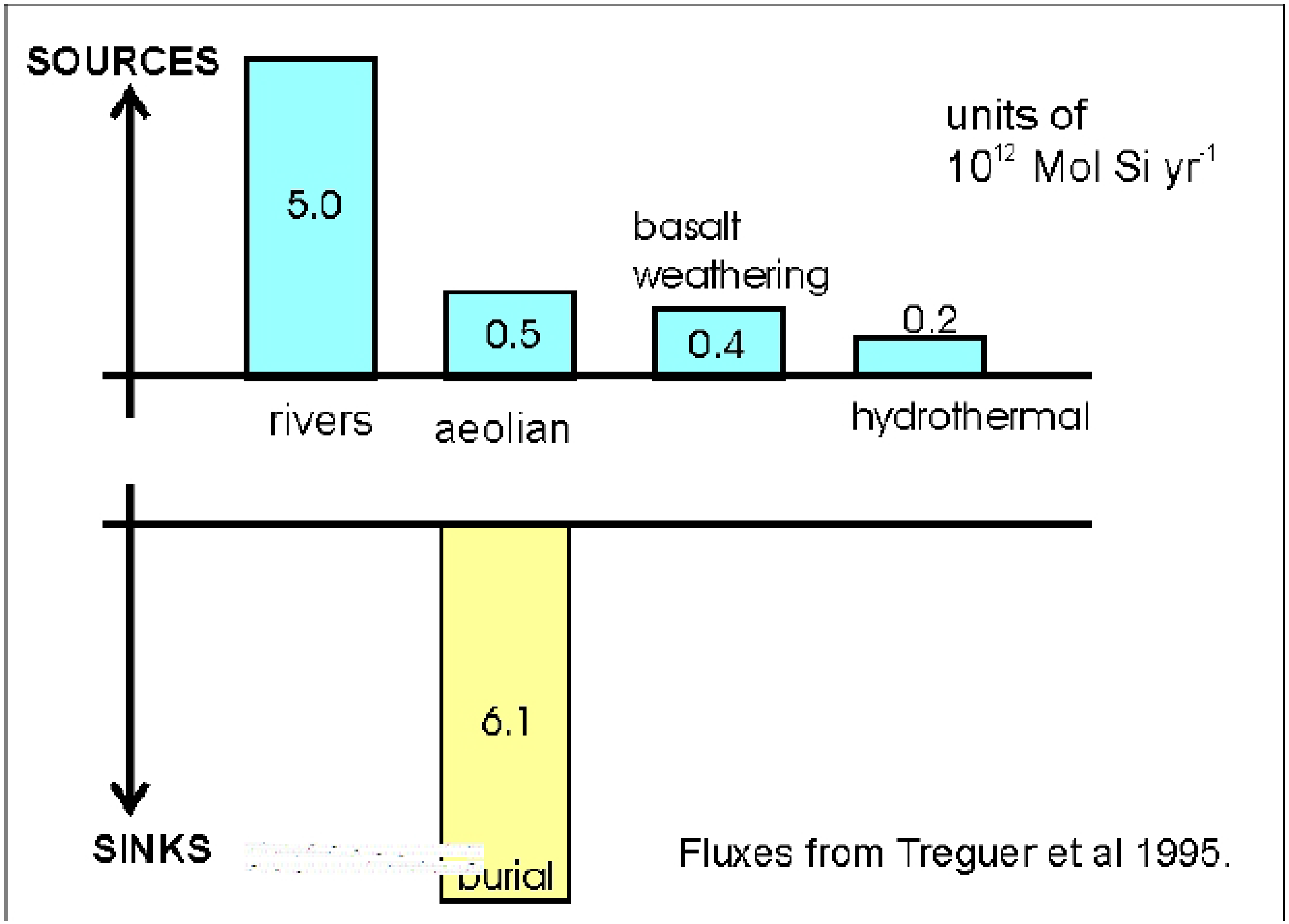
Silicon budget of the ocean





Adapted from Treguer et al. (1995)

Magnitude of Si fluxes in the ocean.

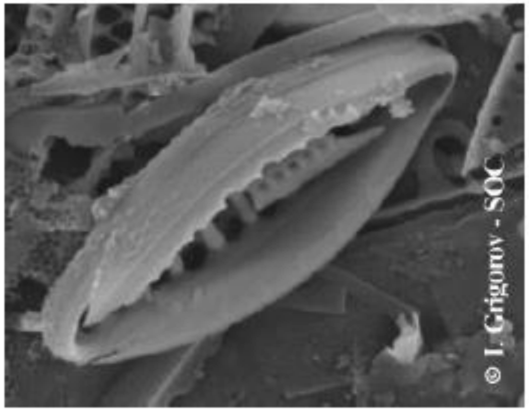


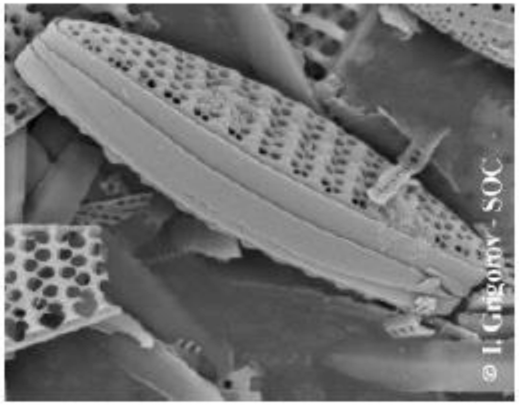
“There have been a number of attempts to construct a balanced budget for dissolved silica in the oceans. While the uncertainties are not so great as those for nitrogen, the budgets have still required considerable guesswork.”

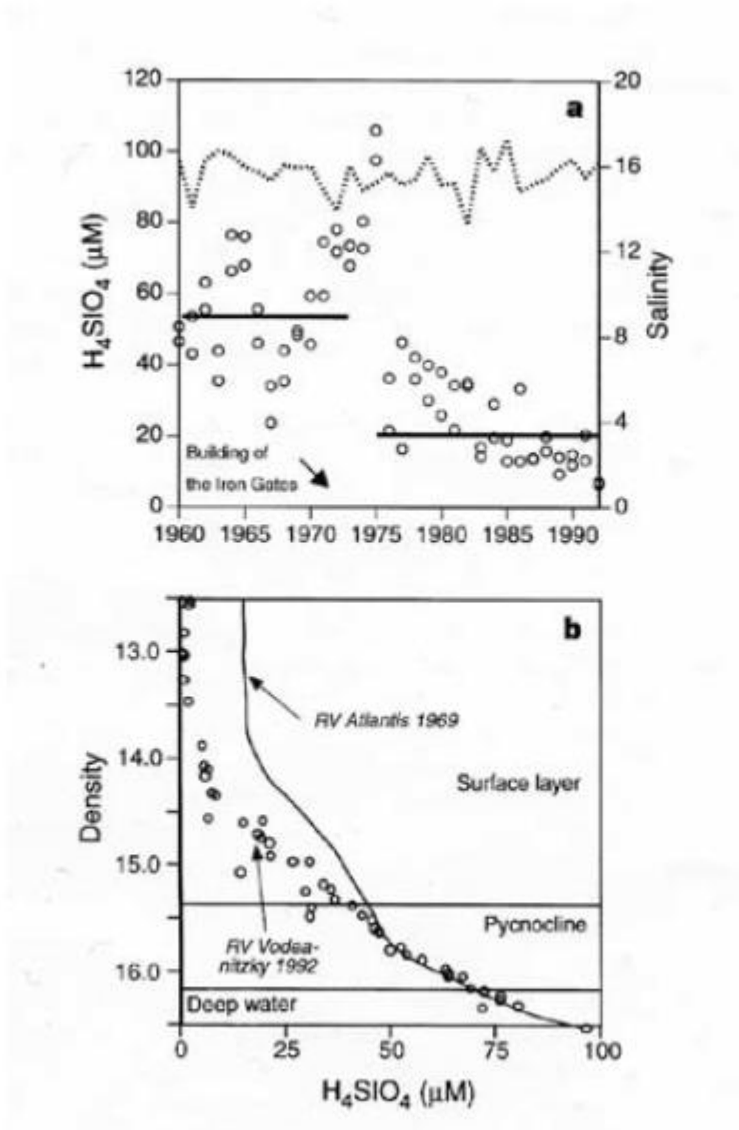
(M.E.Q. Pilson “An Introduction to the Chemistry of the Sea”, Prentice Hall, 1998)

Variable Frustule Thicknesses.

Diatoms which grow in high-silicate environments develop thicker frustules (become more heavily silicified). This is seen particularly in the Southern Ocean, for instance in the abundant species *Fragilariopsis kerguelensis*.







Effect of Damming on Black Sea Silicate Concentrations.

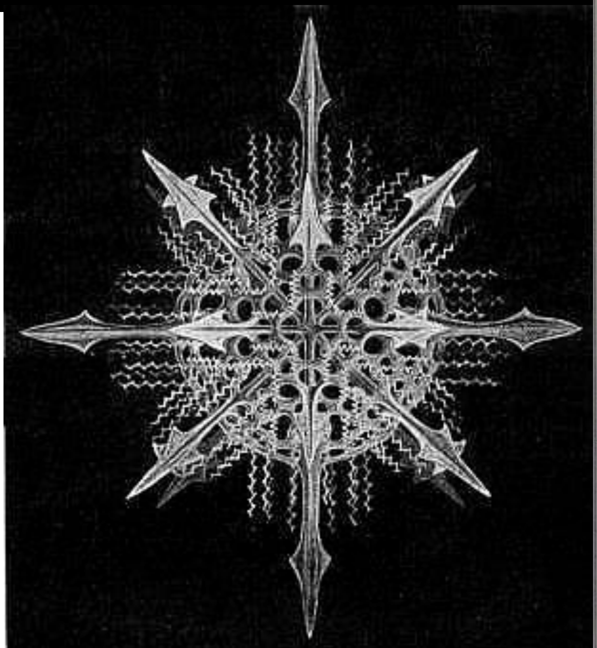
C Humborg et al (1997)
Nature, **386**: 385-388.

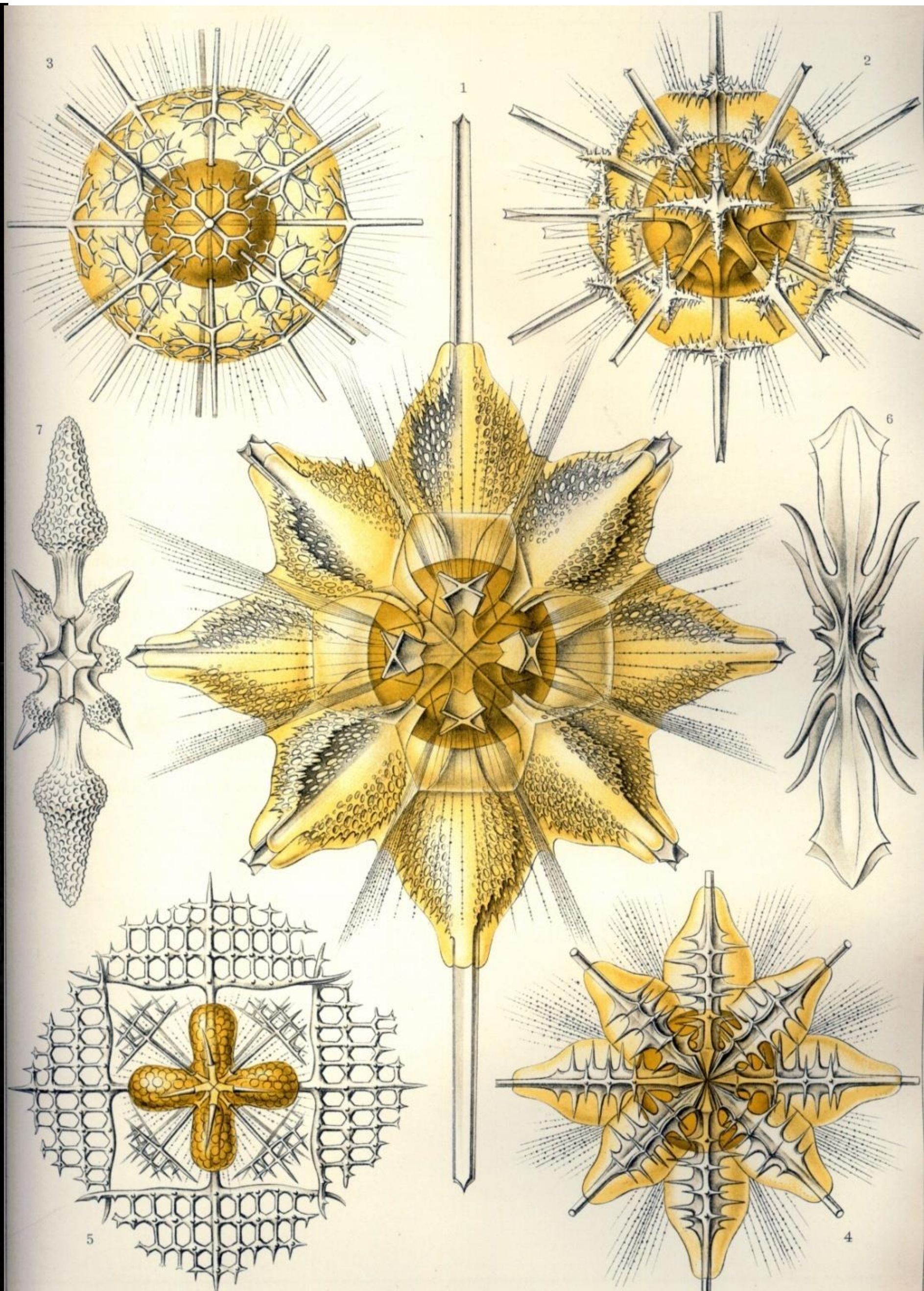
Black Sea *E. huxleyi* bloom

In contrast to nitrogen and phosphorus, rivers may presently be supplying less silicic acid to the ocean than during pre-industrial times.

Concentration of silicic acid in the Mississippi has declined by 50% since measurements began.

Turner RE & Rabelais NN (1991) Bioscience, 41: 140-147.





Celestine

$SrSO_4$