The $CaCO_3$ – biological pumps in the ocean

Jonthan Erez

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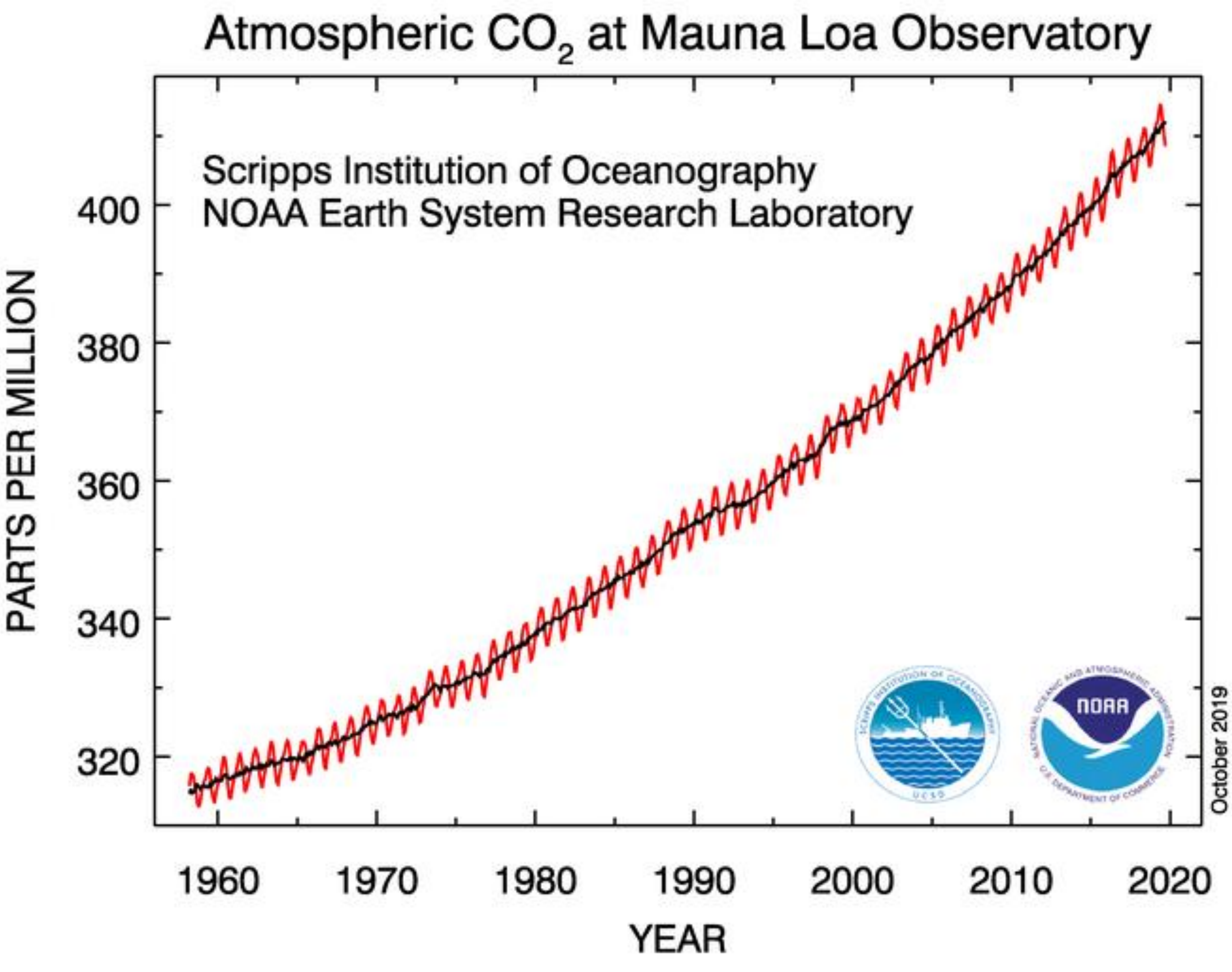
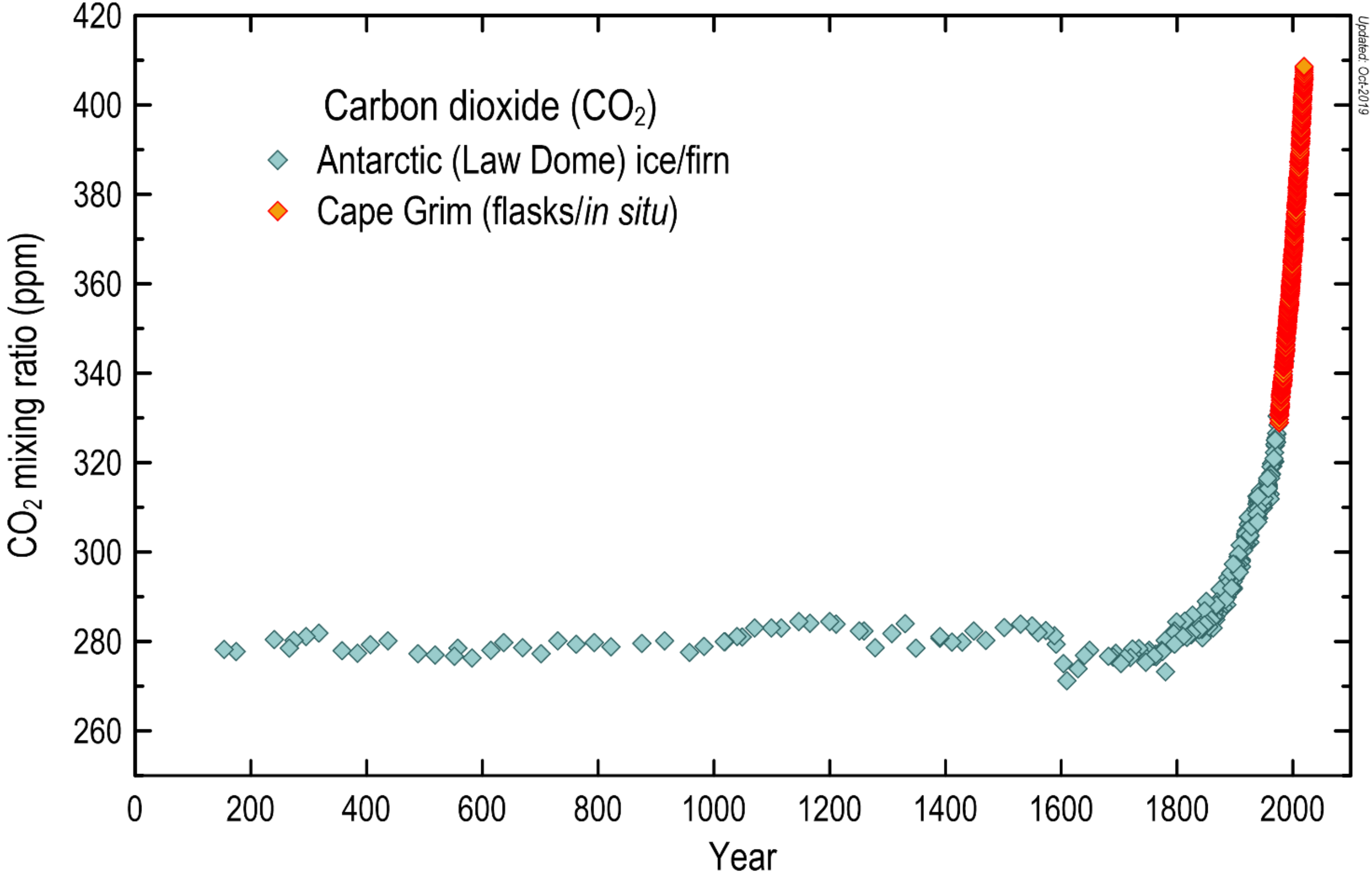
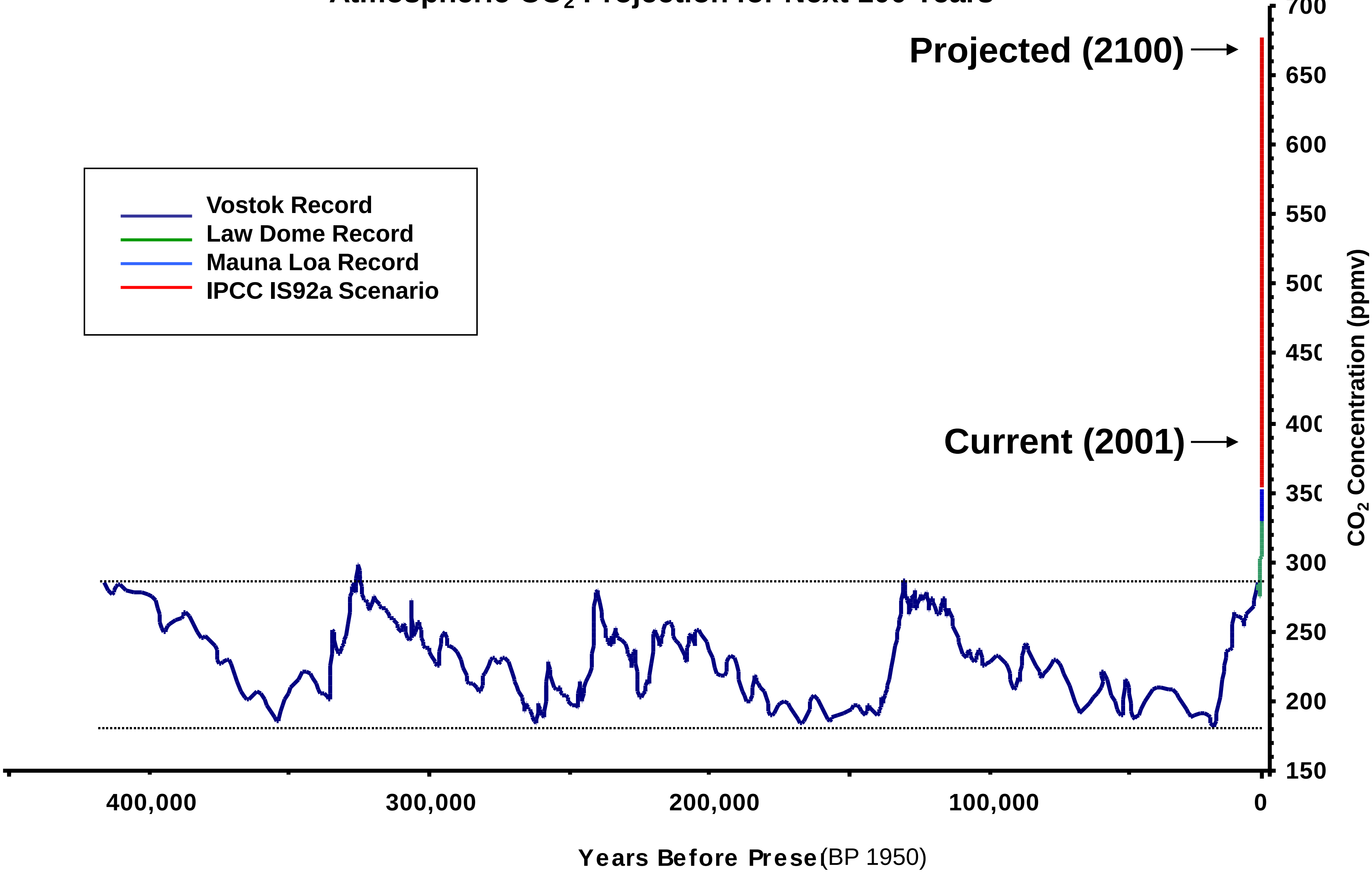

Atmospheric CO_2 at Mauna Loa Observatory
Scripps Institution of Oceanography
NOAA Earth System Research Laboratory
PARTS PER MILLION
400
380
360
340
320
1960
1970
1980
1990
2000
2010
2020
YEAR
October 2019
NOAA

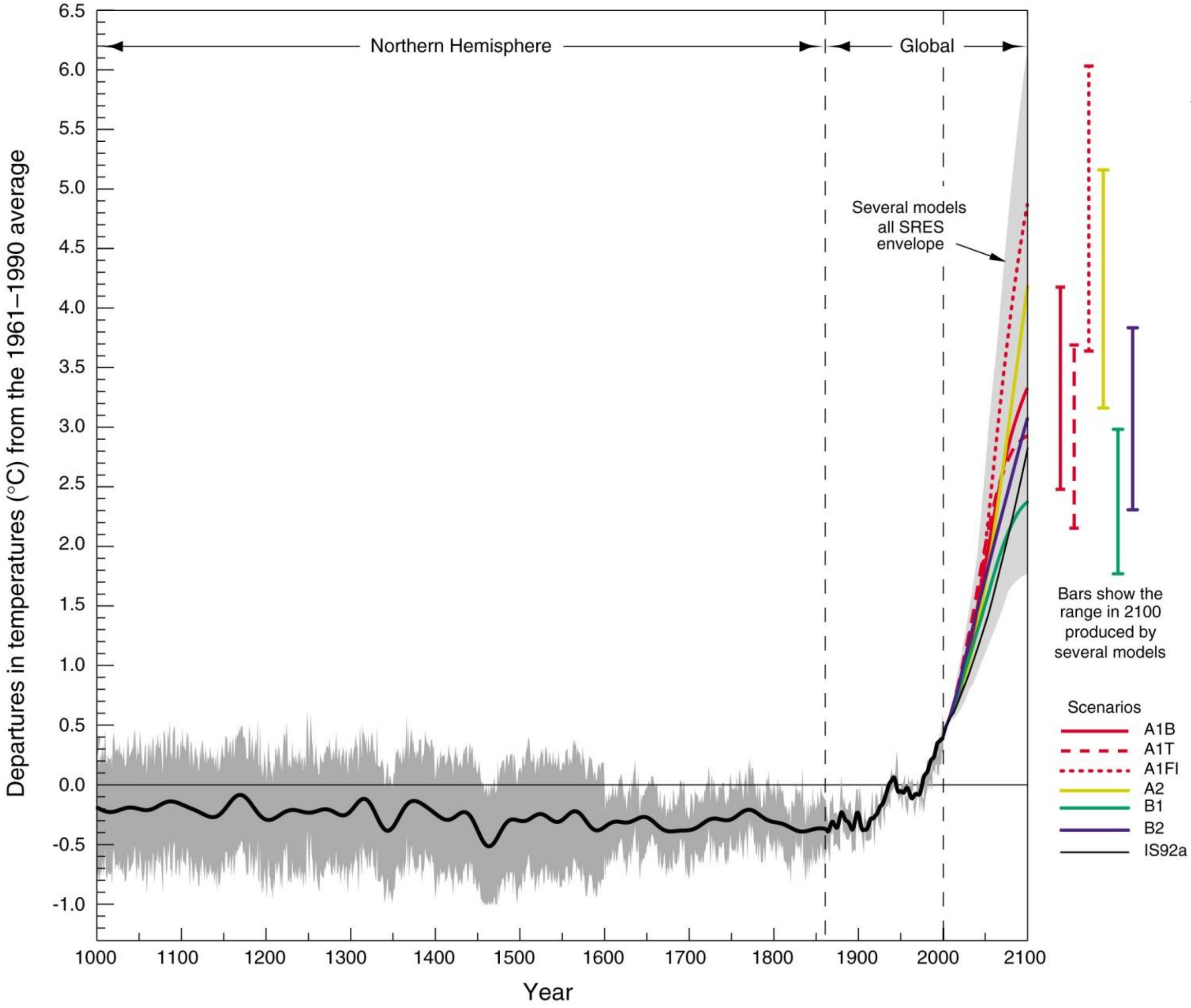


Carbon dioxide (CO_2)
Antarctic (Law Dome) ice/firn
Cape Grim (flasks/*in situ*)
CO_2 mixing ratio (ppm)
420
400
380
360
340
320
300
280
260
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Year
Updated: Oct-2019

CO_2 Concentration in Ice Cores and Atmospheric CO_2 Projection for Next 100 Years



Source: C. D. Keeling and T. P. Whorf; Etheridge *et.al.;* Barnola *et.al.;* (*PAGES* / IGBP); IPCC



Global temperature will rise from 1.4-5.8˚C over this century unless greenhouse gas emissions are greatly reduced

Source: IPCC Third Assessment Report, WG1

Processes that affect the global carbon cycle

- Geophysical – Plate tectonics, volcanism and the configuration of the oceans and continents
- Atmosphere physics and chemistry
- The land ecosystem
- **The oceans: Physics, chemistry and biology**
- Feedback mechanisms and the effects of global change in the ocean

Geochemical Carbon Cycle

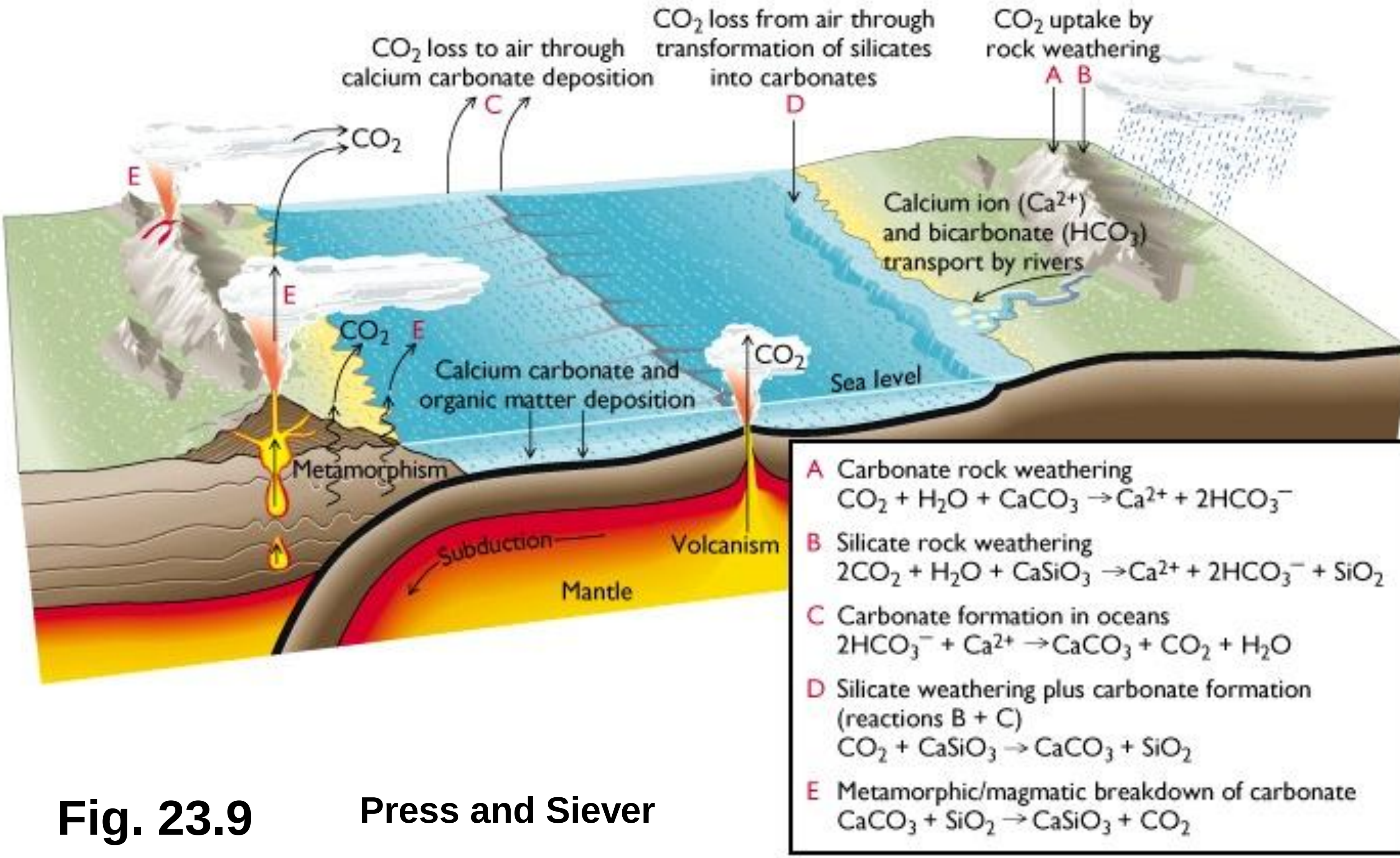
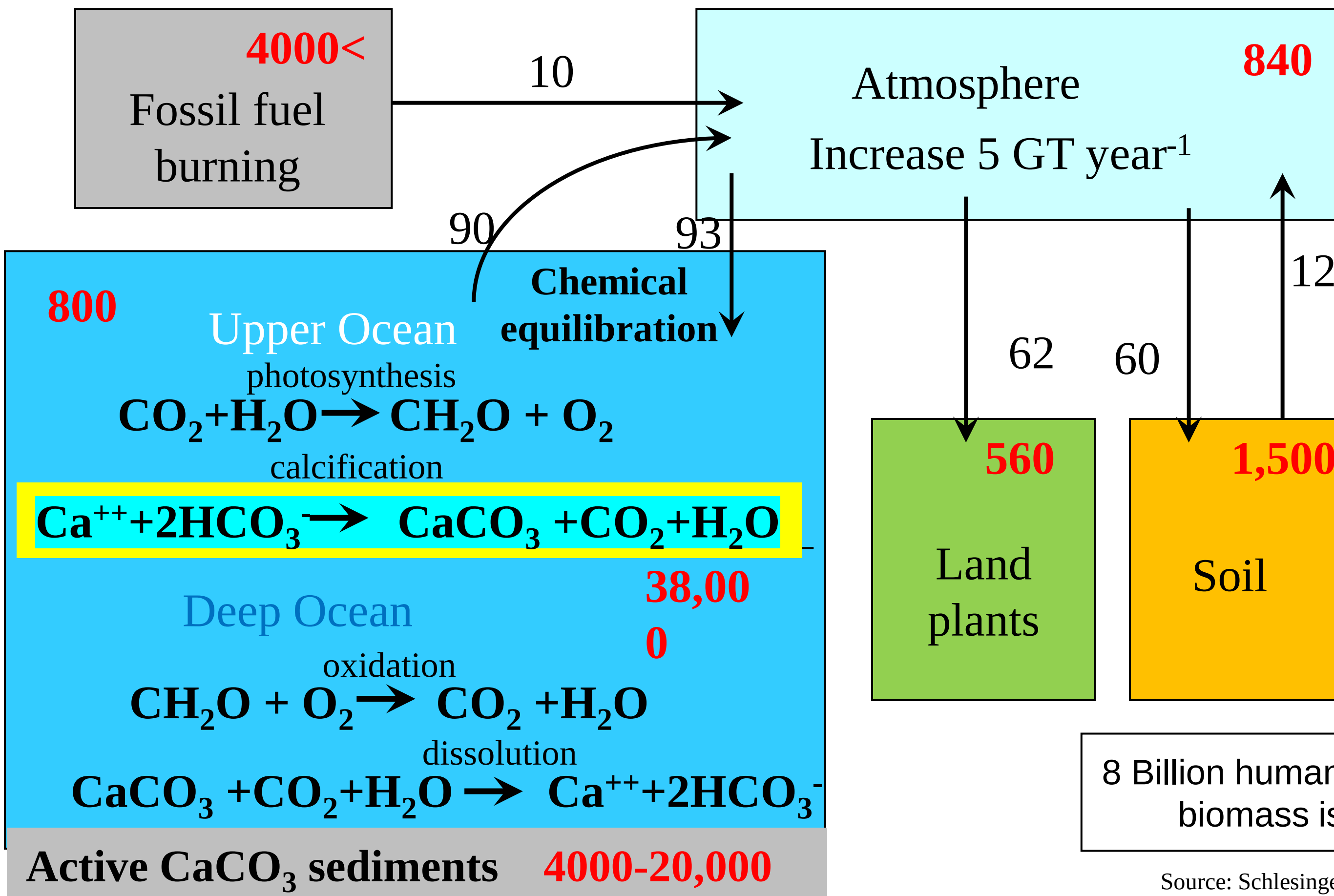


Fig. 23.9 **Press and Siever**

MODIFIED MODEL OF THE GLOBAL CARBON CYCLE (2018)

Reservoir sizes in 10^{15} gC=GTC

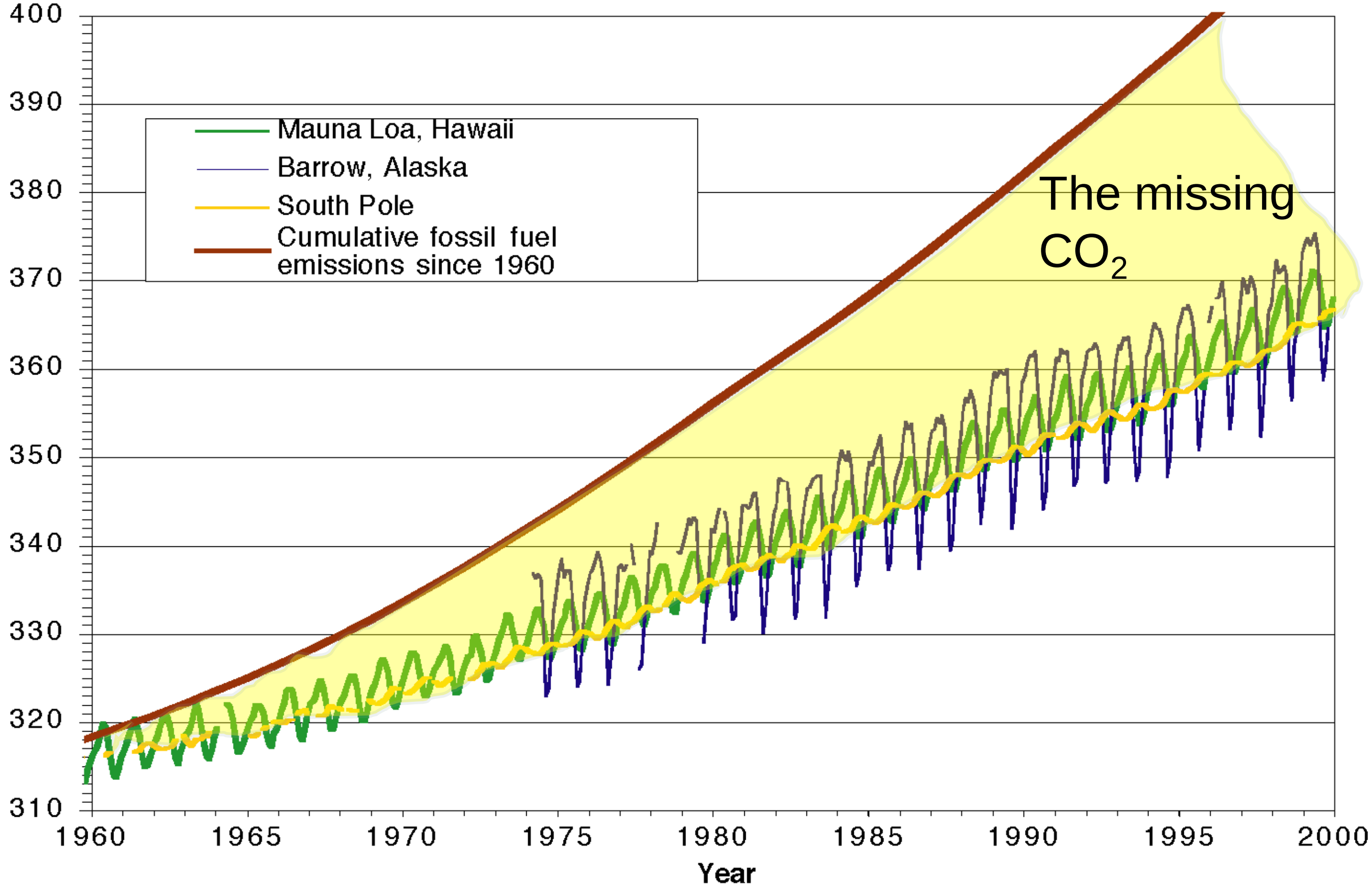
Fluxes in 10^{15} gC year^{-1}



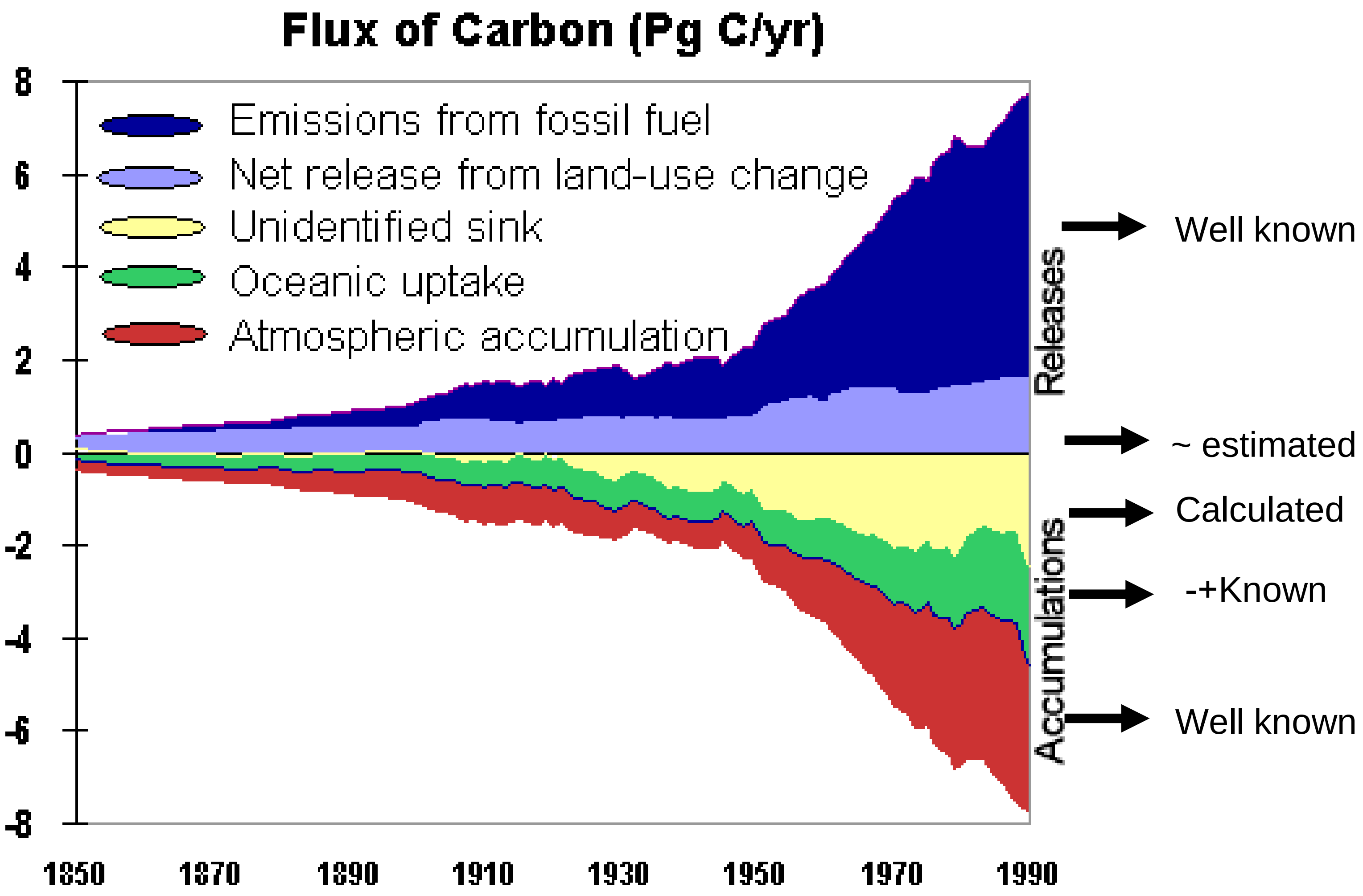
8 Billion humans on Earth, their biomass is only **0.06 GT C**

Source: Schlesinger 1997

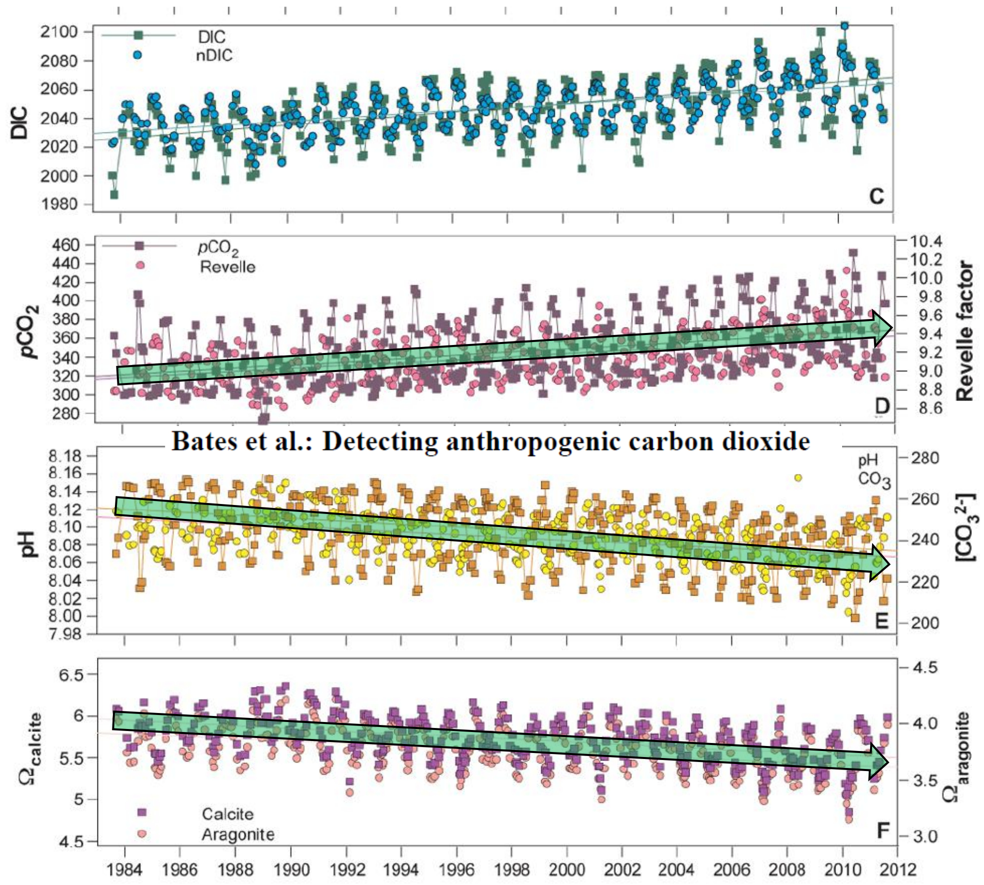
The emission of CO_2 are higher than the accumulation in the Atmosphere



W. Knorr


Flux of Carbon (Pg C/yr)
Emissions from fossil fuel
Net release from land-use change
Unidentified sink
Oceanic uptake
Atmospheric accumulation
8
6
4
2
0
-2
-4
-6
-8
1850
1870
1890
1910
1930
1950
1970
1990
Releases
Accumulations
Well known
~ estimated
Calculated
-+Known
Well known

BATS Bermuda Atlantic time series: 1984 - 2012



Bates et al 2013 Biogeosciences

$$CO_{2(g)}$$

4 equations and 6 unknowns. Need to measure at least 2 parameters to solve the system

K_H

$$\underline{CO_{2(g)}} \leftrightarrows \underline{CO_{2(aq)}}$$

k_0

$$CO_{2(aq)} + H_2O \leftrightarrows \underline{H_2CO_3}$$

k_1

$$H_2CO_3 \leftrightarrows \underline{HCO_3}^- + \underline{H}^+$$

k_2

$$HCO_3^- \leftrightarrows \underline{CO_3^{-2}} + H^+$$

$$CO_{2(gas)} \Leftrightarrow CO_{2(aq.)} \rightarrow \boxed{\frac{CO_{2(aq.)}}{CO_{2(gas)}} = K_H}, (mole \cdot kg^{-1} \cdot atm^{-1})$$

$$CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_3 \rightarrow \frac{CO_{2(aq)}}{H_2CO_3} = K_0^{-1} \approx 700$$

we define a new variable CO_2^* as follows

$$CO_2^* \Leftrightarrow CO_{2(aq.)} + H_2CO_3$$

$$CO_2^* \Leftrightarrow HCO_3^- + H^+ \rightarrow \boxed{\frac{HCO_3^- \cdot H^+}{CO_2^*} = K_1}$$

$K_1 = 10^{-6}$
$pK_1 = 6$

$$HCO_3^- \Leftrightarrow CO_3^{-2} + H^+ \rightarrow \boxed{\frac{CO_3^{-2} \cdot H^+}{HCO_3^-} = K_2}$$

$K_2 = 10^{-9}$
$pK_2 = 9$

$$\boldsymbol{DIC = \Sigma CO_2 = C_T = Ci}$$

$$C_T = CO_{2(aq)} + H_2CO_3 + HCO_3^- + CO_3^{-2}$$

DIC can be measured in a vacuum line where a known amount of seawater is acidified with strong acid (H_3PO_4) to very low pH. All the DIC is converted into CO_2 gas which is purified and measured with a digital manometer or an IRGA (Infra Red Gas Analyzer)

$CO_2 = \alpha_0 * C_T$, $HCO_3^- = \alpha_1 * C_T$, $CO_3^{2-} = \alpha_2 * C_T$

$$CO_2 = \alpha_0 \cdot C_T = \frac{H^2}{H^2 + K_1 \cdot H + K_1 \cdot K_2} \cdot C_T$$

$$HCO_3^- = \alpha_1 \cdot C_T = \frac{H \cdot K_1}{H^2 + K_1 \cdot H + K_1 \cdot K_2} \cdot C_T$$

$$CO_3^{2-} = \alpha_2 \cdot C_T = \frac{K_1 \cdot K_2}{H^2 + K_1 \cdot H + K_1 \cdot K_2} \cdot C_T$$

$$CO_2 = \alpha_0 \cdot C_T = \frac{H^2}{H^2 + K_1 \cdot H + K_1 \cdot K_2} \cdot C_T$$

For pH=8 $H^2 = 10^{-16}$

$$HCO_3^- = \alpha_1 \cdot C_T = \frac{H \cdot K_1}{H^2 + K_1 \cdot H + K_1 \cdot K_2} \cdot C_T$$

$H \bullet K_1 = 10^{-14}$

$$CO_3^{2-} = \alpha_2 \cdot C_T = \frac{K_1 \cdot K_2}{H^2 + K_1 \cdot H + K_1 \cdot K_2} \cdot C_T$$

$K_1 \bullet K_2 = 10^{-15}$

Normal seawater

pH is 8 i.e. $H = 10^{-8}$

$K_1 = 10^{-6}$

$K_2 = 10^{-9}$

Therefore HCO_3^- is 100 times higher then CO_2 and 10 times higher then CO_3^{2-}

$$K_1 = \frac{H \cdot HCO_3}{CO_2} \qquad \frac{K_1}{H} = \frac{HCO_3}{CO_2}$$

$$\log \frac{HCO_3}{CO_2} = pH - pK_1$$

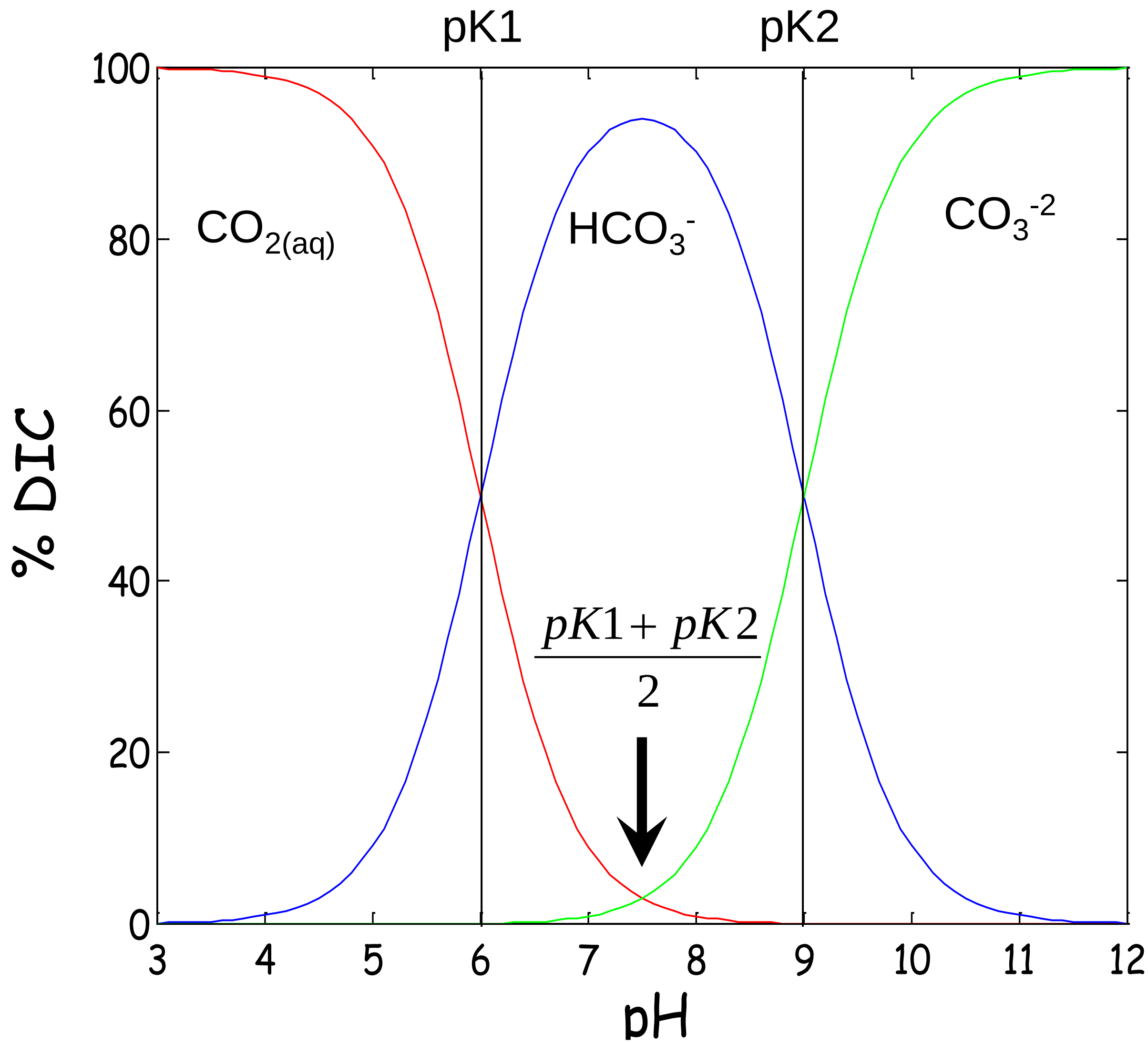
Note that when $HCO_3 = CO_2$
$pH = pK_1$

$$K_2 = \frac{H \cdot CO_3}{HCO_3} \qquad \frac{K_2}{H} = \frac{CO_3}{HCO_3}$$

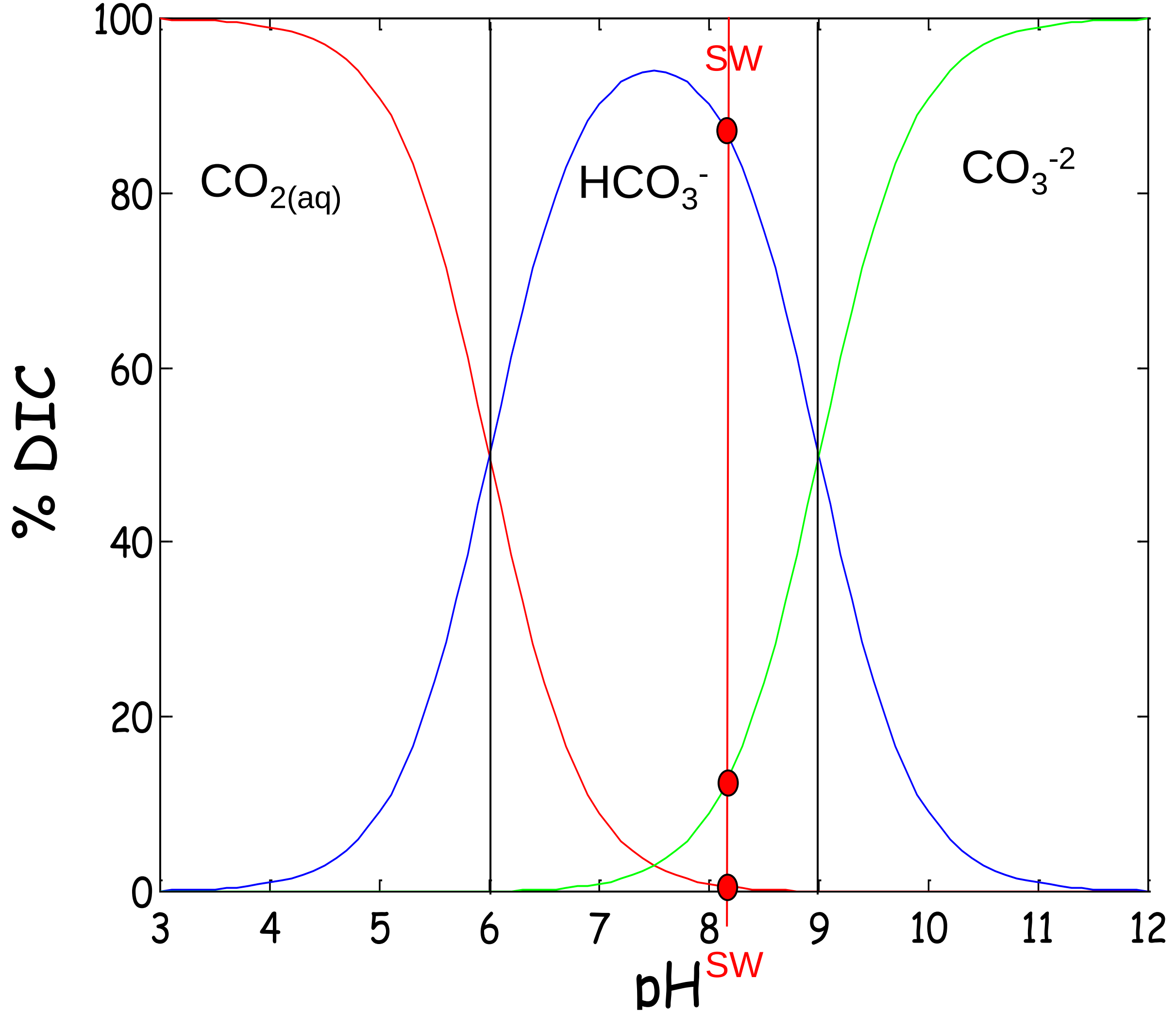
$$\log \frac{HCO_3}{CO_3} = pK_2 - pH$$

Note that when $HCO_3 = CO_3$
$pH = pK_2$

The bells shape diagram



The bells shape diagram



Alkalinity

Charge balance in seawater using the major ions

$$\boldsymbol{Na}^{+} + \boldsymbol{K}^{+} + 2\boldsymbol{Ca}^{+2} + 2\boldsymbol{Mg}^{+2} + \boldsymbol{H}^{+} - \boldsymbol{Cl}^{-} - 2\boldsymbol{SO}_4^{-2} -$$

$$\boldsymbol{HCO}_3^{-} - 2\boldsymbol{CO}_3^{-2} - \boldsymbol{OH}^{-} - \boldsymbol{B(OH)}_4^{-} = 0$$

This can be rearranged to separate the anions of the weak acids:

$$\boldsymbol{Na}^{+} + \boldsymbol{K}^{+} + 2\boldsymbol{Ca}^{+2} + 2\boldsymbol{Mg}^{+2} - \boldsymbol{Cl}^{-} - 2\boldsymbol{SO}_4^{-2} =$$

$$\underline{\underline{\boldsymbol{HCO}_3^{-} + 2\boldsymbol{CO}_3^{-2} + \boldsymbol{B(OH)}_4^{-} + \boldsymbol{OH}^{-} - \boldsymbol{H}^{+}}}$$

$$\underline{\underline{= \boldsymbol{ALK}}}$$

Hence the sum of the cations of the strong bases – the sum of the anions of the strong acids = the sum of the anions of the weak acids DEFINED AS THE TOTAL ALKALINITY

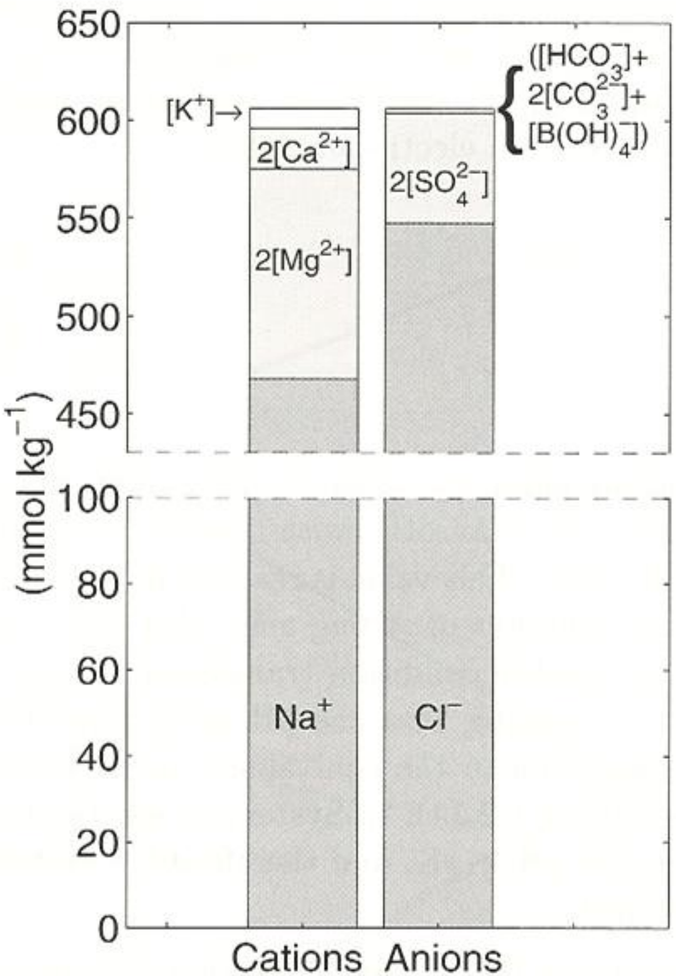


Figure 1.2.15: Charge balance of the major ions in seawater (cf. Broecker and Peng, 1998). The small excess charge of the conservative cations over anions is mainly balanced by $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-]$.

Note that Alk is measured in Equivalents which the Moles of a species multiplied by it charge. This is because we make a charge balance

$$
\begin{aligned}
[\mathrm{Na}^+] + 2[\mathrm{Mg}^{2+}] + 2[\mathrm{Ca}^{2+}] + [\mathrm{K}^+] + \ldots + [\mathrm{H}^+]_\mathrm{F} & \\
-[\mathrm{Cl}^-] - 2[\mathrm{SO}_4^{2-}] - [\mathrm{NO}_3^-] & \\
-[\mathrm{HCO}_3^-] - 2[\mathrm{CO}_3^{2-}] - [\mathrm{B(OH)}_4^-] - [\mathrm{OH}^-] - \ldots &= 0 \qquad (1.2.37)
\end{aligned}
$$

or

Change in carbonate alkalinity with pH

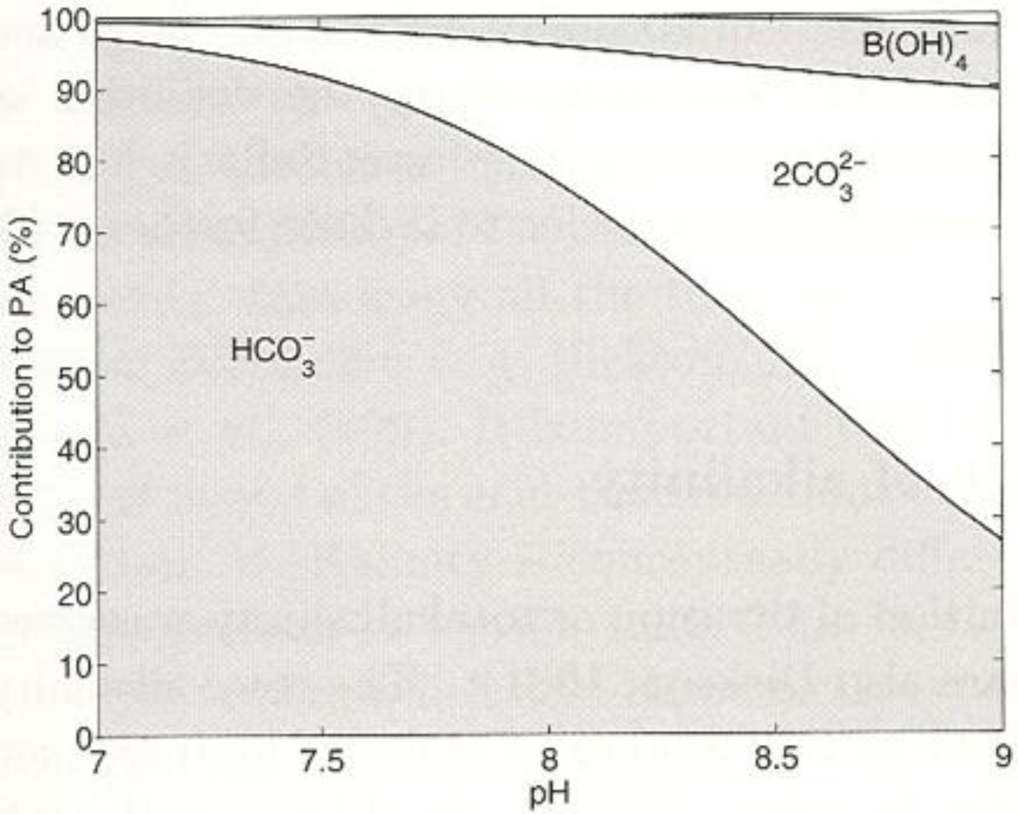


Figure 1.2.10: Relative contribution of various compounds to PA as a function of pH (DIC = 2000 μmol kg^{-1}, T_c = 25°C, S = 35). Areas show the percentage of each compound HCO_3^- (lower shaded area and left vertical axis), $2CO_3^{2-}$ (large white area), $B(OH)_4^-$ (upper shaded area), and OH^- (upper small white area).

What is hiding behind this strange definition of alkalinity?

- Imagine liter of distilled water (pH =7) to which we add 1 mmole of Na(OH). Now the alkalinity is 1 mEq/L (very high pH).
- Now we take 1 mmole of HCl and add to the solution and the pH is again 7 (no alkalinity because Na=Cl and H=OH
- What we did is equal to taking 1 mmole of NaCl and adding it to distilled water
- Conclusion: seawater is made of NaCl, $MgSO_4$, KCl, and $CaCl_2$ $MgCl_2$ with Alk =0
- Then the “inteligent designer” added little $CaCO_3$ and $NaB(OH)_4$ and created the TOTAL ALKALINITY
- So what is it good for?

Usefulness of Alkalinity

- Easy to measure with high precision and accuracy
- Does not change as samples are changing their pressure and temperature
- Conservative with salinity (major ions)
- **Helps to calculate the carbonate chemistry**
- Essential to calculate the oceanic carbon cycle and more…..
- Measure directly dissolution and precipitation of $CaCO_3$
- $Ca^{+2} + 2HCO_3^- \leftrightarrows CaCO_3 + H_2O + CO_2$

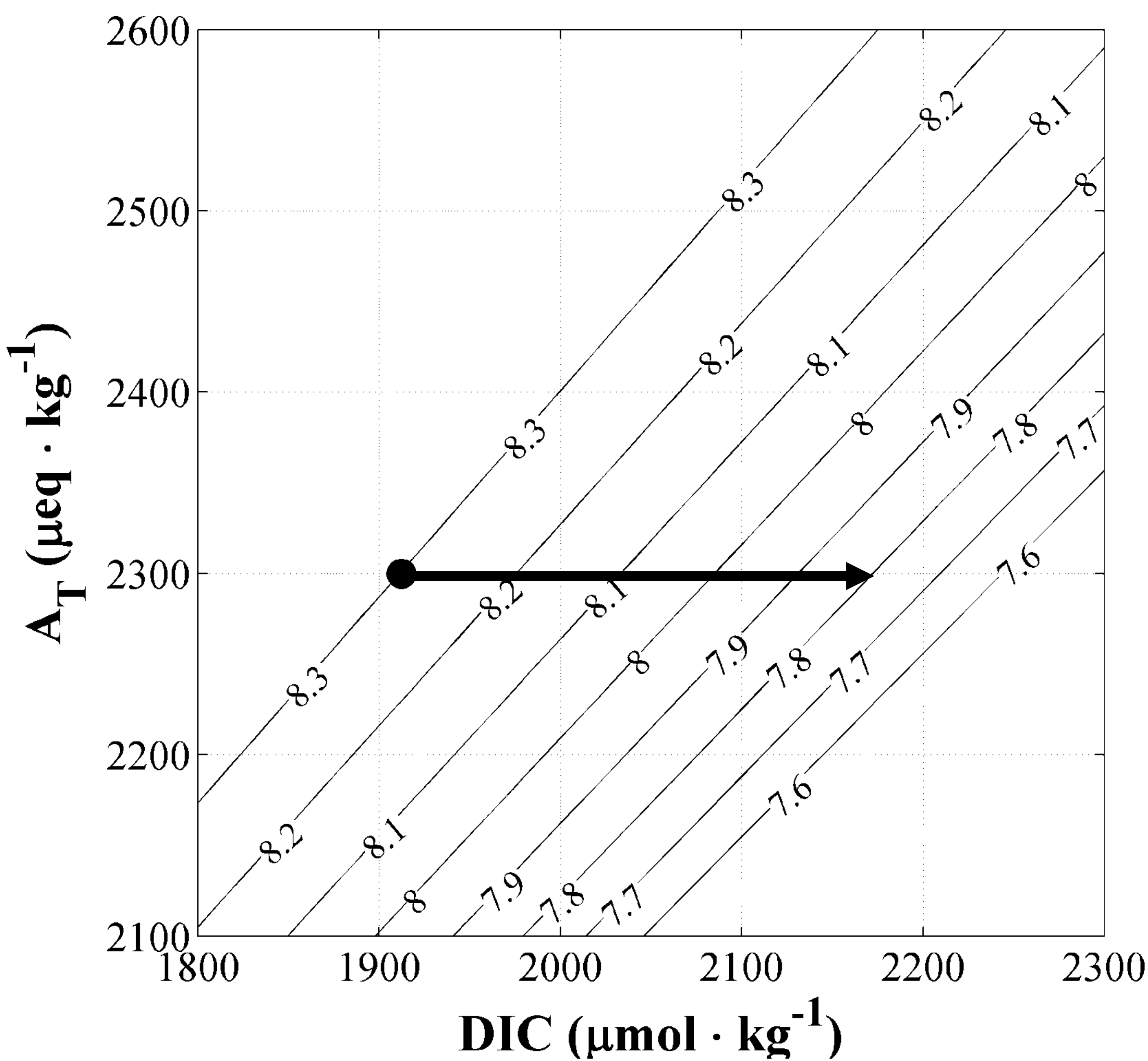
Deffeyess diagrams

$$ALK = HCO_3^{-} + 2\cdot CO_3^{-2} + B(OH)_4^{-} + OH^{-} - H^{+}$$

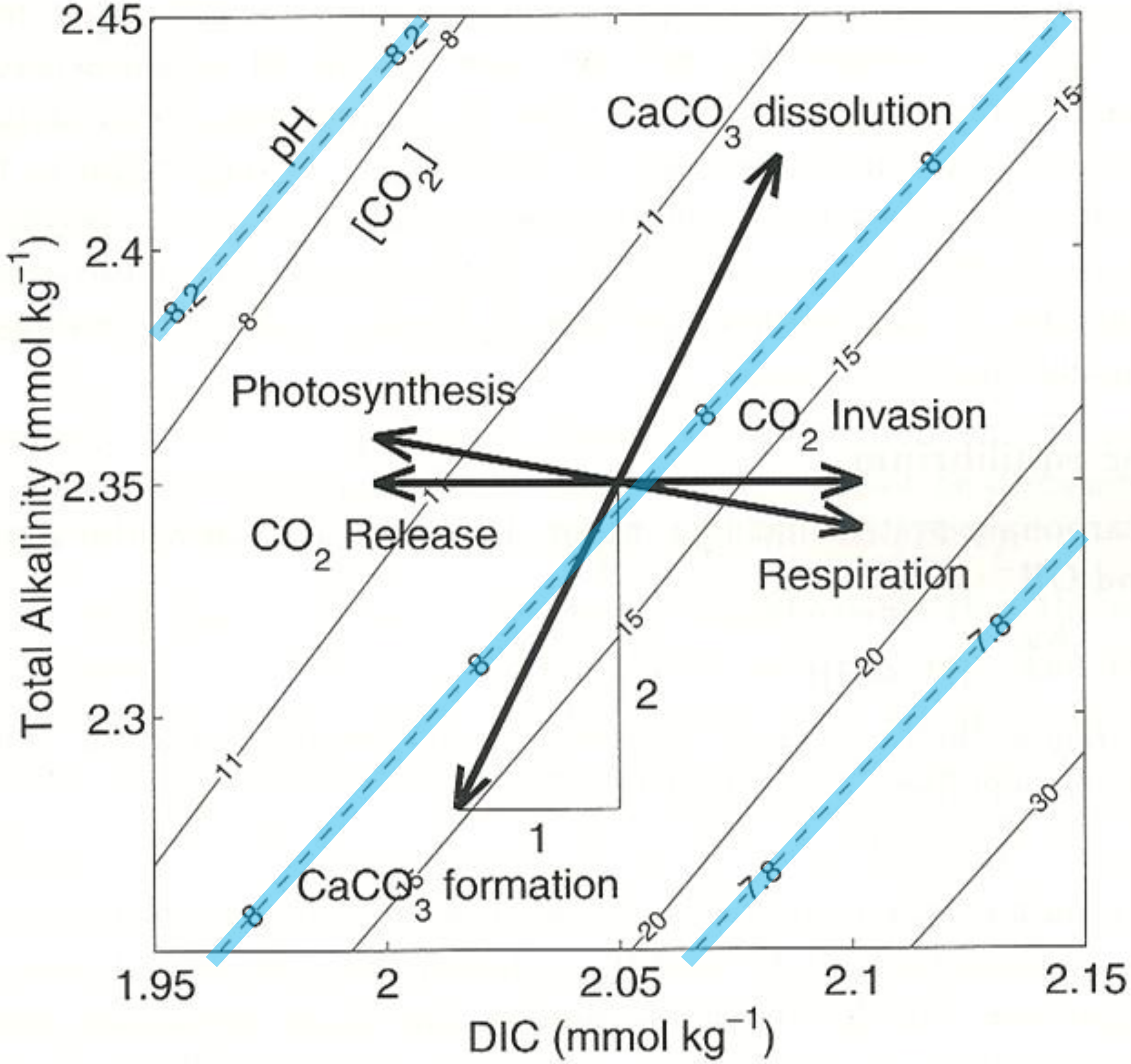
$$ALK = C_T\cdot(\alpha_1 + 2\cdot\alpha_2) + B(OH)_4^{-} + OH^{-} - H^{+}$$

$$A = C_T\cdot\left(\alpha_1 + 2\alpha_2\right) + \frac{K_w}{H^{+}} - H^{+} + B(OH)_4^{-}$$

For a given pH α values are constant hence ALK as a function of CT has is a linear line of the type: y = ax+b

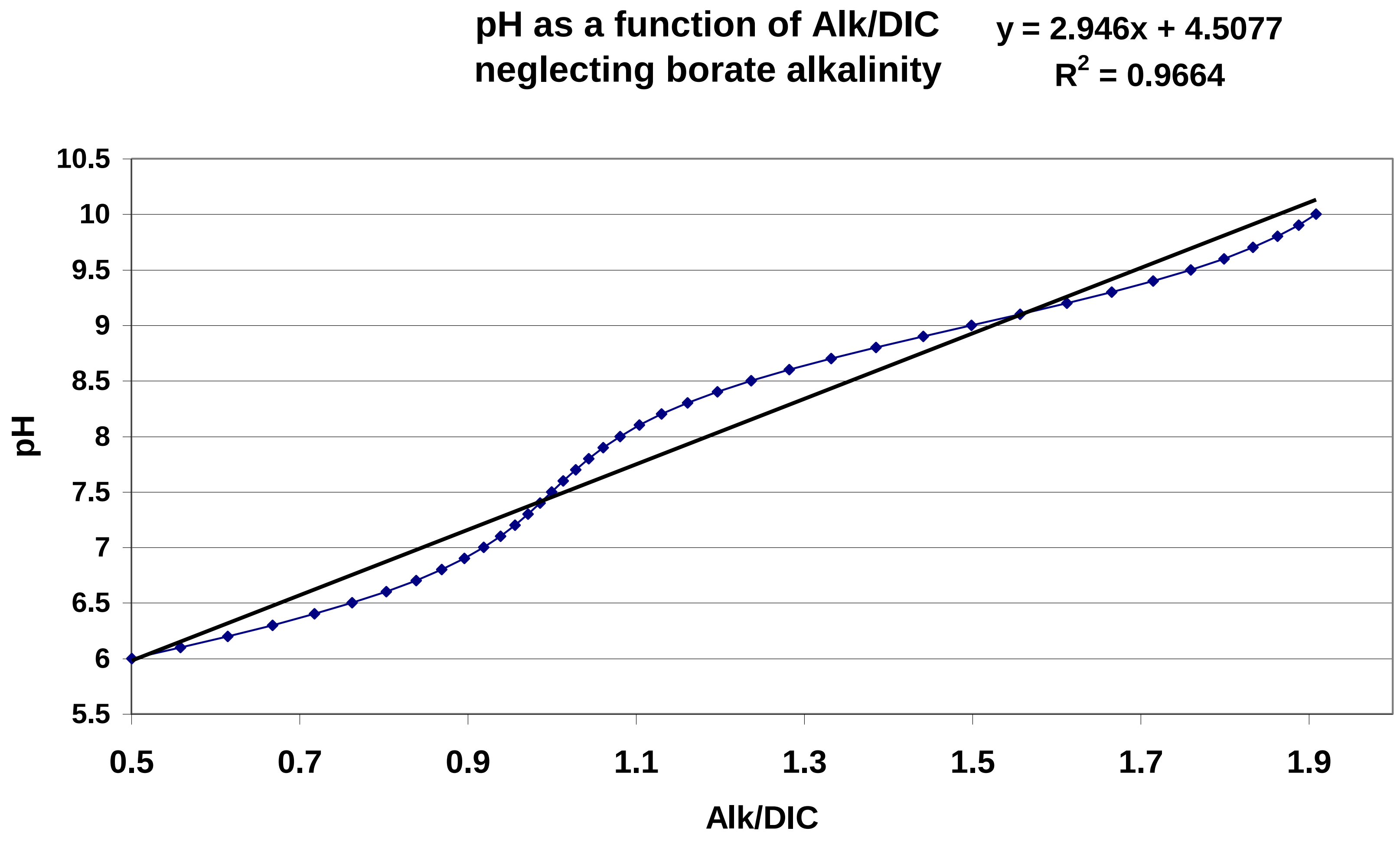


2600
2500
2400
2300
2200
2100
1800
1900
2000
2100
2200
2300
A_T (μeq · kg^-1)
DIC (μmol · kg^-1)
8.3
8.2
8.1
8
7.9
7.8
7.7
7.6



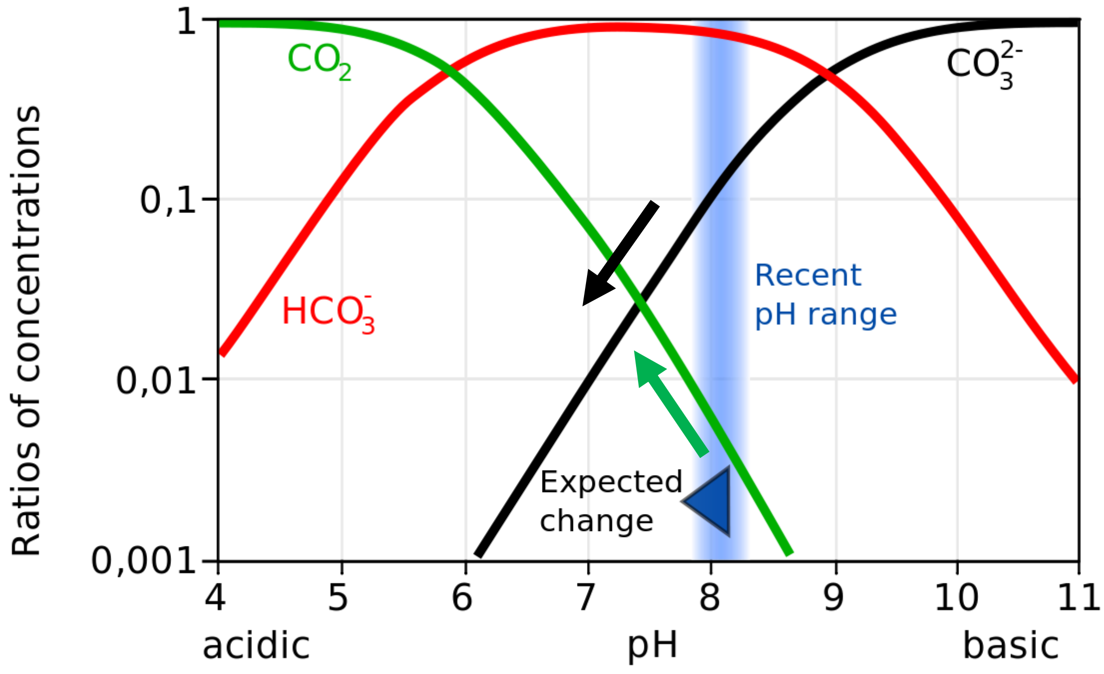
$$Ca^{+2} + 2HCO_3^{-} \leftrightarrows CaCO_3 + H_2O + CO_2$$

pH $\propto$ Alk/DIC

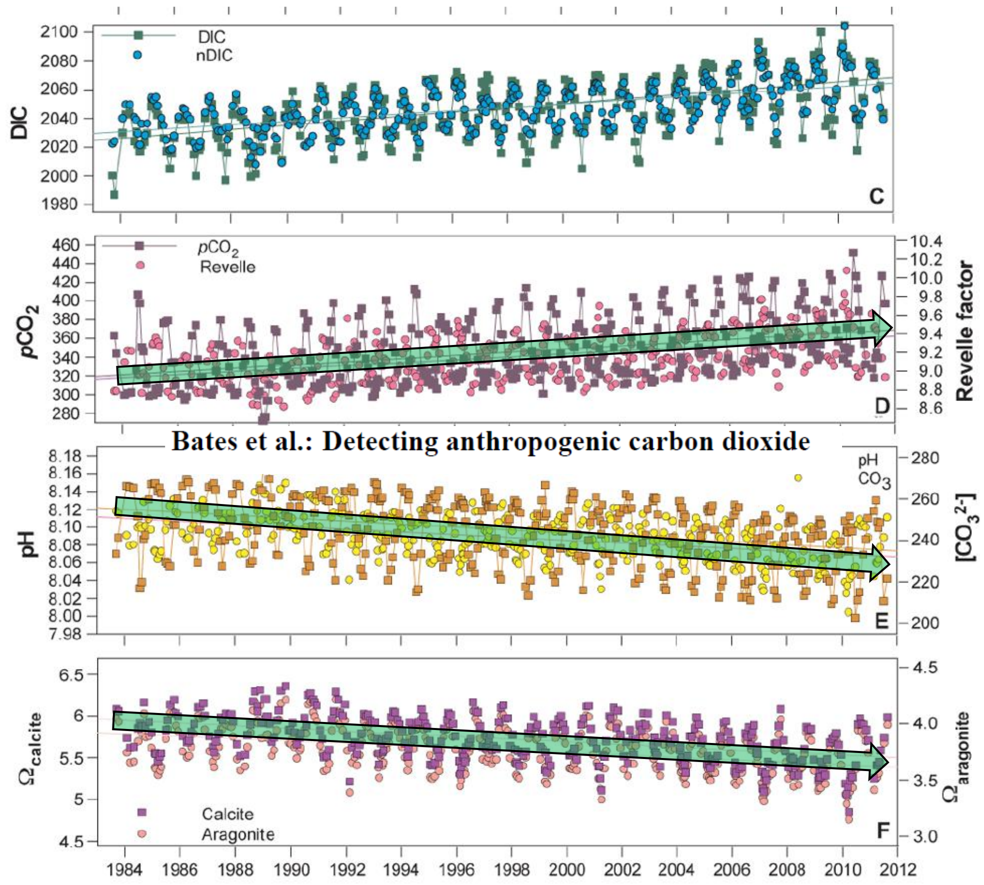


Equilibrium of the carbonate system in the ocean under acidification

Calcification: $Ca^{2+} + 2HCO_3^- \leftrightarrows CaCO_3 + \uparrow CO_2 + H_2O$
reduction of $CaCO_3$ precipitation of in the ocean is a positive feedback to ocean acidification. To understand this we need to define Alkalinity



BATS Bermuda Atlantic time series: 1984 - 2012



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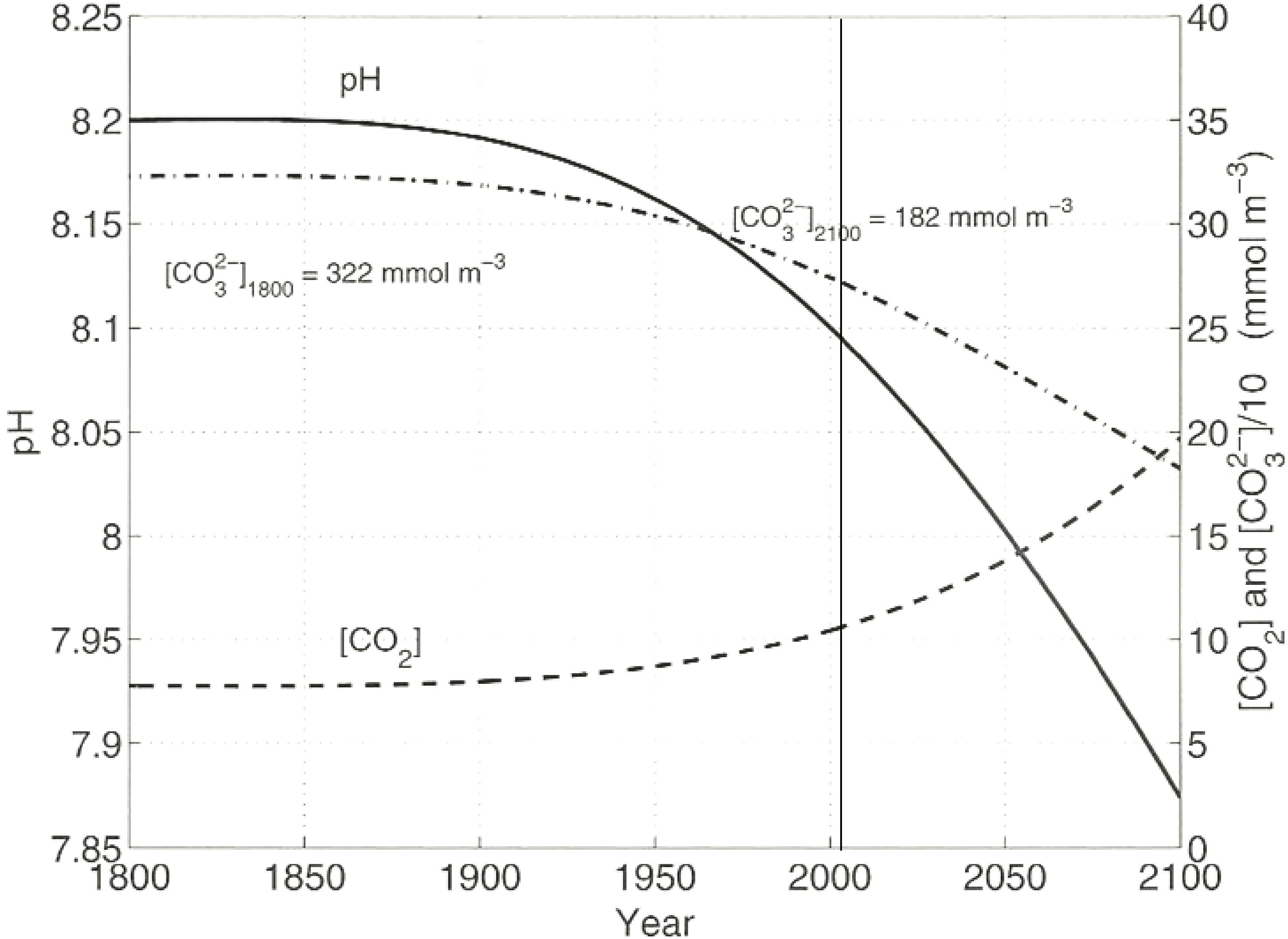


Figure 1.6.27: Changes of CO_2, CO_3^{2-}, and pH in the surface ocean calculated according to the business as usual scenario IS92a ($T_c = 25°$C, $S = 35$).

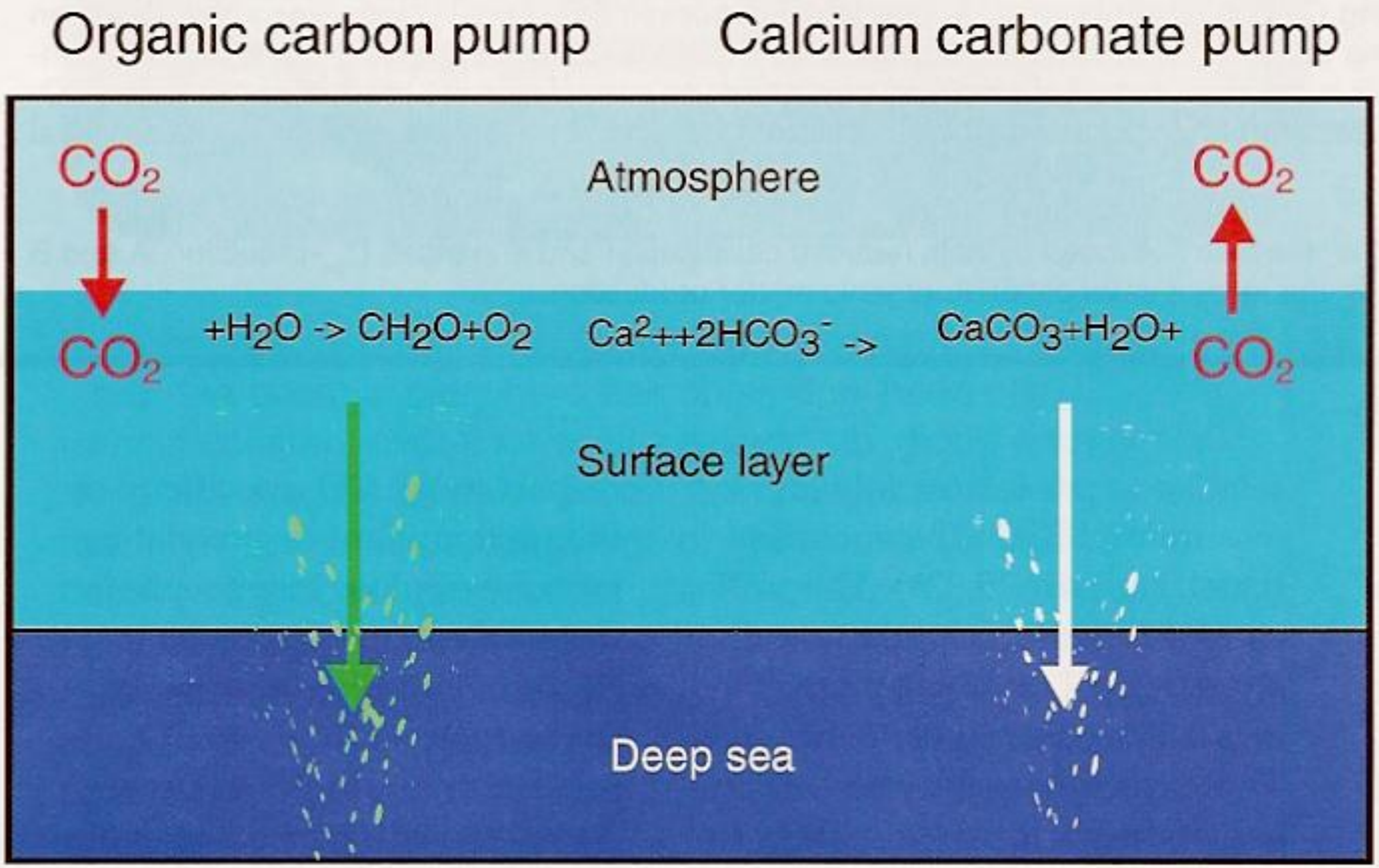
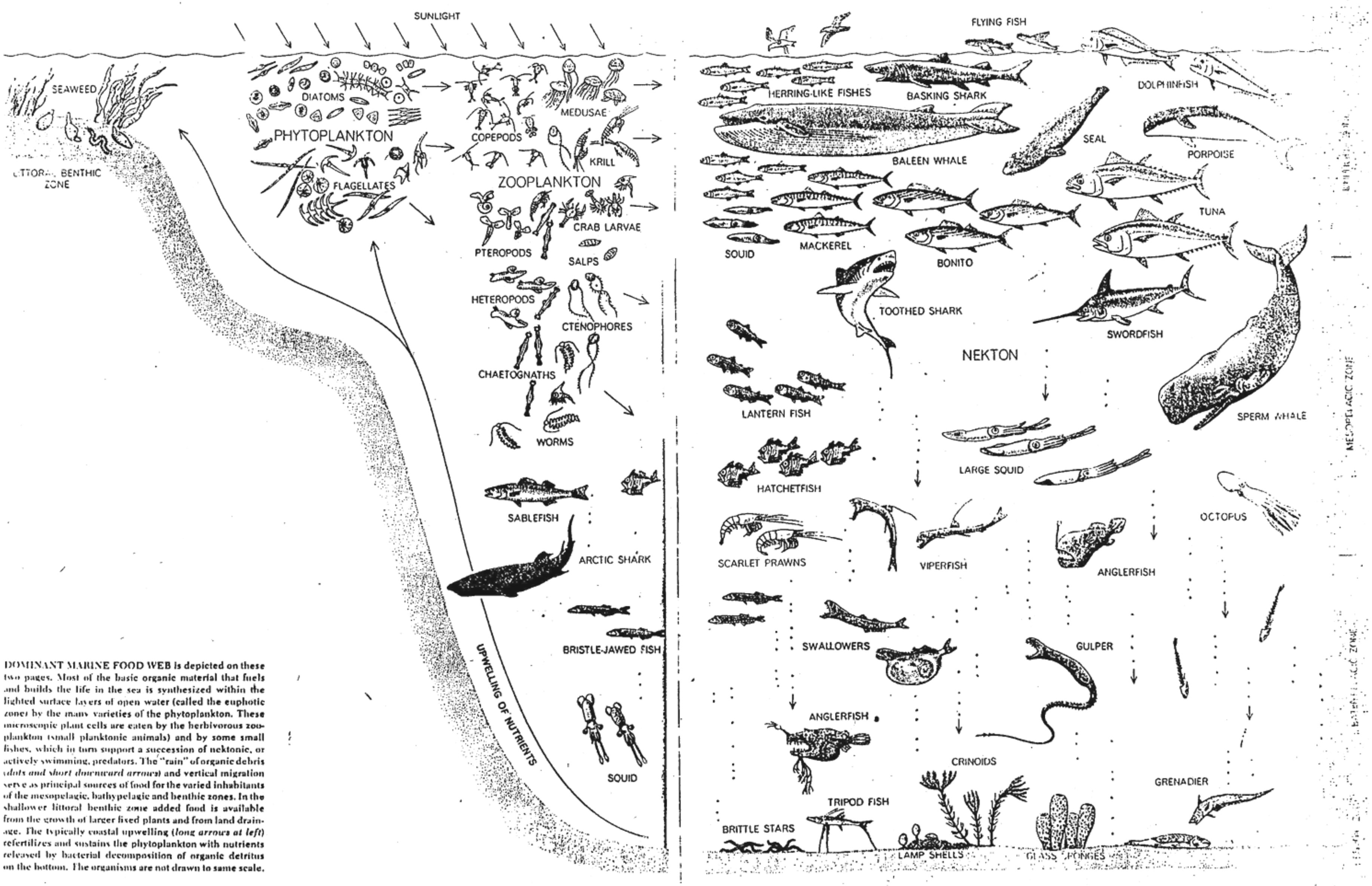


Figure 2. The biological carbon pumps: Photosynthetic carbon fixation in the surface layer of the flux of organic matter to depth, termed organic carbon pump, generates a CO_2 sink in the ocean. In contrast, calcium carbonate production and its transport to depth, referred to as the calcium carbonate pump, releases CO_2 in the surface layer. The relative strengths of these two processes largely determine the biologically-mediated ocean atmosphere CO_2 exchange.

6



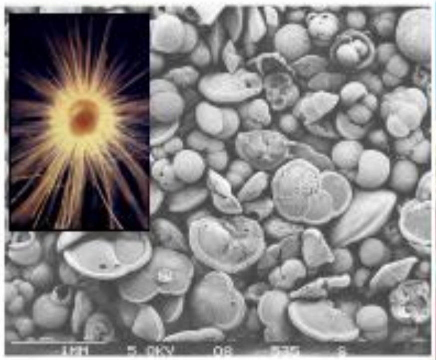
DOMINANT MARINE FOOD WEB is depicted on these two pages. Most of the basic organic material that fuels and builds the life in the sea is synthesized within the lighted surface layers of open water (called the euphotic zone) by the many varieties of the phytoplankton. These microscopic plant cells are eaten by the herbivorous zooplankton (small planktonic animals) and by some small fishes, which in turn support a succession of nektonic, or actively swimming, predators. The "rain" of organic debris (*dots and short downward arrows*) and vertical migration serve as principal sources of food for the varied inhabitants of the mesopelagic, bathypelagic and benthic zones. In the shallower littoral benthic zone added food is available from the growth of larger fixed plants and from land drainage. The typically coastal upwelling (*long arrows at left*) refertilizes and sustains the phytoplankton with nutrients released by bacterial decomposition of organic detritus on the bottom. The organisms are not drawn to same scale.

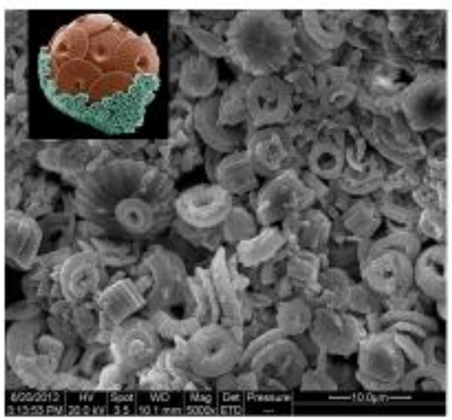
Diatoms

Ocean calcification

To the atmosphere

$$Ca^{+2} + 2HCO_3^- \leftrightarrows CaCO_3 + H_2O + \uparrow CO_2$$





$CaCO_3$ production in the ocean
Total of ~ 1 GT per year
Only 20% accumulates

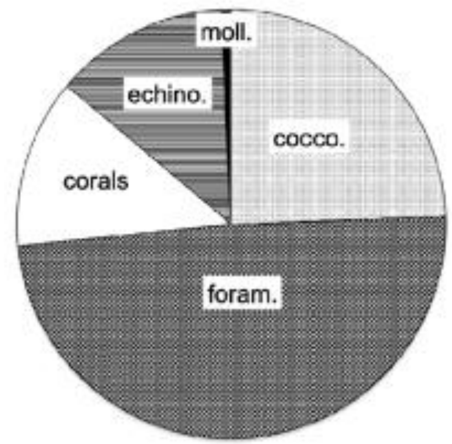
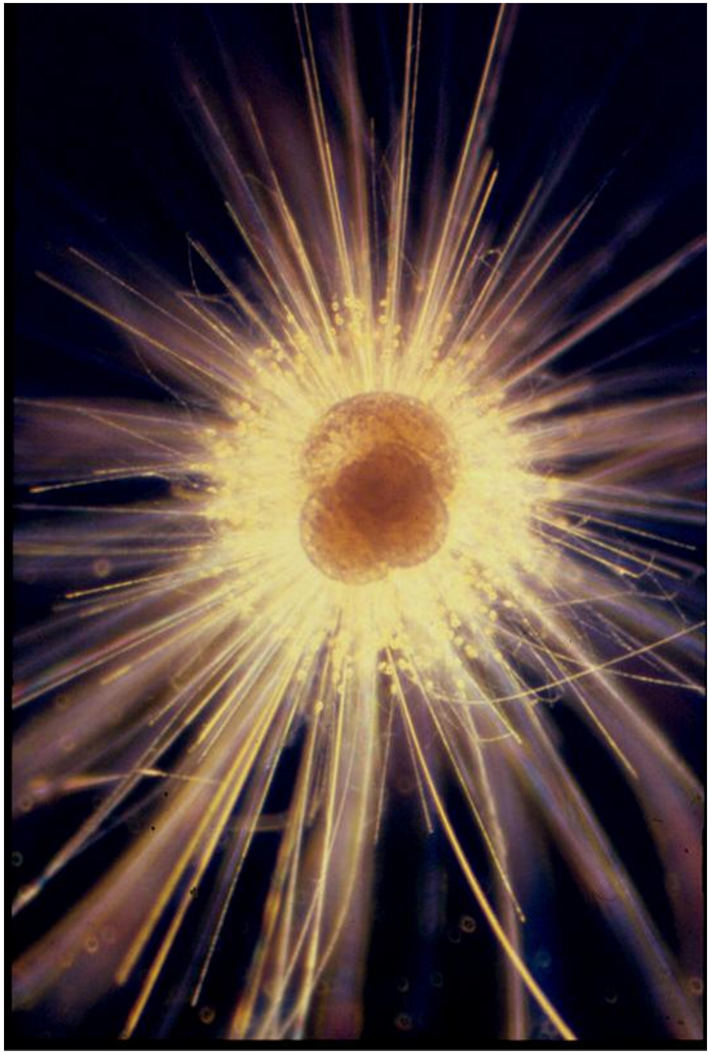
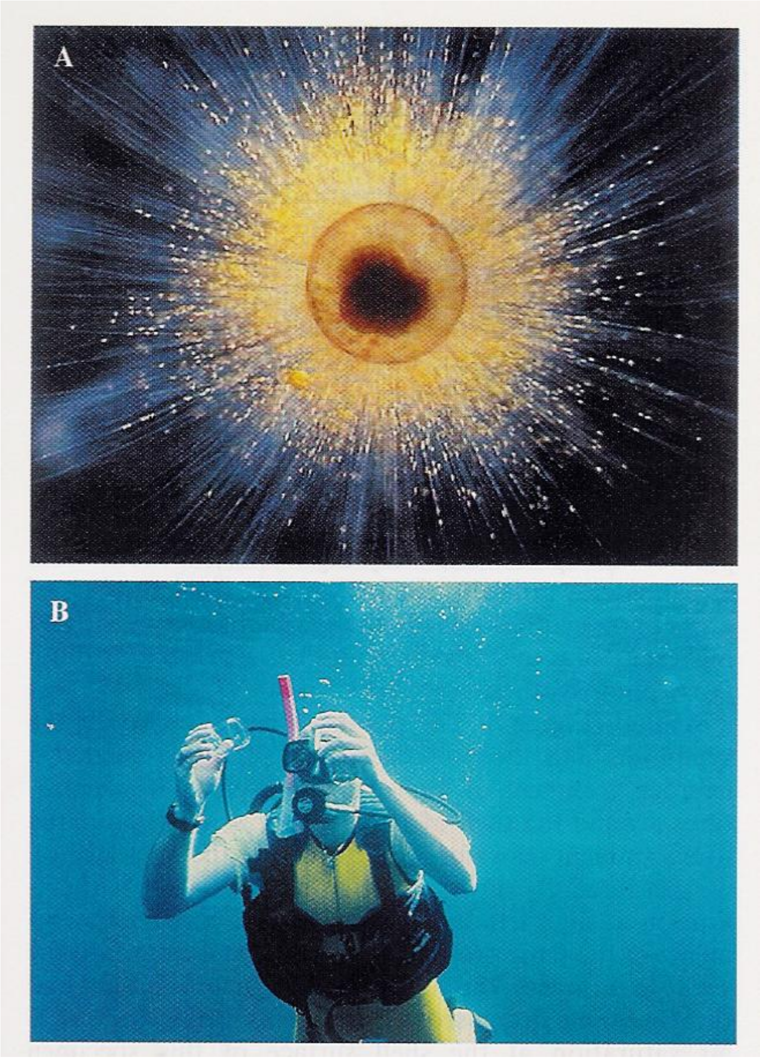


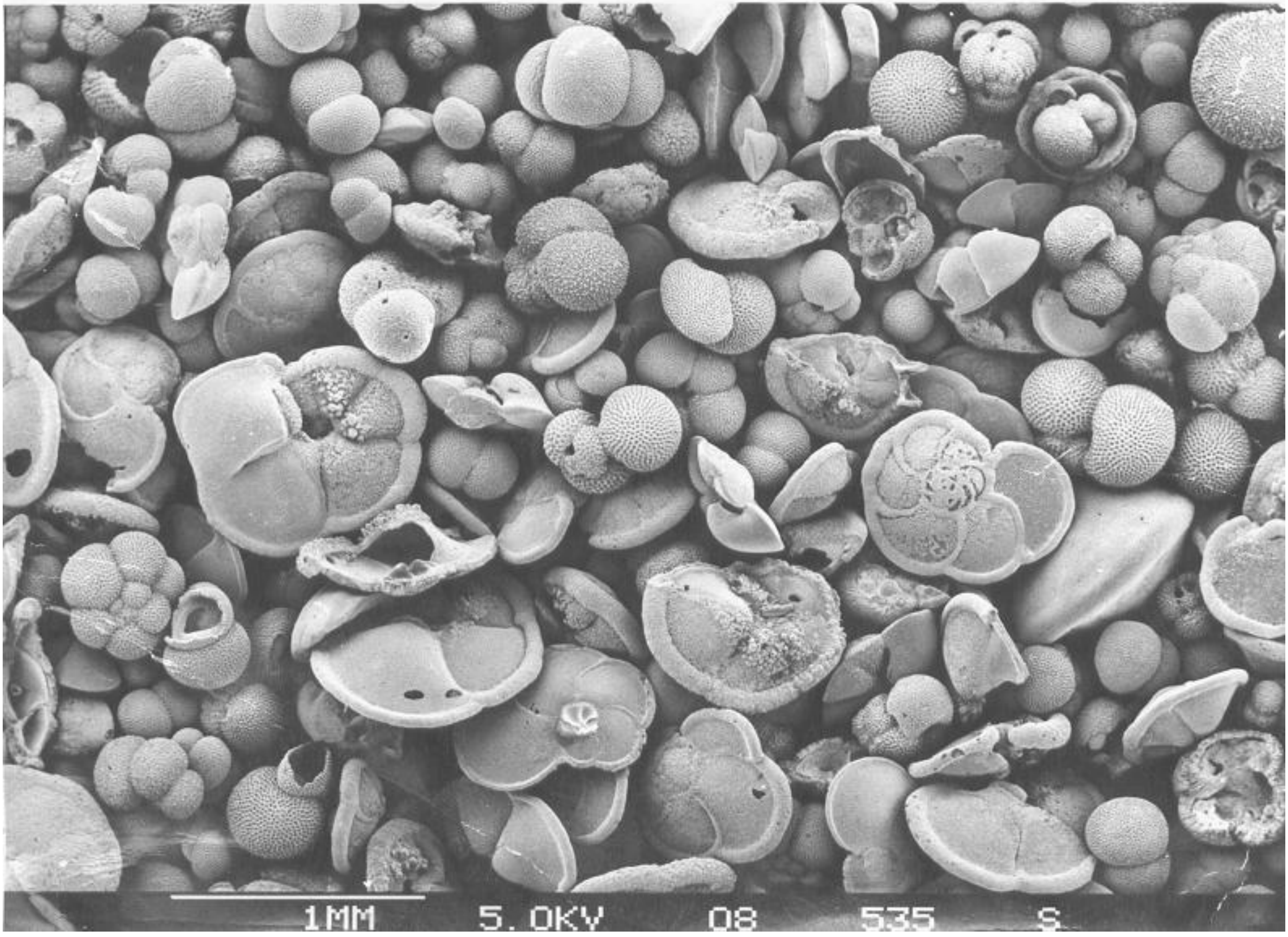
Fig. 9. Calcium carbonate global production by the major marine calcifiers (Gt $CaCO_3$ yr^{-1}).

Tambutte et al 2011 JEMBE

Foraminifera precipitate $CaCO_3$ by a complex genetically controlled biomineralization process. Symbiotic algae are often involved.






1MM
5.0KV
08
535
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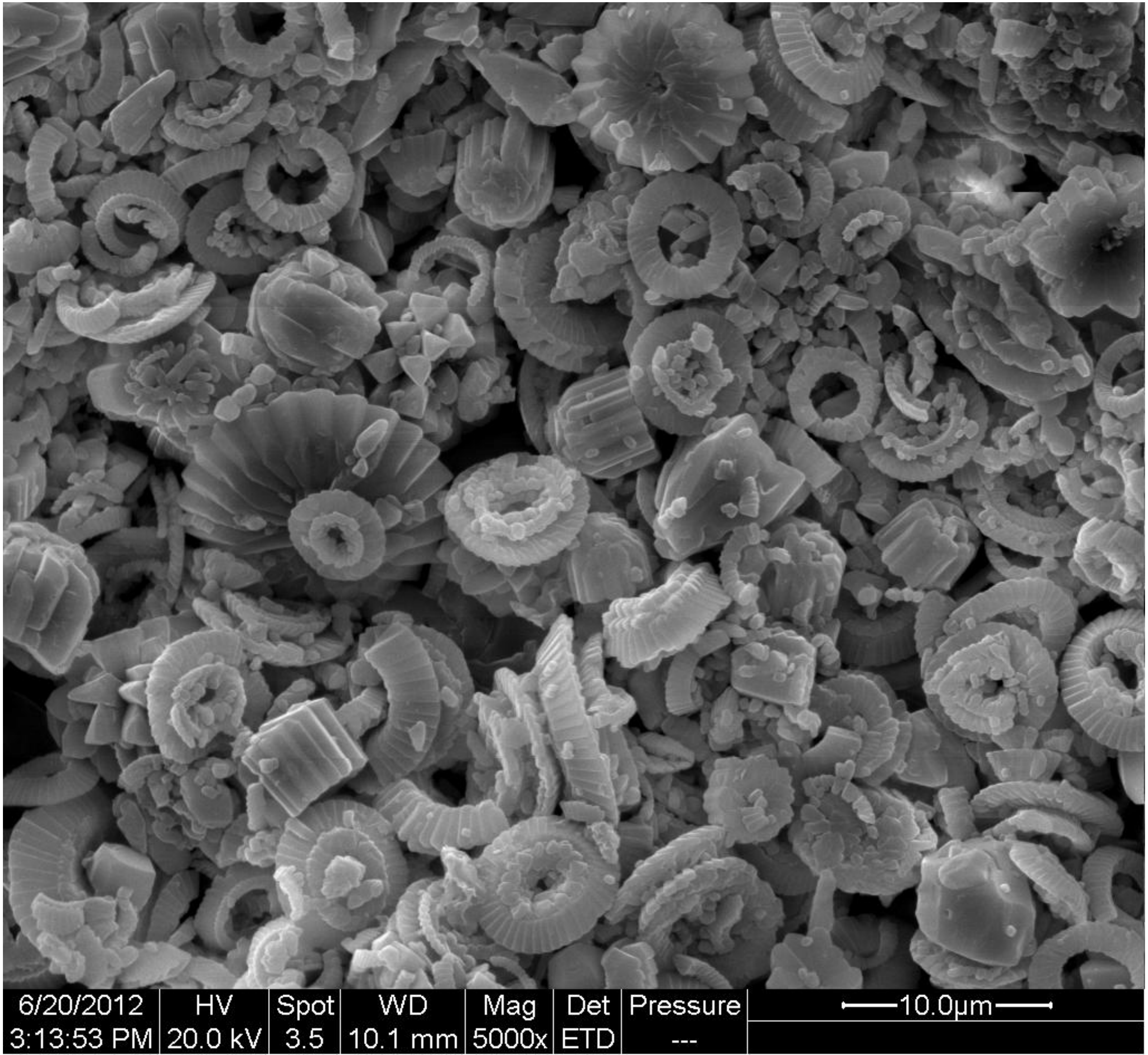
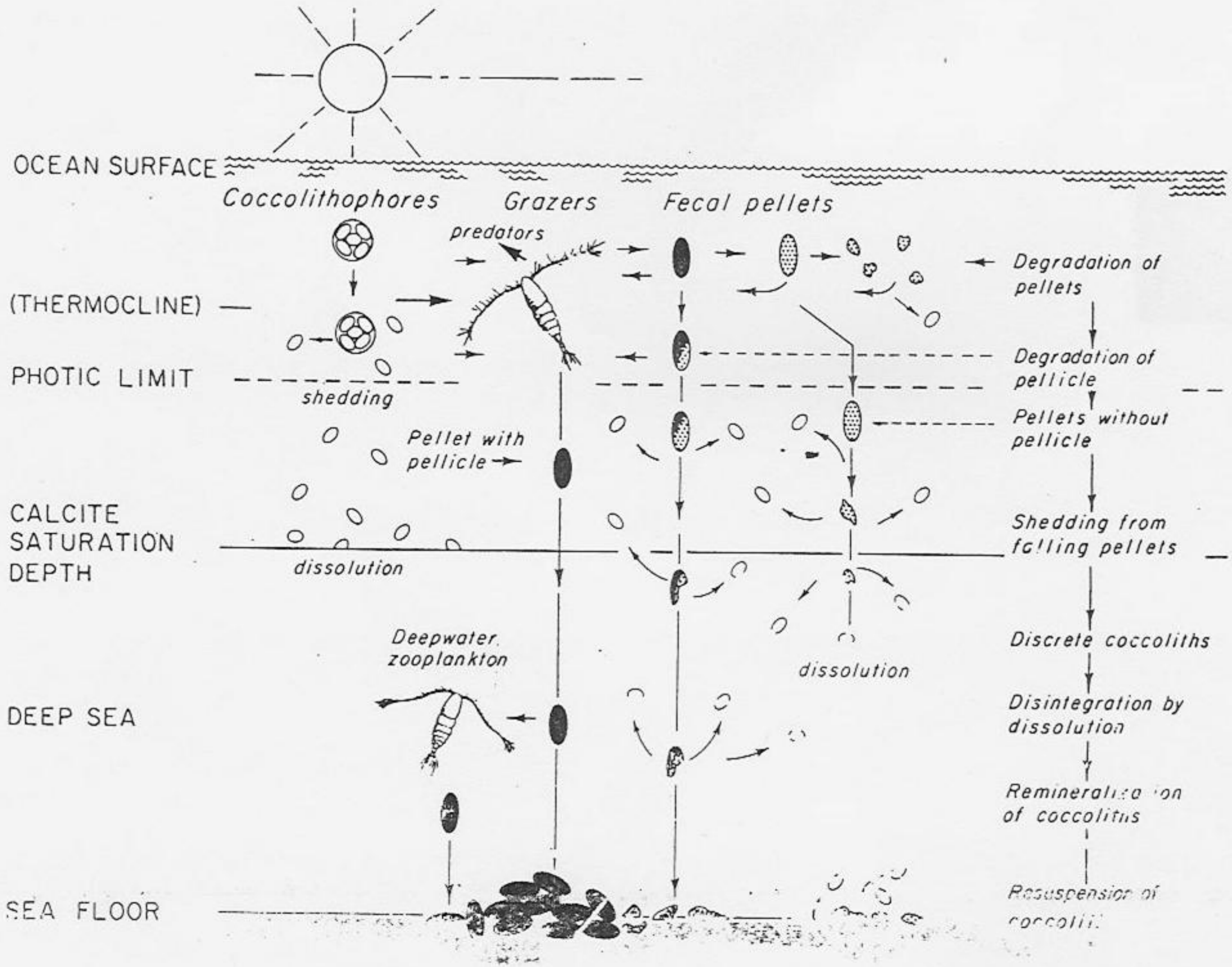


https://www.e-education.psu.edu/earth103/sites/www.e-education.psu.edu.earth103/files/module05/141_001.jpg



Sinking rates of coccoliths; in a pellet - 150m day; a discrete coccolith - 0.15 m day

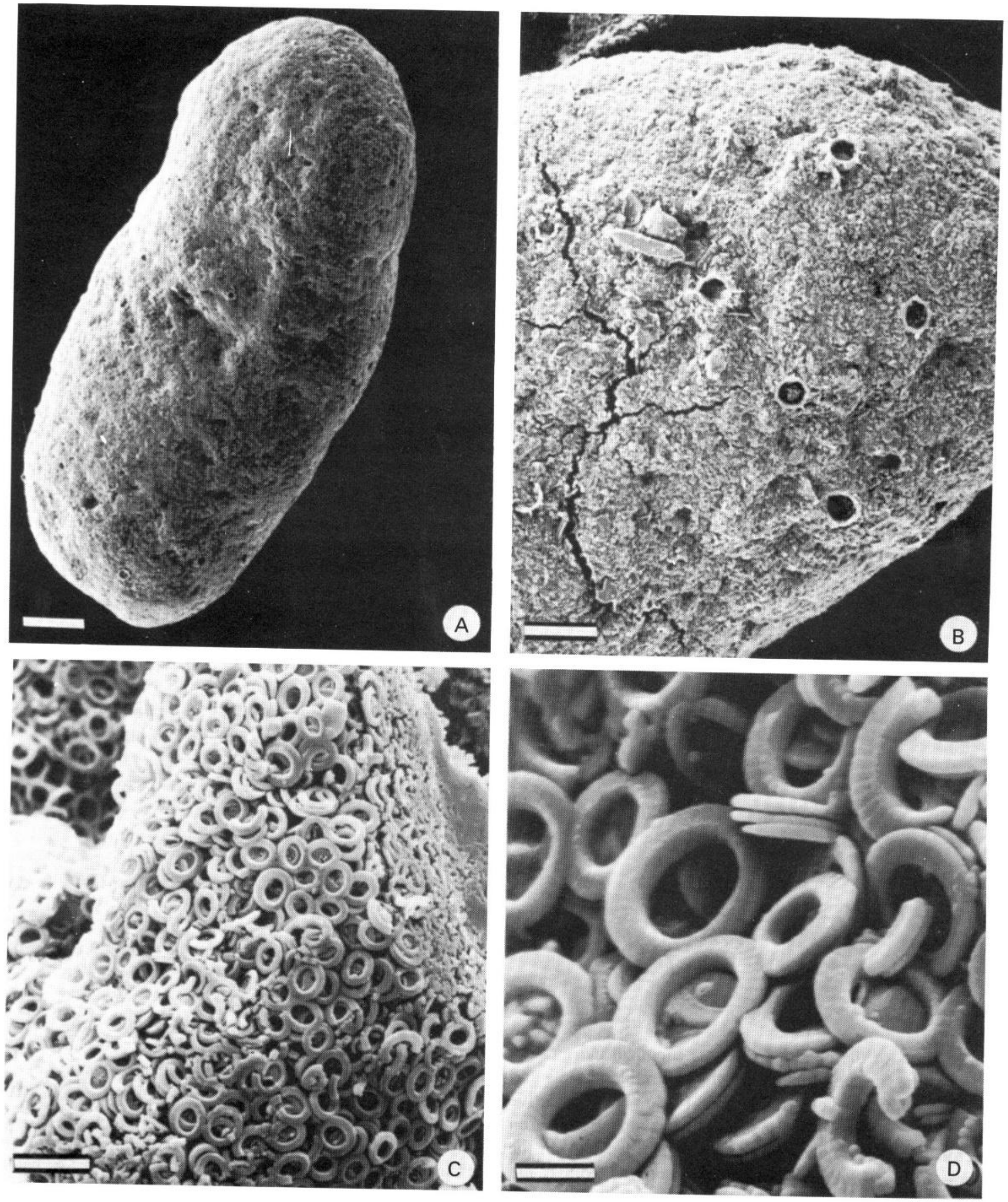
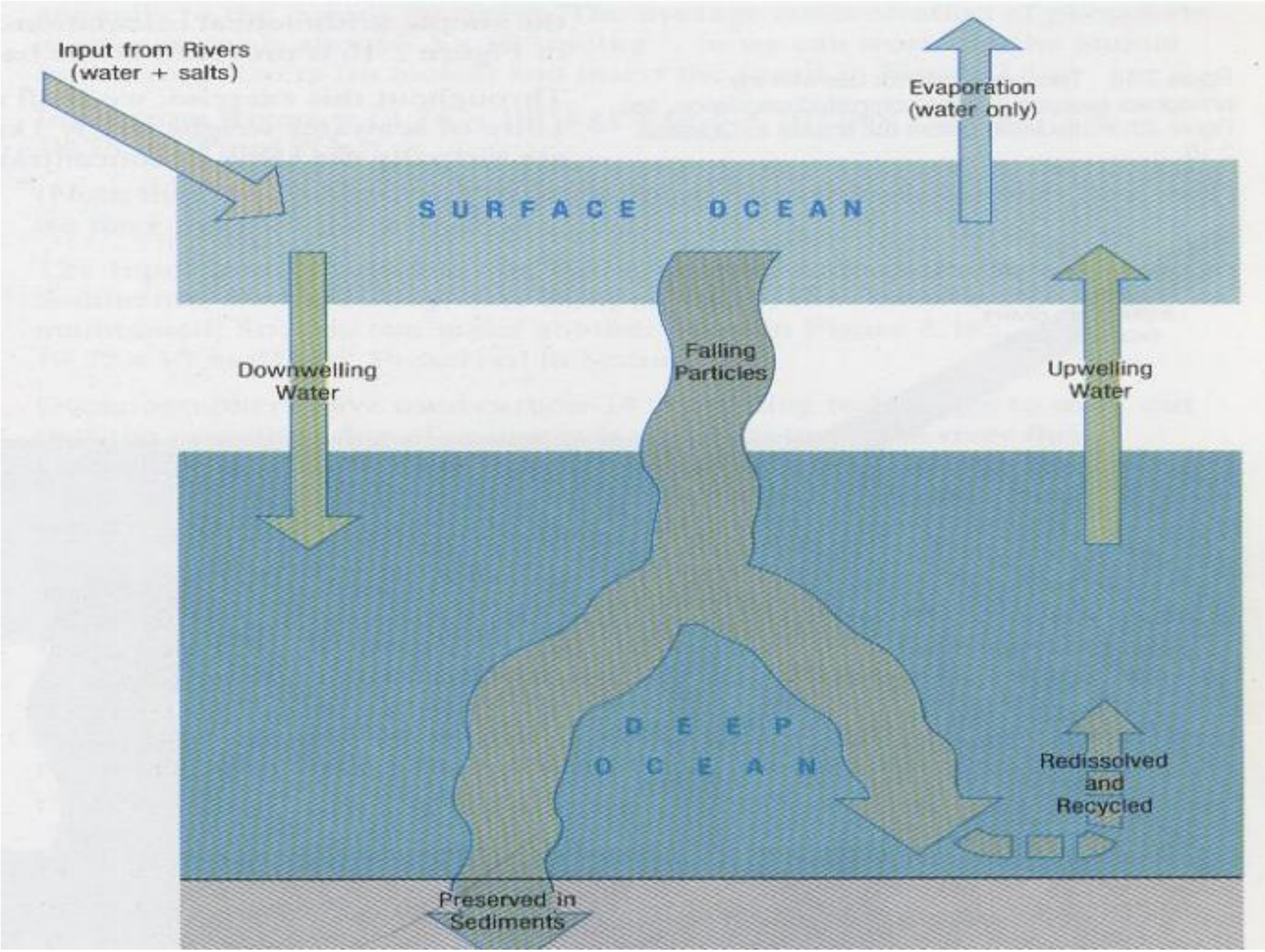
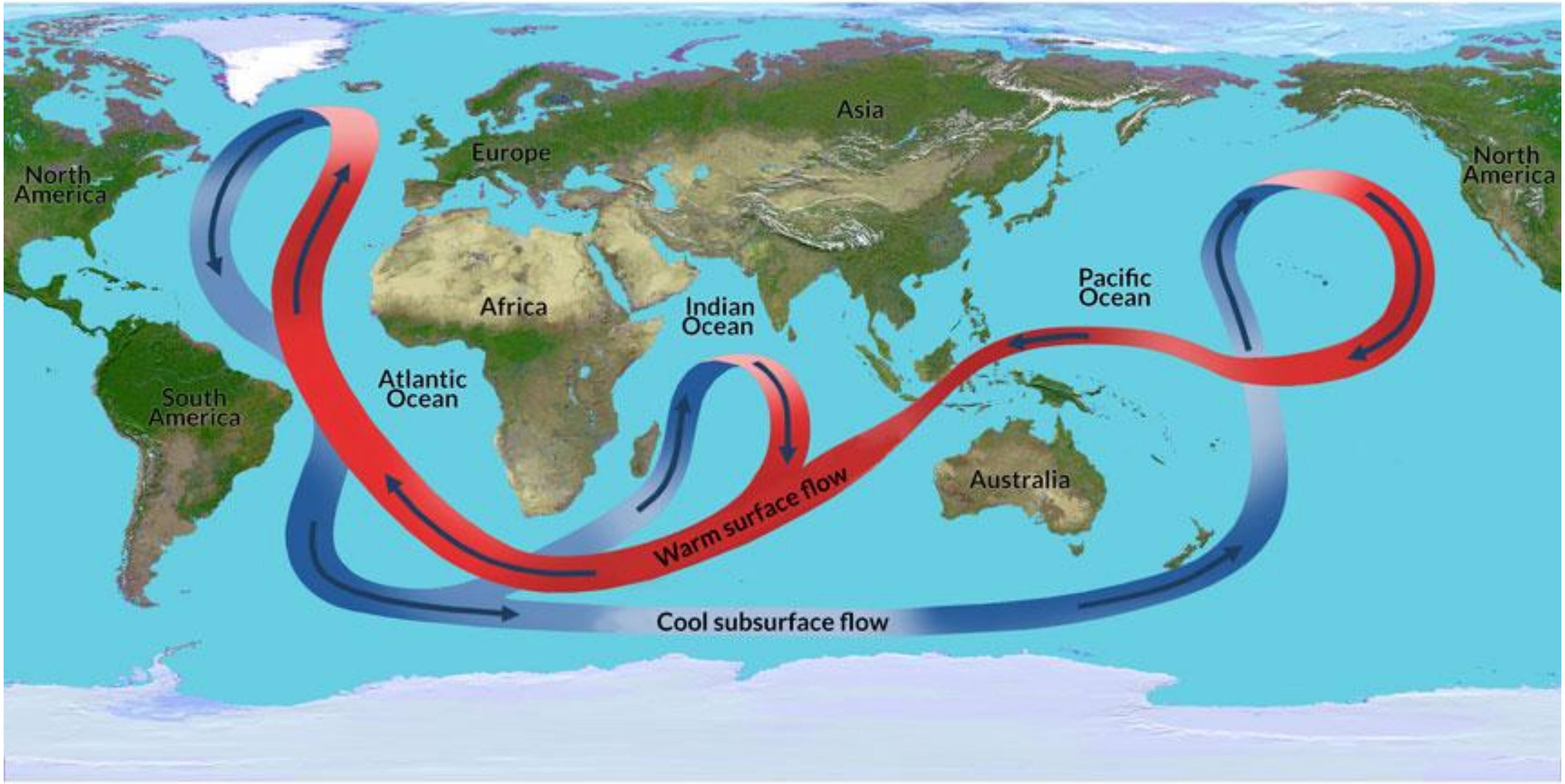
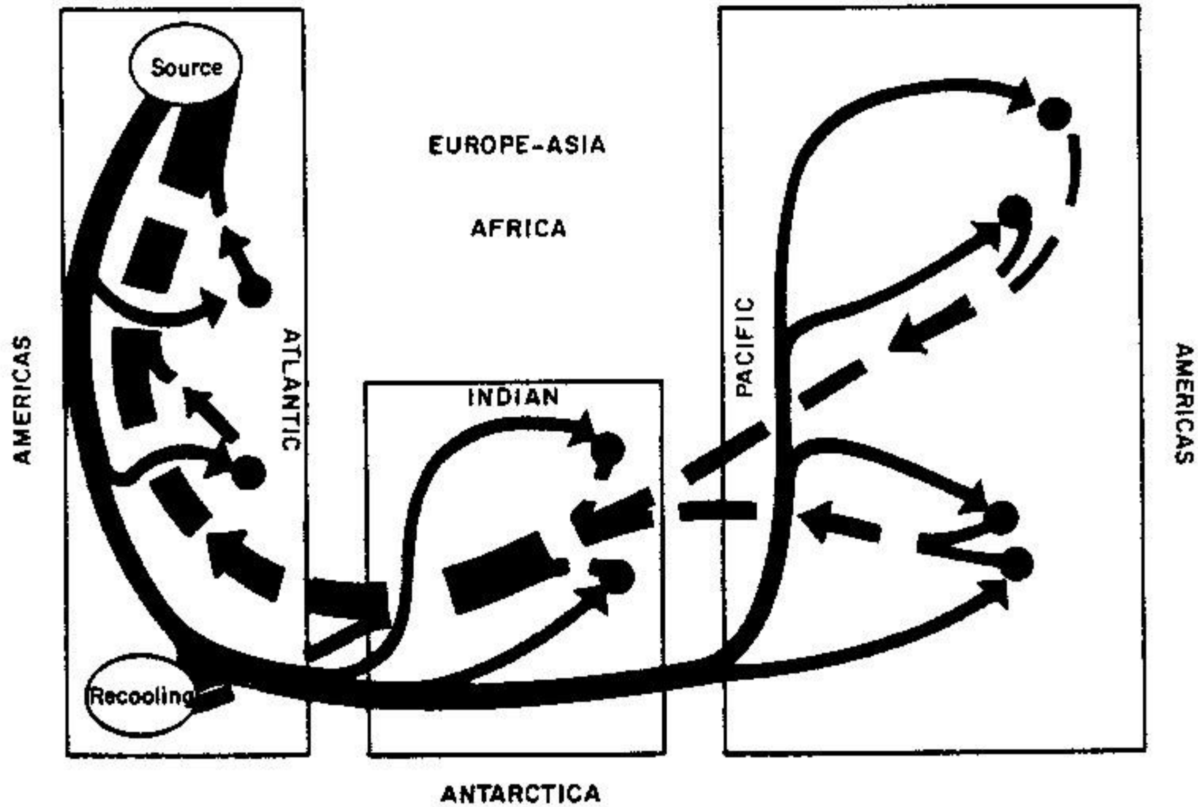


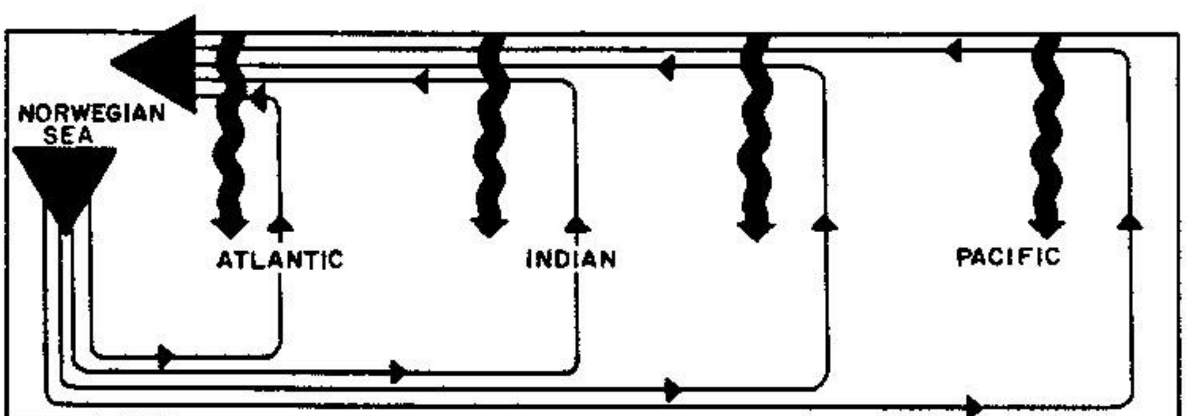
Fig. 2. Fecal Pellets. A. Typical fecal pellet. Scale bar is 100 µm. B. Close-up of the surface of a fecal pellet. Circular objects on the surface are silicoflagellates. Scale bar is 50 µm. C. and D. Close-up of the surface of a fecal pellet composed entirely of the coccolithophore *Umbilicosphaera sibogae* . Scale bars are 10 µm and 2 µm, respectively. SEM photos compliments of C. Pilskaln; C. and D. from Pilskaln (1985).


Input from Rivers
(water + salts)
Evaporation
(water only)
SURFACE OCEAN
Downwelling
Water
Falling
Particles
Upwelling
Water
DEEP
OCEAN
Redissolved
and
Recycled
Preserved in
Sediments

The general circulation of the oceans




Source
EUROPE-ASIA
AFRICA
AMERICAS
ATLANTIC
INDIAN
PACIFIC
AMERICAS
Recooling
ANTARCTICA


NORWEGIAN SEA
ATLANTIC
INDIAN
PACIFIC

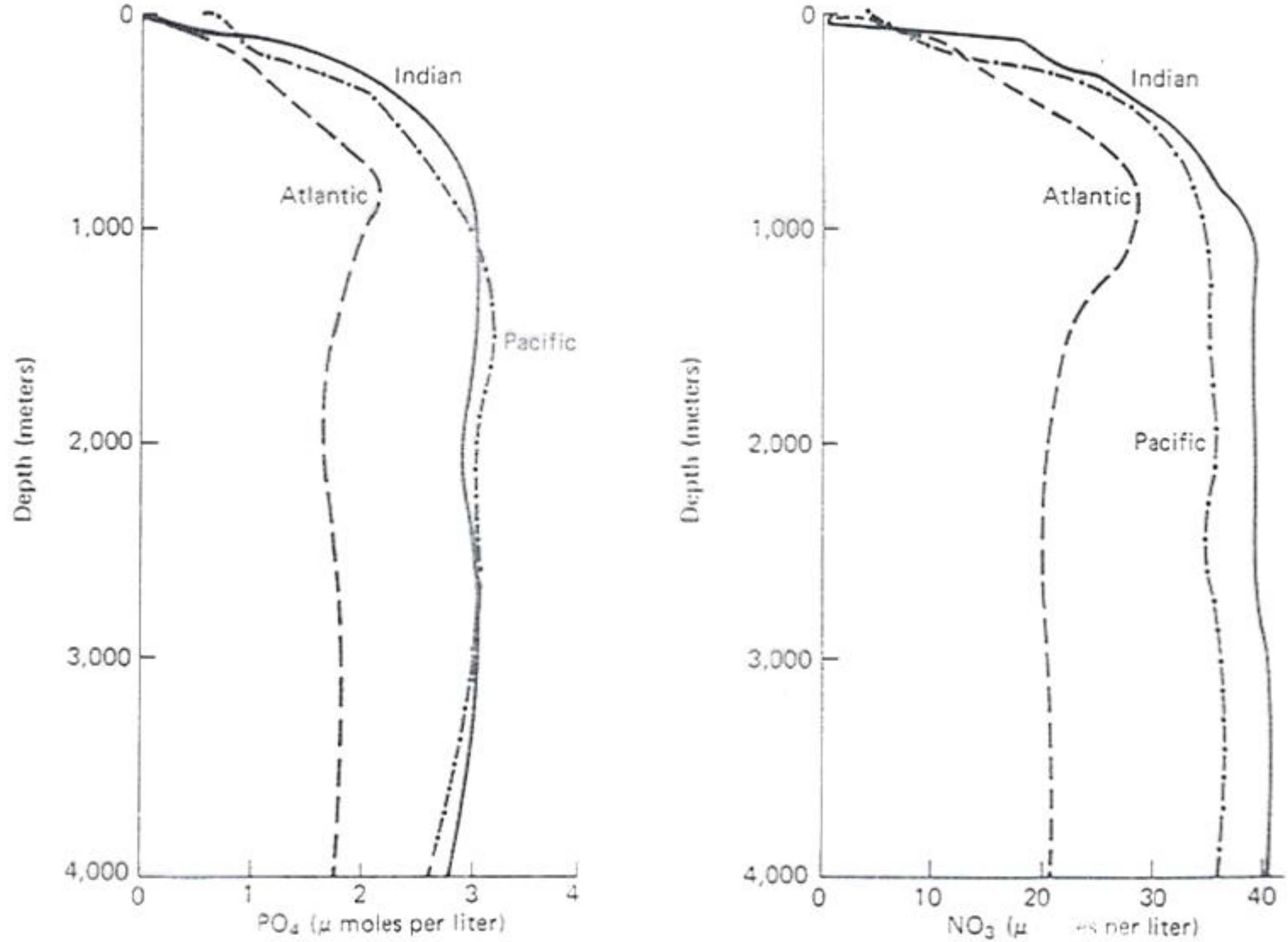
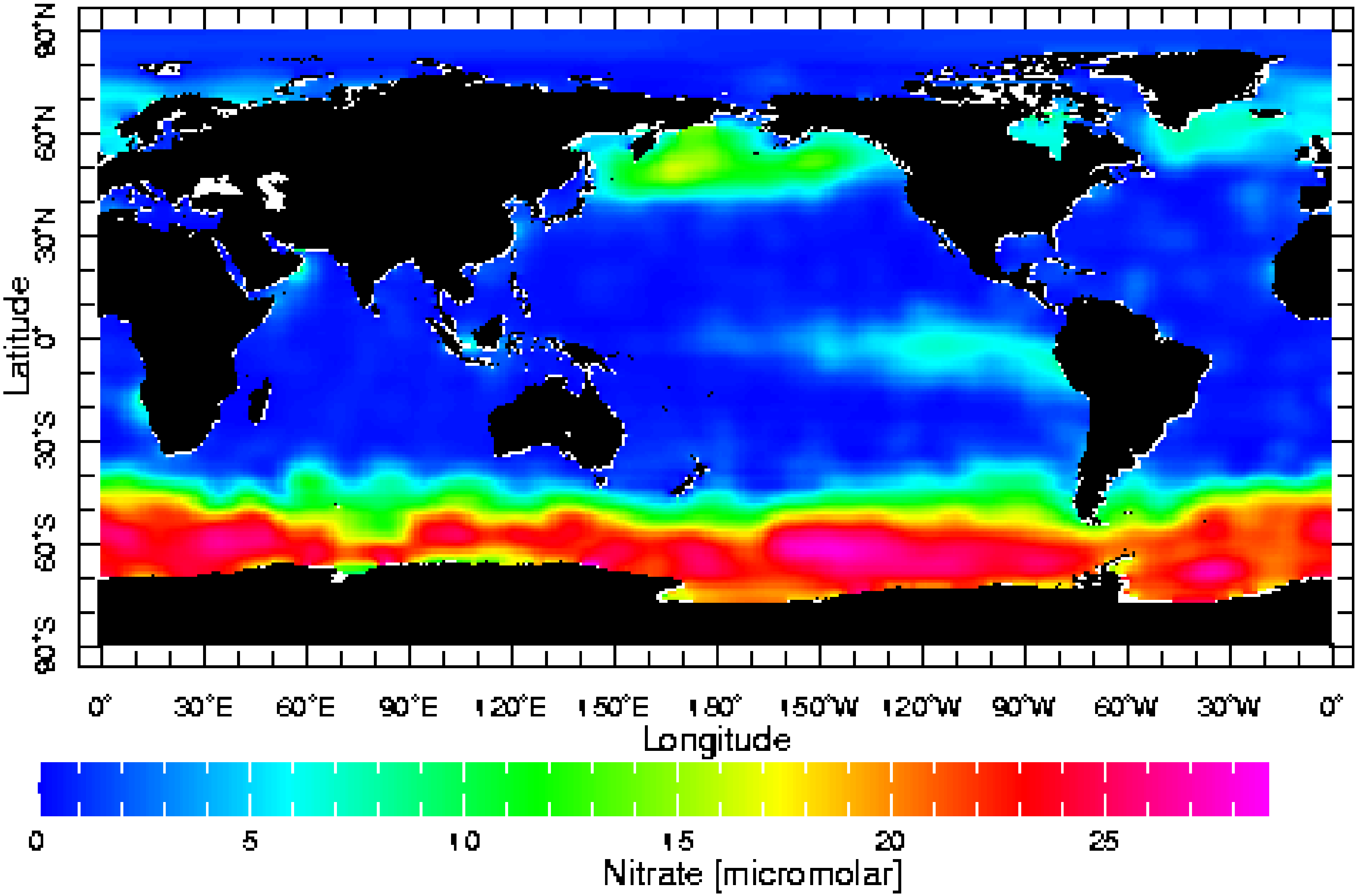
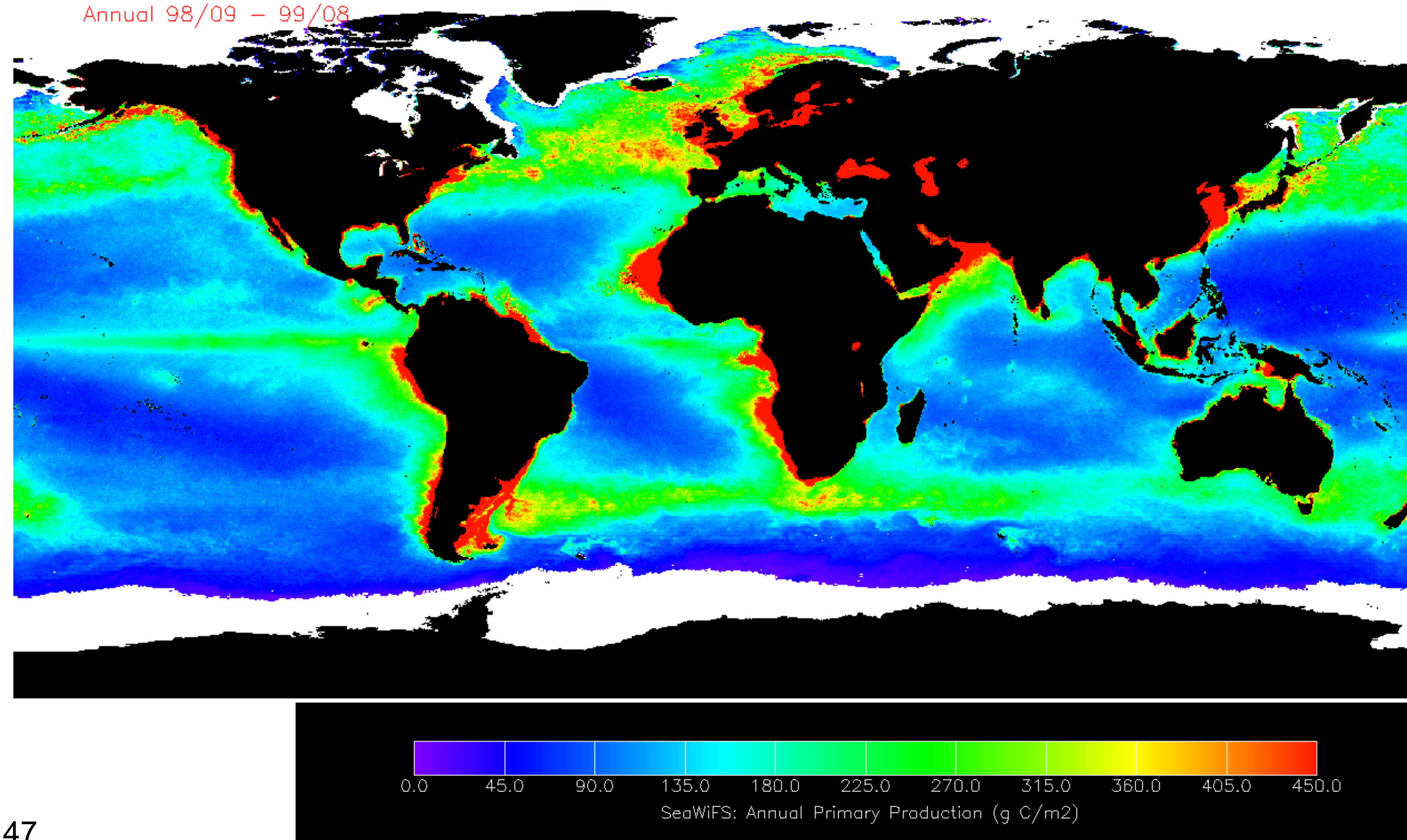


FIGURE 9.2 Vertical distributions of the nutrient components, phosphate and nitrate, in typical water columns in the Atlantic, Pacific, and Indian Oceans. (After Sverdrup, Johnson, and Fleming, 1942).

Surface distribution of nitrate



Surface water productivity



Productivity Study

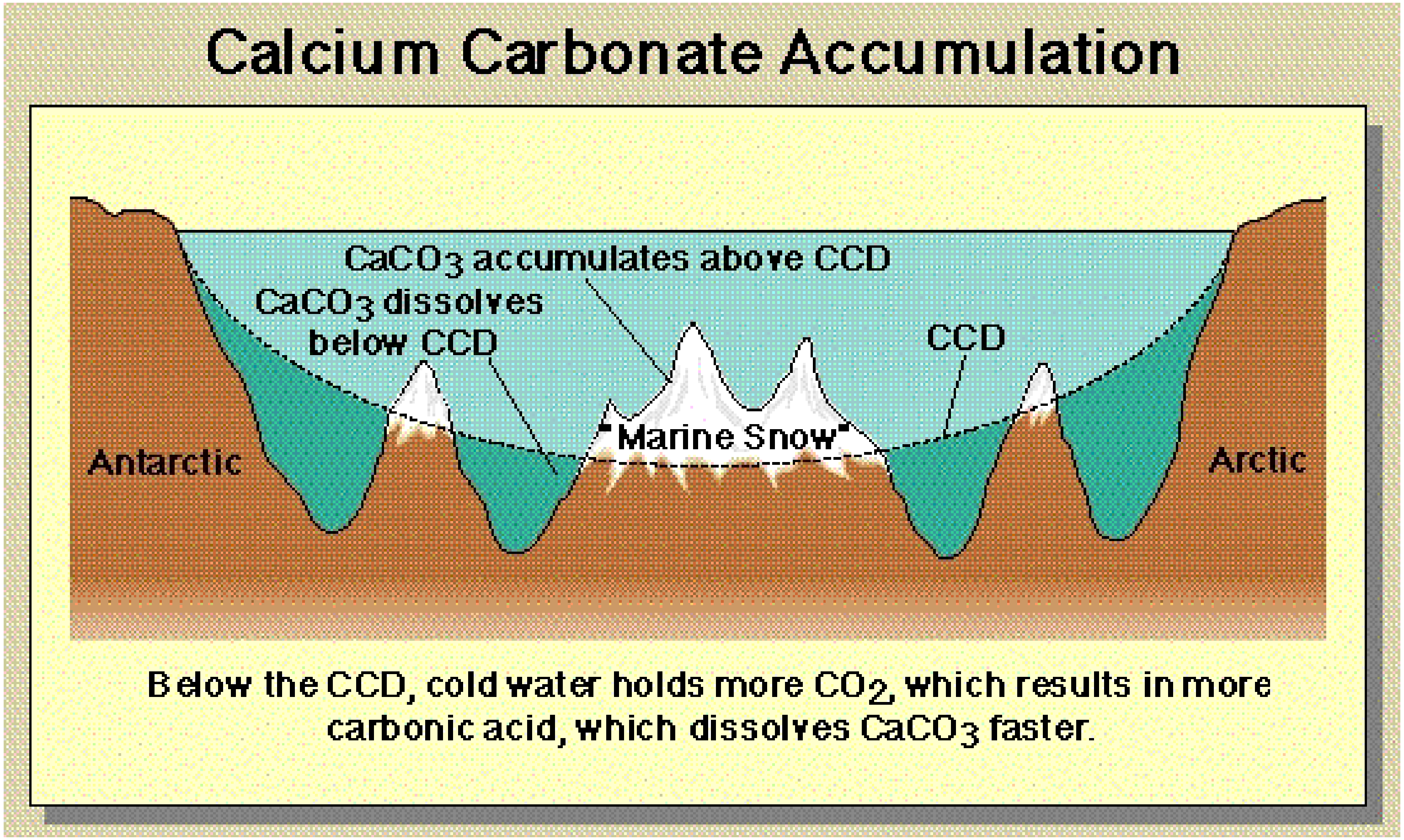
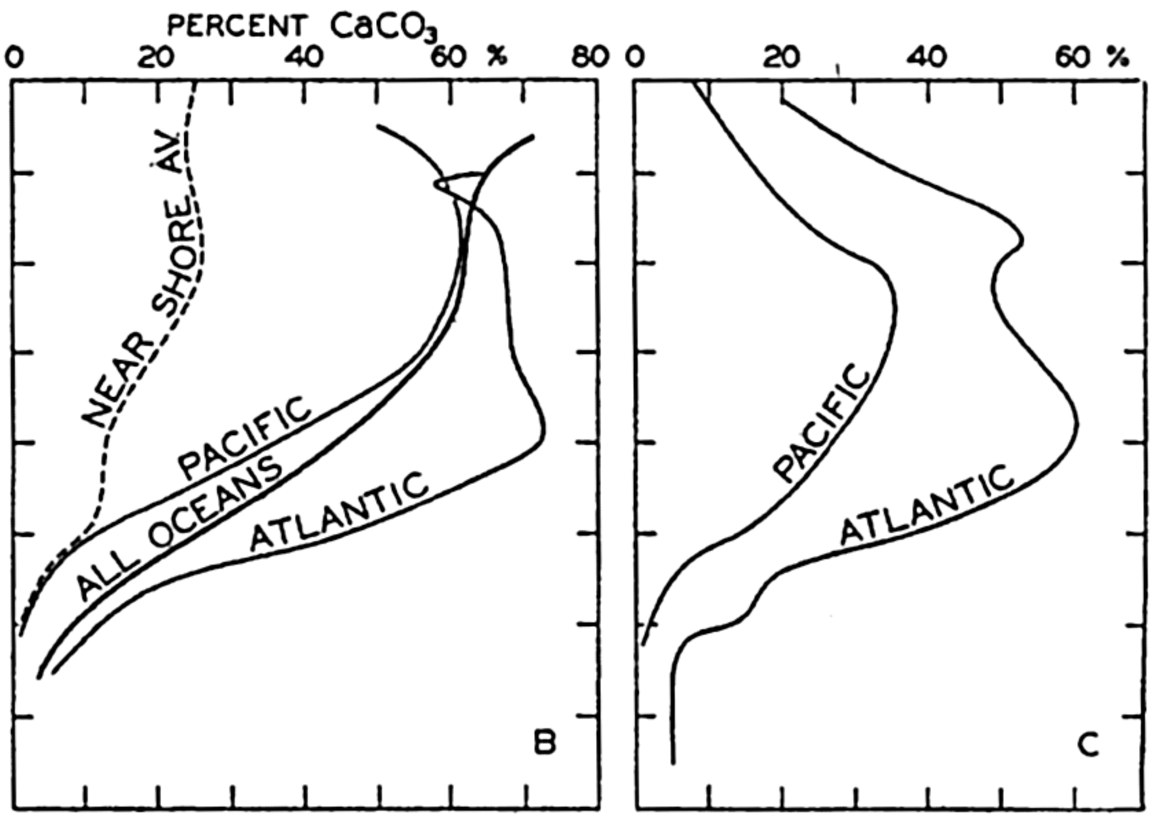
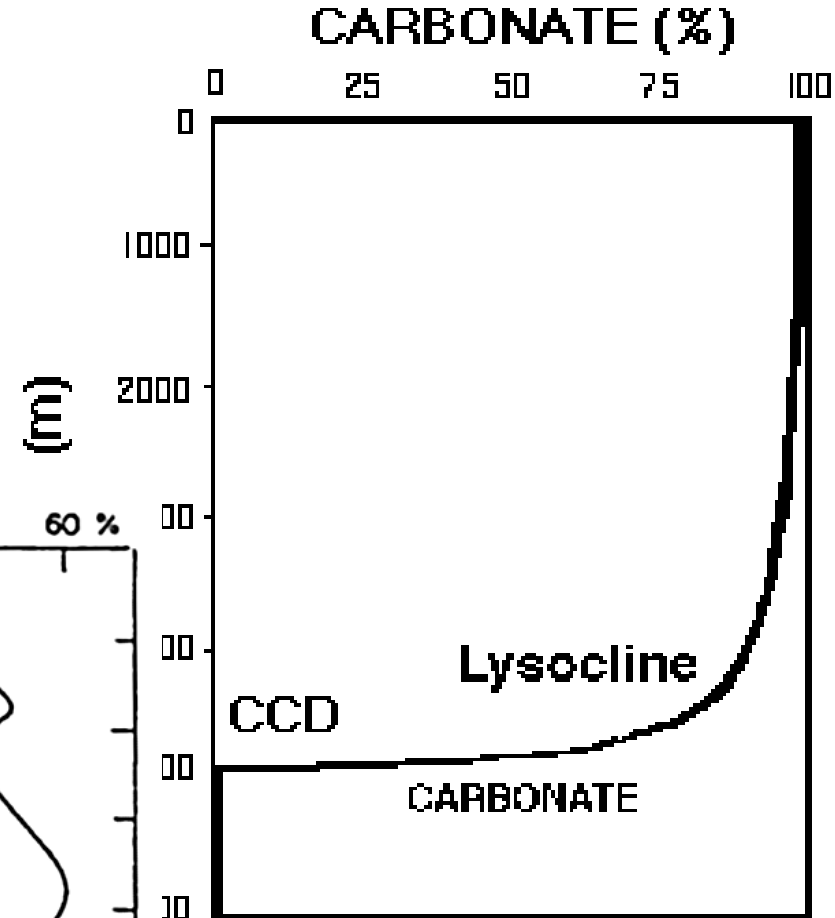


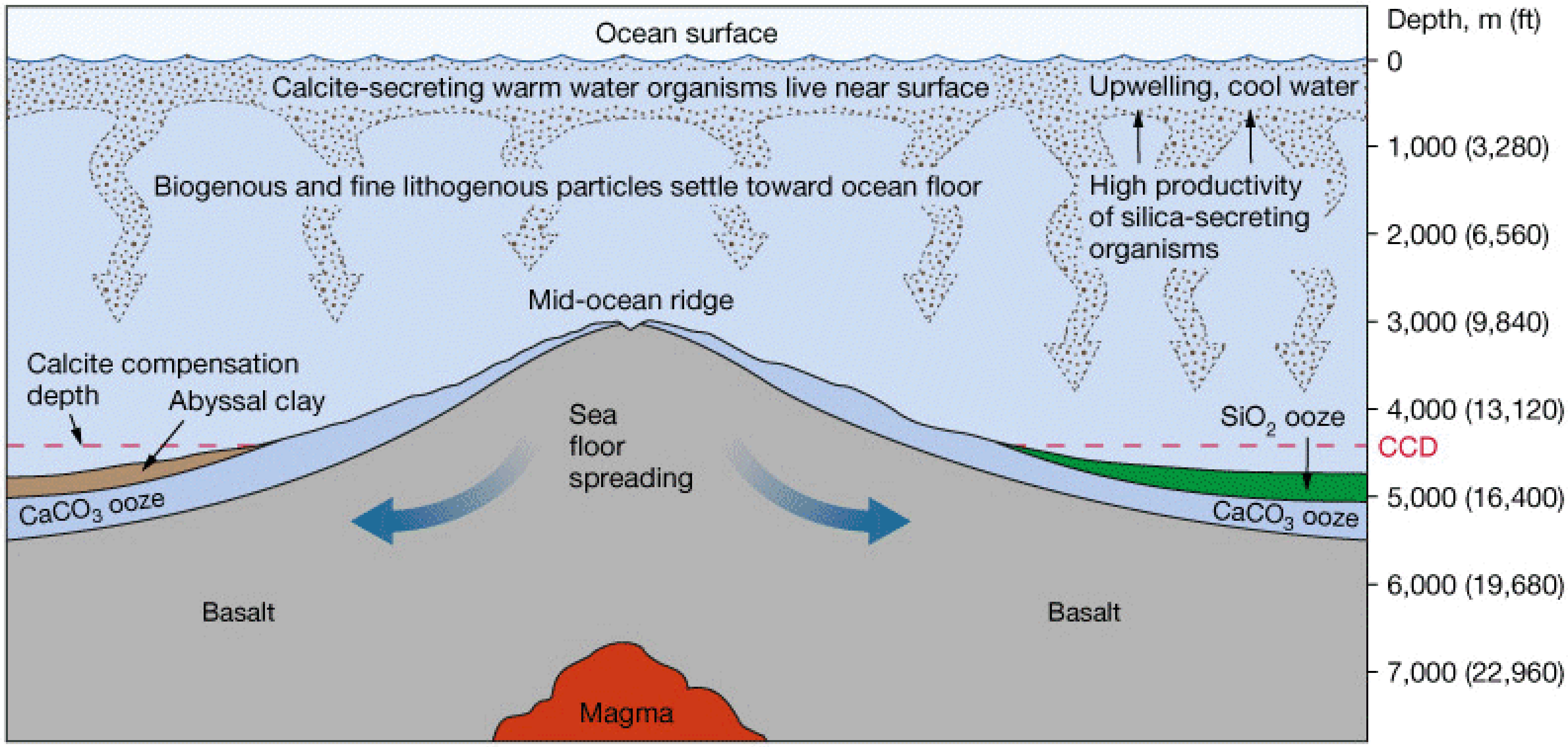
Diagram showing the sediment "snow line" in the oceans. The dashed line shows the calcium carbonate compensation depth (CCD). At this depth, the rate at which calcareous sediments accumulate equals the rate at which those sediments dissolve. The CCD varies with temperature: the "snow line" is lower in warmer waters and higher in colder waters.

CALCITE COMPENSATION DEPTH

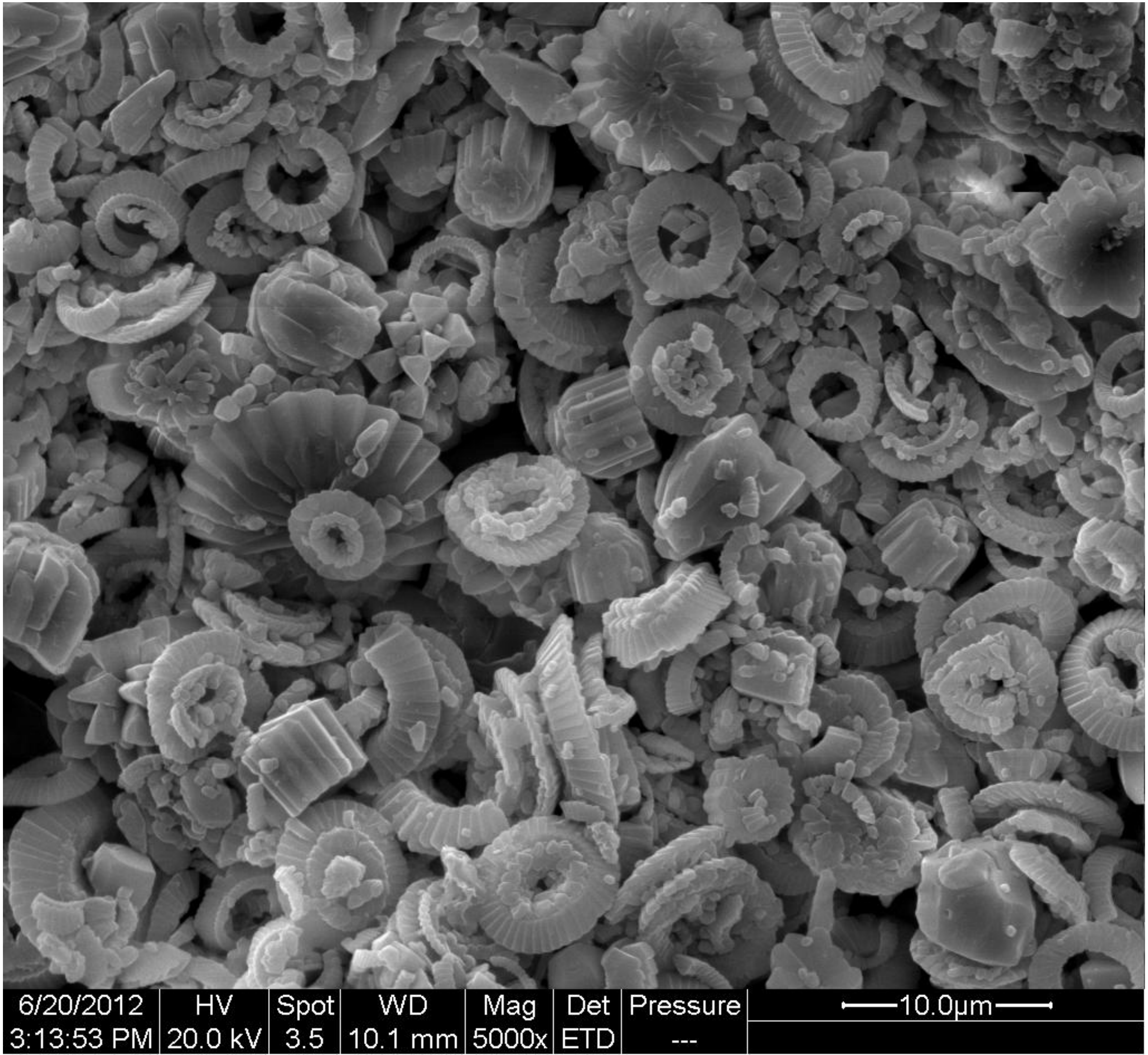
The **CCD**



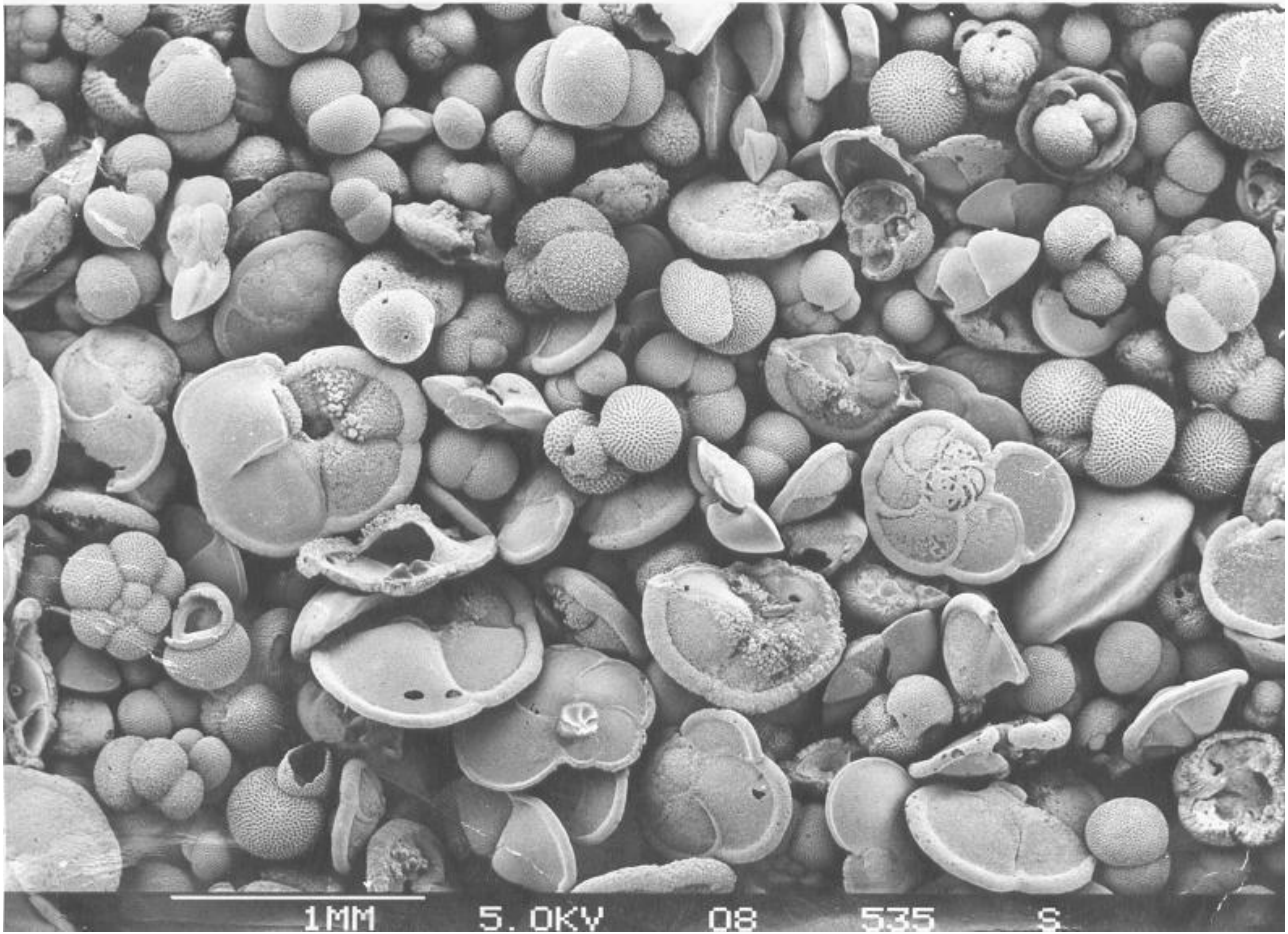


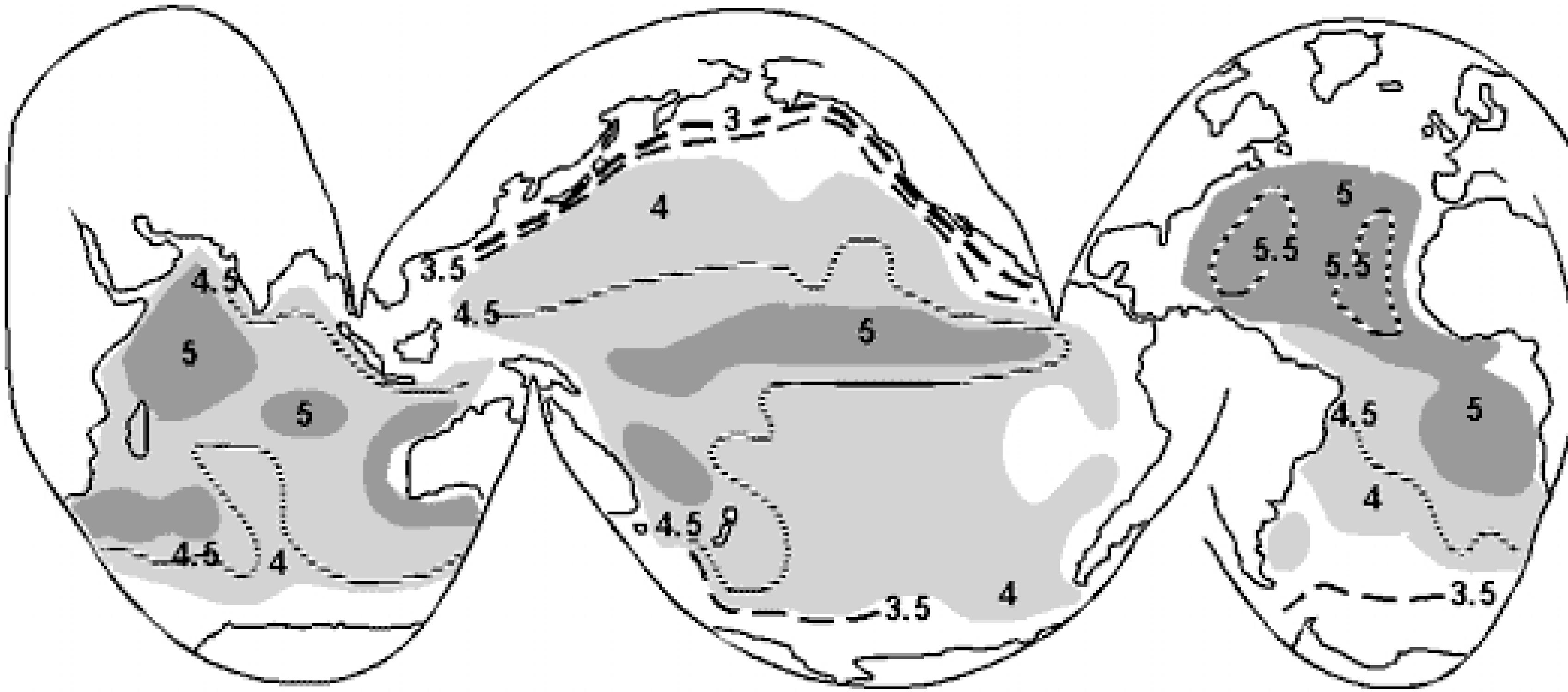


Ocean surface
Depth, m (ft)
0
1,000 (3,280)
2,000 (6,560)
3,000 (9,840)
4,000 (13,120)
5,000 (16,400)
6,000 (19,680)
7,000 (22,960)
Calcite-secreting warm water organisms live near surface
Upwelling, cool water
Biogenous and fine lithogenous particles settle toward ocean floor
High productivity of silica-secreting organisms
Mid-ocean ridge
Calcite compensation depth
Abyssal clay
SiO_2 ooze
CCD
$CaCO_3$ ooze
Sea floor spreading
$CaCO_3$ ooze
Basalt
Basalt
Magma



https://www.e-education.psu.edu/earth103/sites/www.e-education.psu.edu.earth103/files/module05/141_001.jpg


1MM
5.0KV
08
535
S



Topography of the calcium carbonate compensation depth (CCD), i.e., the depth in kilometers below which little or no CaCO3 accumulates

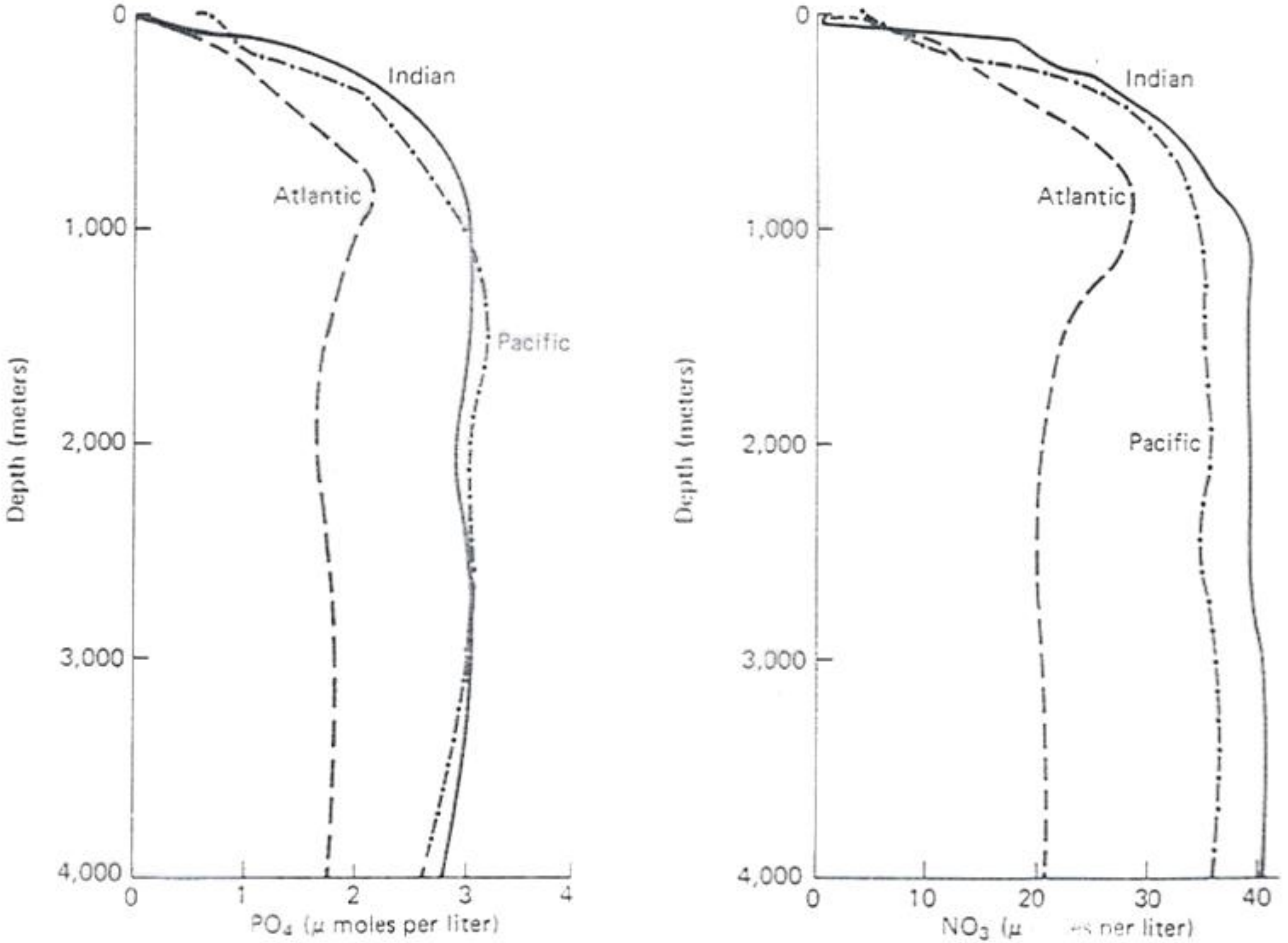
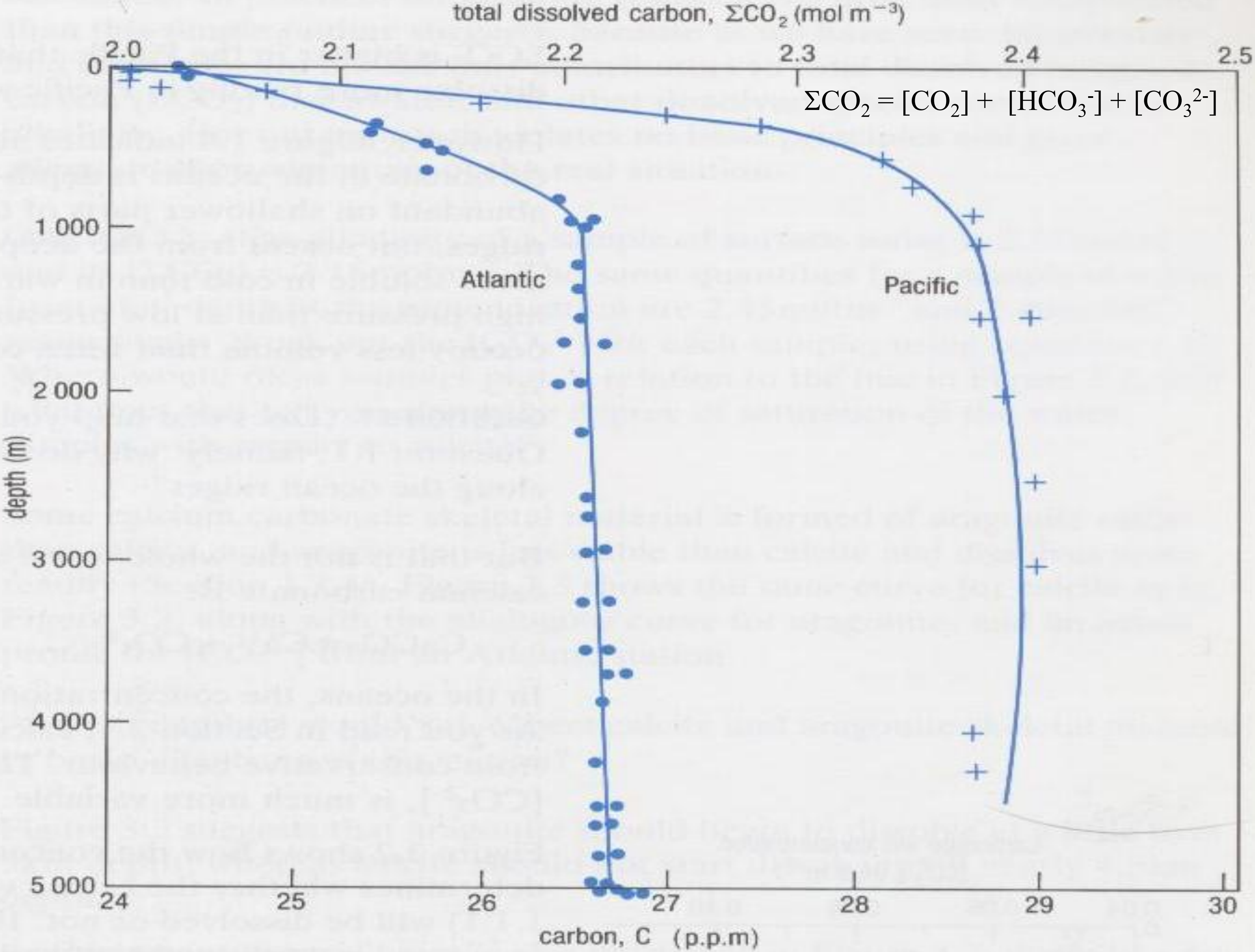
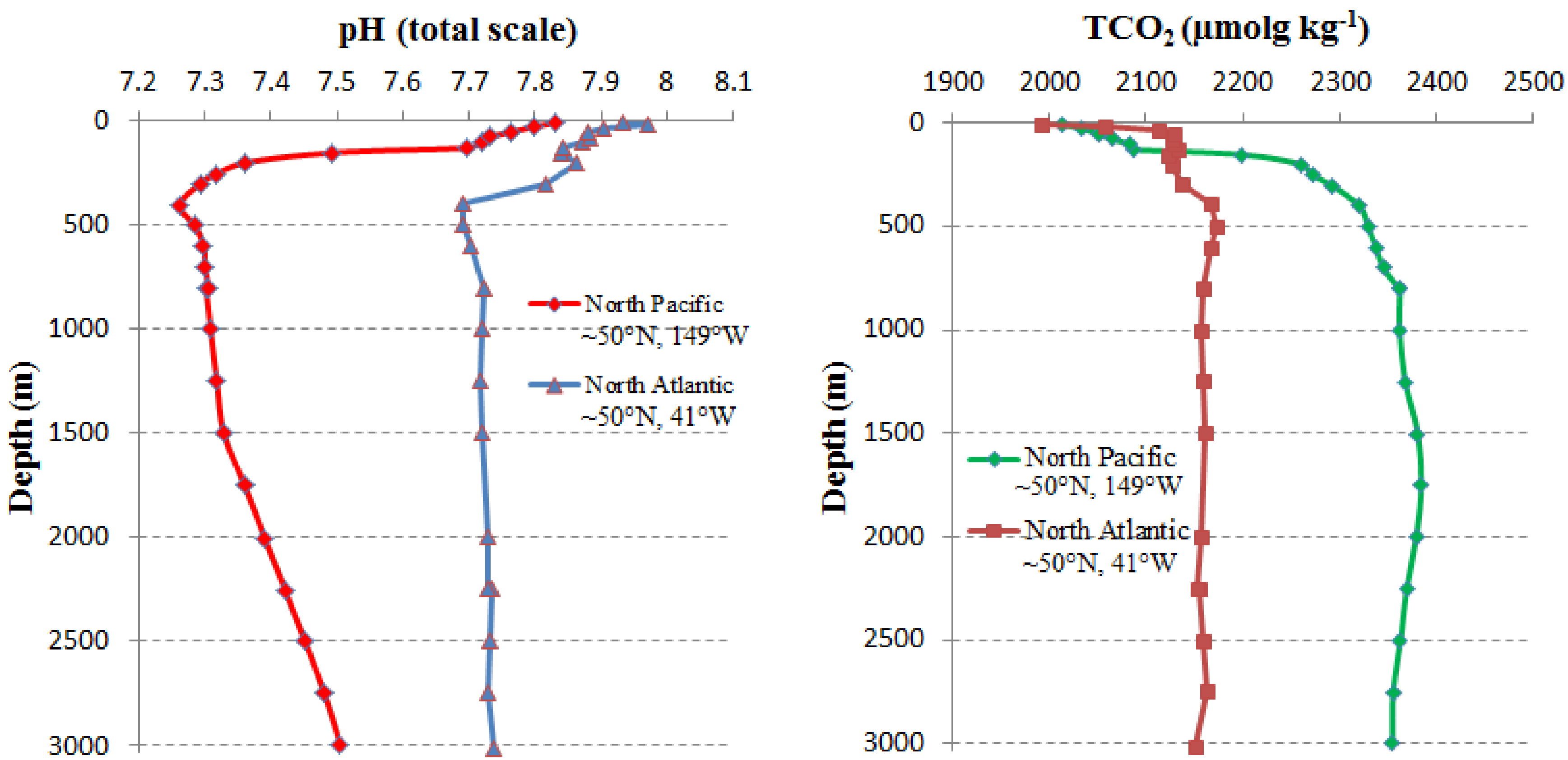


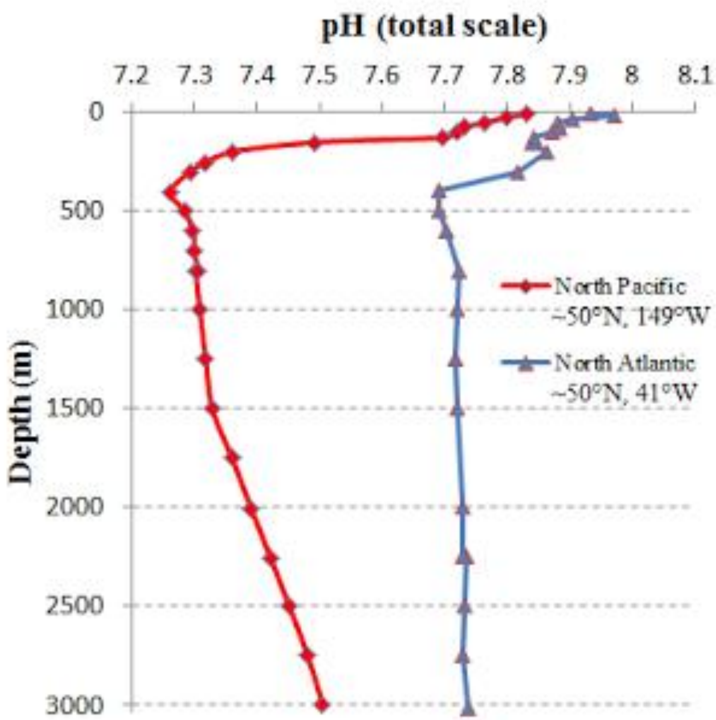
FIGURE 9.2 Vertical distributions of the nutrient components, phosphate and nitrate, in typical water columns in the Atlantic, Pacific, and Indian Oceans. (After Sverdrup, Johnson, and Fleming, 1942).

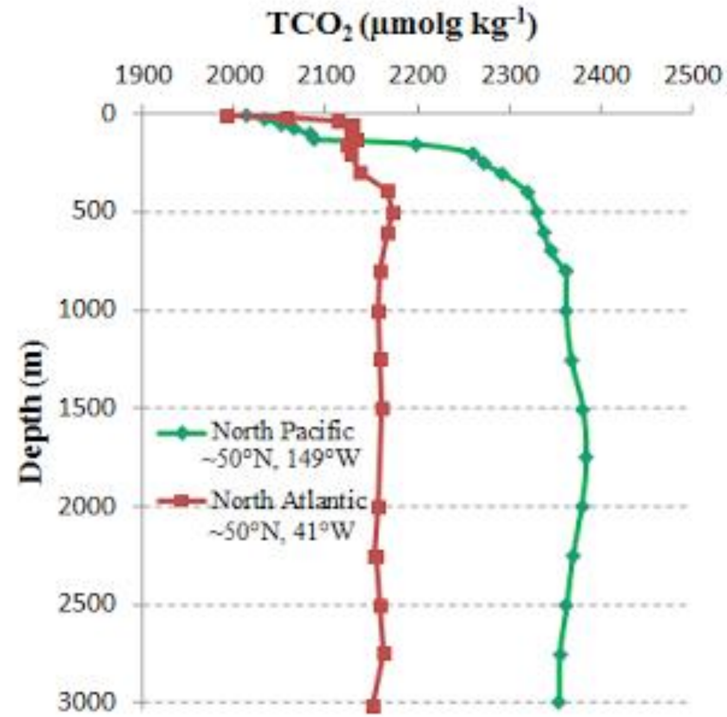

total dissolved carbon, ΣCO_2 (mol m^{-3})
2.0
2.1
2.2
2.3
2.4
2.5
$\Sigma CO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$
0
1 000
2 000
3 000
4 000
5 000
depth (m)
Atlantic
Pacific
24
25
26
27
28
29
30
carbon, C (p.p.m)



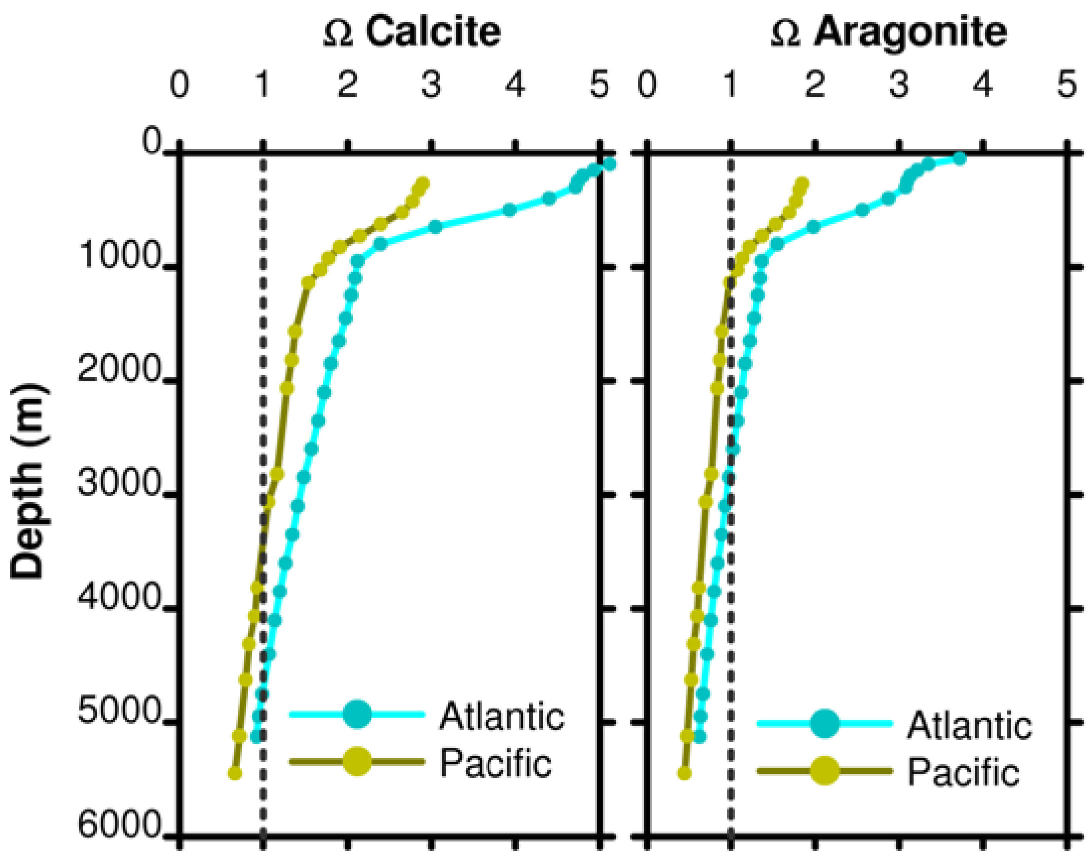
pH (total scale)
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8
8.1
Depth (m)
0
500
1000
1500
2000
2500
3000
North Pacific ~50°N, 149°W
North Atlantic ~50°N, 41°W
TCO_2 (µmolg kg^{-1})
1900
2000
2100
2200
2300
2400
2500
Depth (m)
0
500
1000
1500
2000
2500
3000
North Pacific ~50°N, 149°W
North Atlantic ~50°N, 41°W

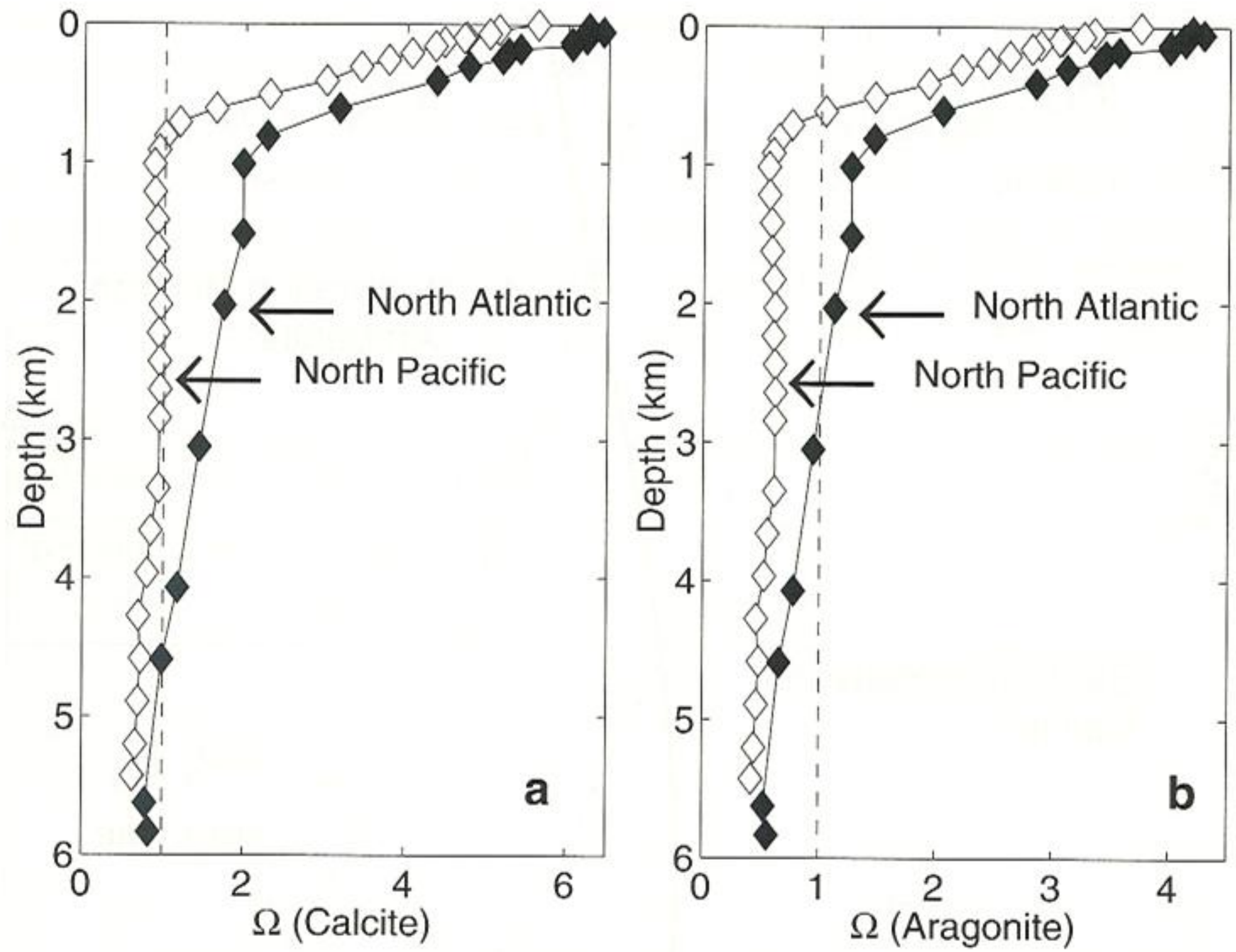
$$TCO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$





Omega profiles in the ocean





$\Omega = [Ca^{2+}] \times [CO_3] / K'sp$

Zeebe and Wolf-Gladrow, 2001

$\Omega = 1$ Equilibrium

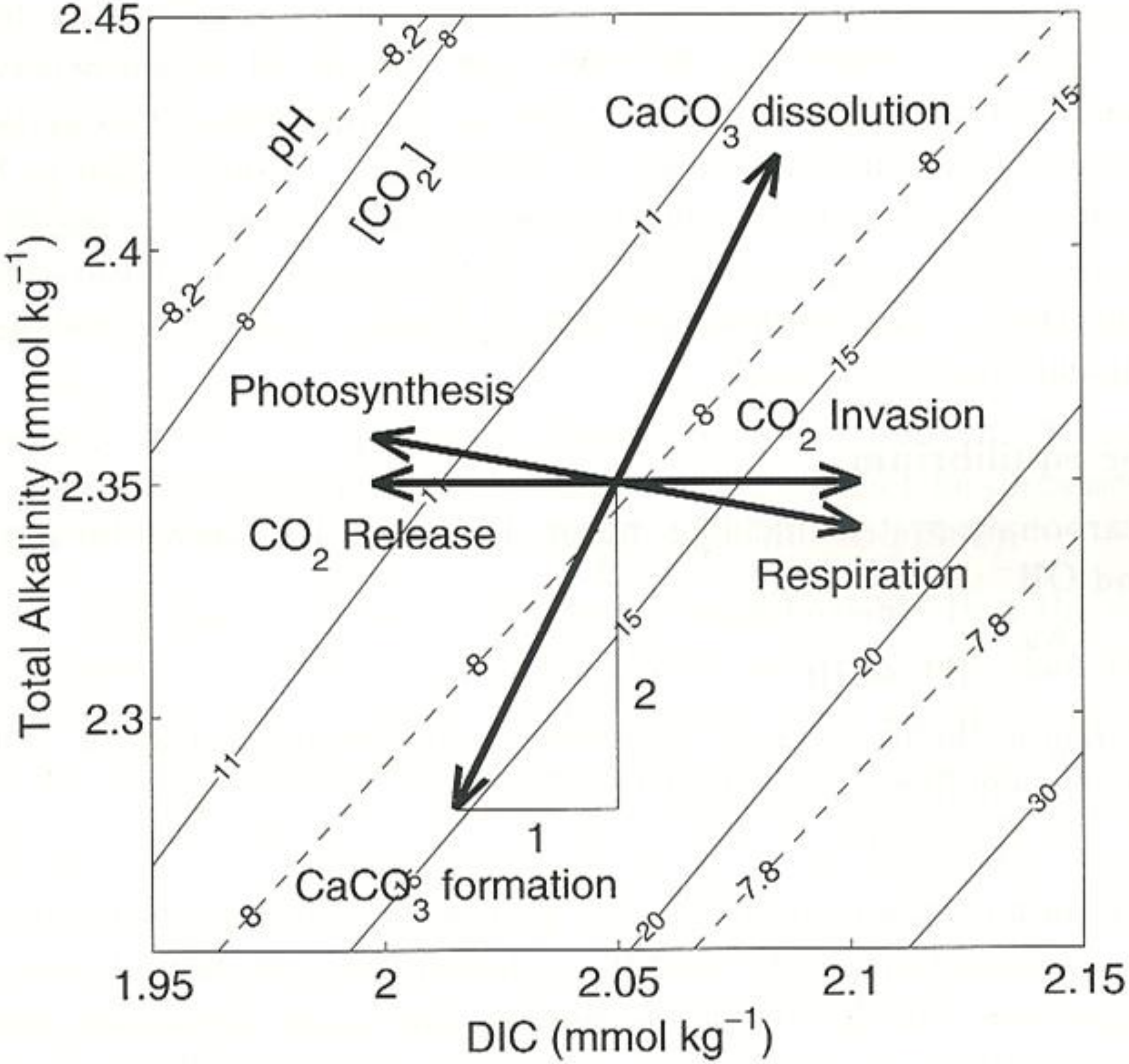


Figure 1.1.3: Effect of various processes on DIC and TA (arrows). Solid and das lines indicate levels of constant dissolved CO_2 (in μmol kg^{-1}) and pH, respectively, : function of DIC and TA. $CaCO_3$ formation, for example, reduces DIC by one and by two units, therefore driving the system to higher CO_2 levels and lower pH. Invasio: atmospheric CO_2 into the ocean increases DIC, while release of CO_2 to the atmospl has the opposite effect. TA stays constant in these two cases.

Pacific).

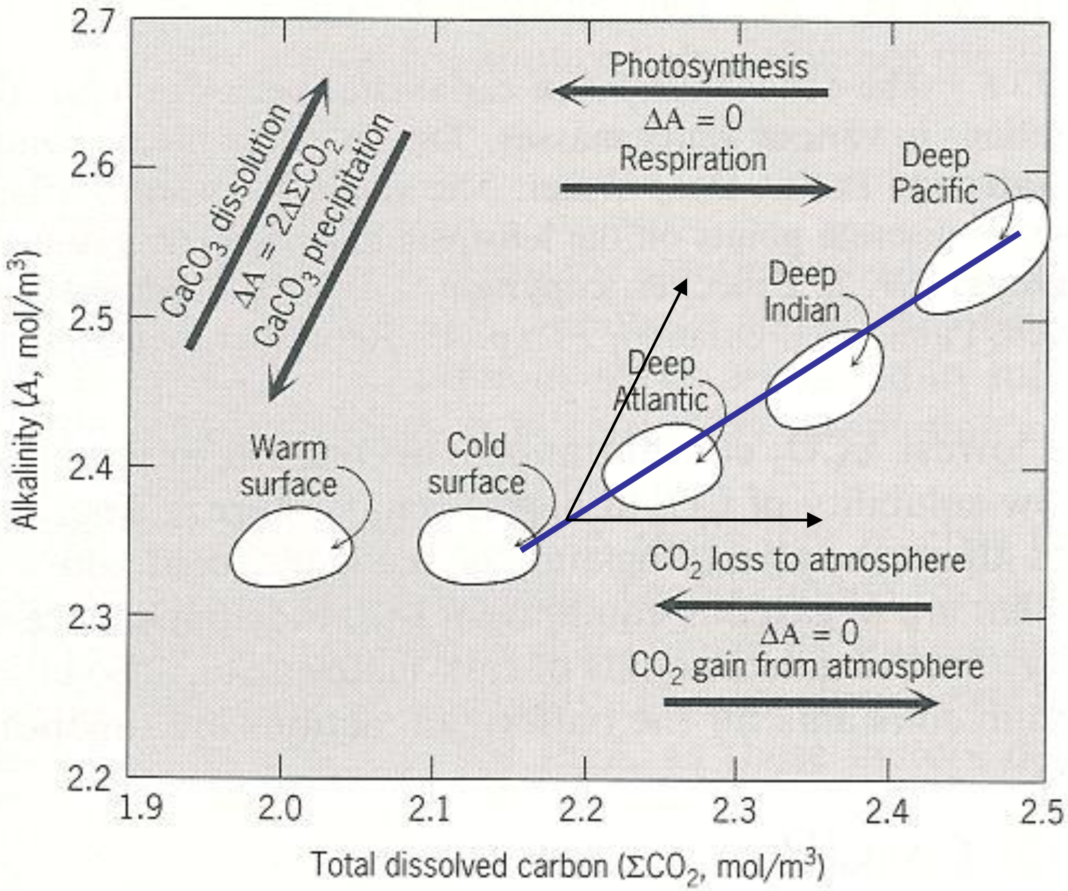


FIGURE 15.7. Relationship between the total dissolved inorganic carbon content and the alkalinity of waters from various parts of the ocean. The arrows indicate the effects of various processes occurring within the sea. *Source:* From *Chemical Oceanography*, W. S. Broecker, copyright © 1974 by Harcourt, Brace and Jovanovich Publishers, Orlando, FL, pp. 14–15. Reprinted by permission.

Peterson experiment

1996

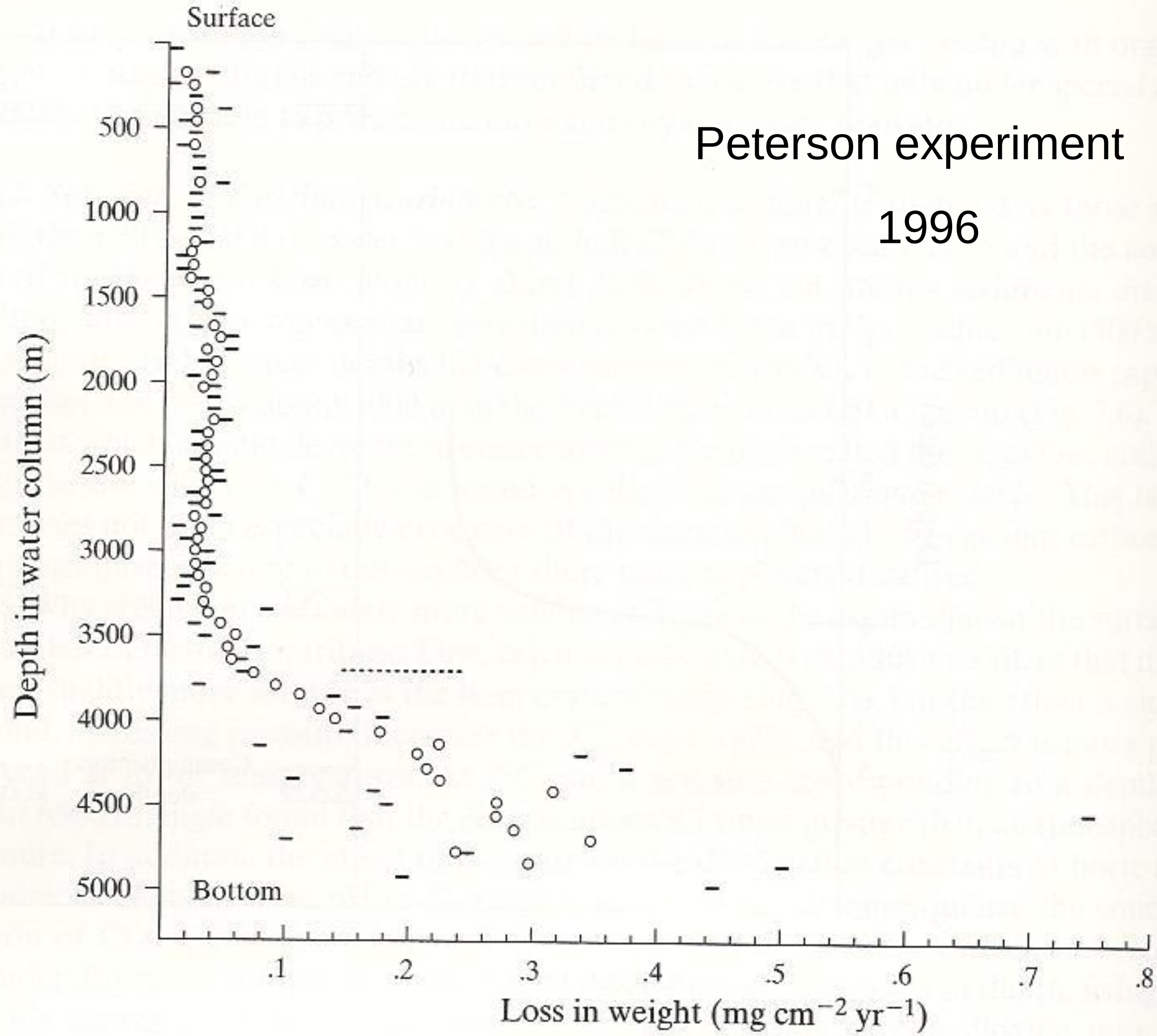


Figure 7.7 *Data from the experimental dissolution rate observations of Peterson (1966). Calcite spheres were suspended for several months at various depths in the eastern Pacific Ocean. Bars show rates of dissolution for individual calcite spheres (length of bars represents uncertainty due to assigned weighing errors). Circles show rates of dissolution averaged over five adjacent spheres. Dashed line shows the level of abrupt increase in rate.* (Reprinted with permission from M. N. A. Peterson, "Calcite: rates of dissolution in a vertical profile in the Central Pacific," *Science* 1954:1542–1544. Copyright 1966 by American Association for the Advancement of Science.)

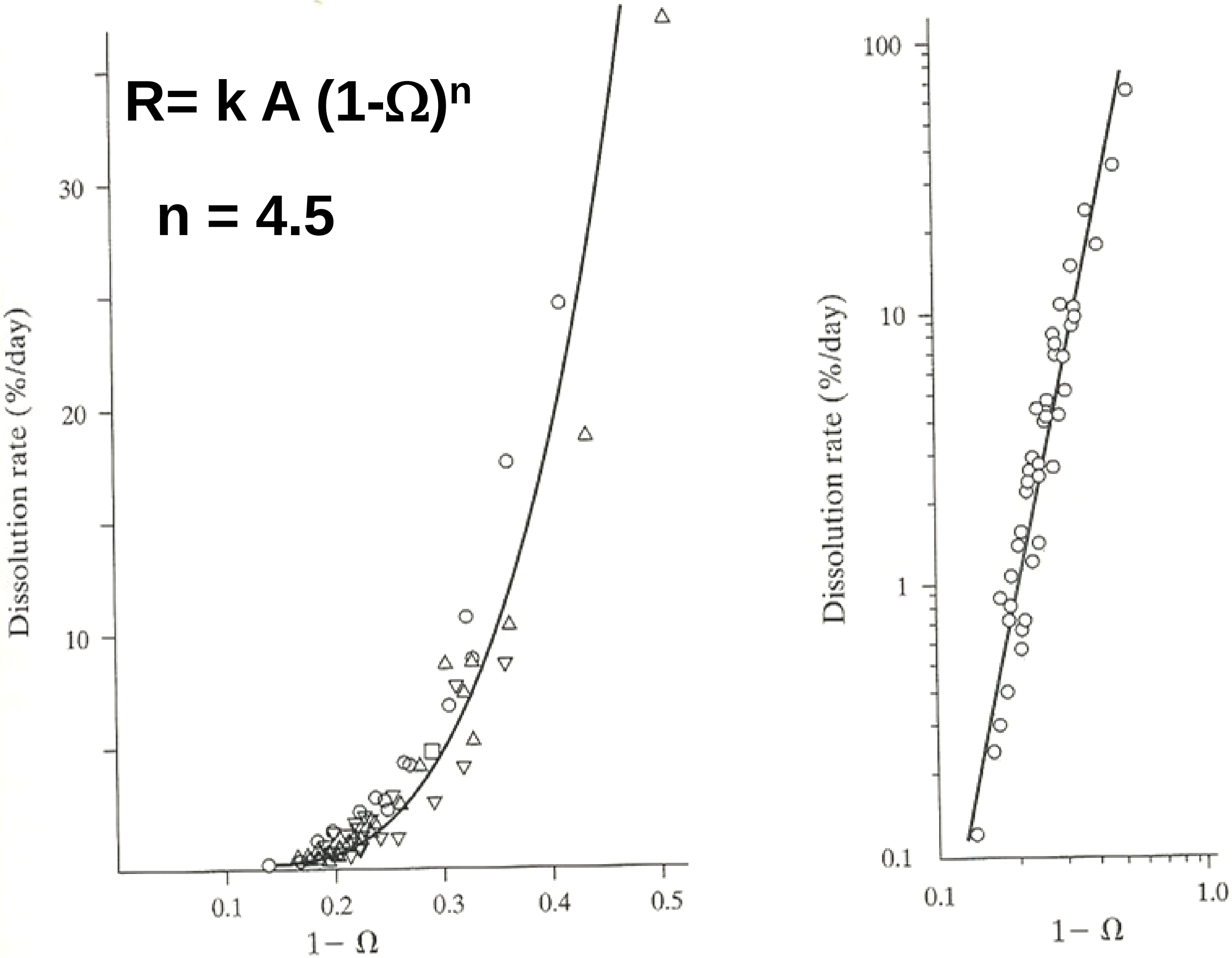
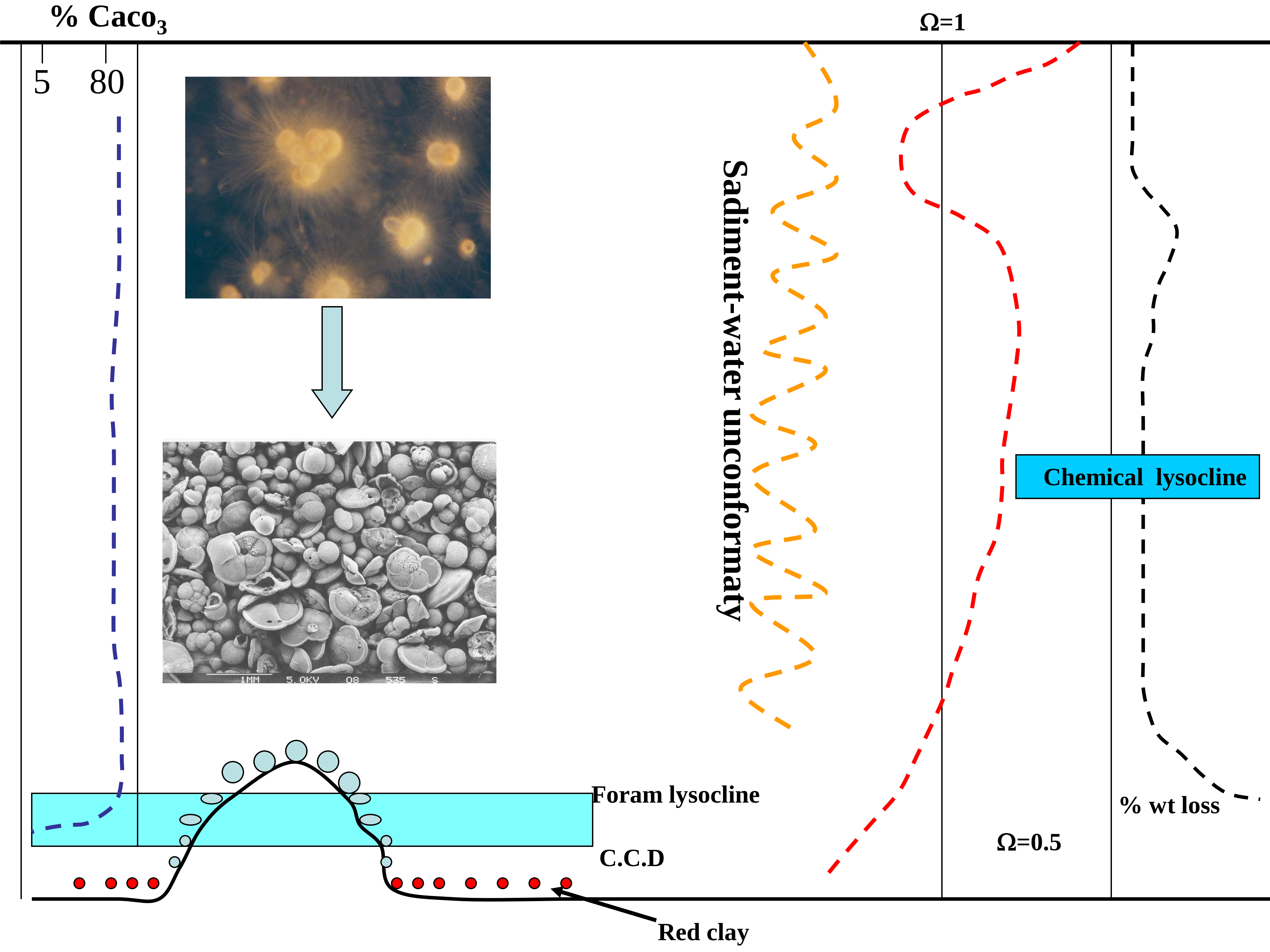


Figure 7.8 *Dissolution rate versus degree of undersaturation for reagent grade calcite (Keir 1980), measured in artificial seawater at 20°C. Undersaturation is expressed by the relationship:*

$$\text{degree of undersaturation} = 1 - \Omega$$

where

$$\Omega = \frac{IP}{K^*_{sp}} = \frac{[Ca^{++}][CO_3^{=}]}{K^*_{sp}}$$


% $CaCO_3$
5
80
Ω=1
Sadiment-water unconformaty
Chemical lysocline
Foram lysocline
C.C.D
Ω=0.5
% wt loss
Red clay
1MM 5.0KV 08 535 S

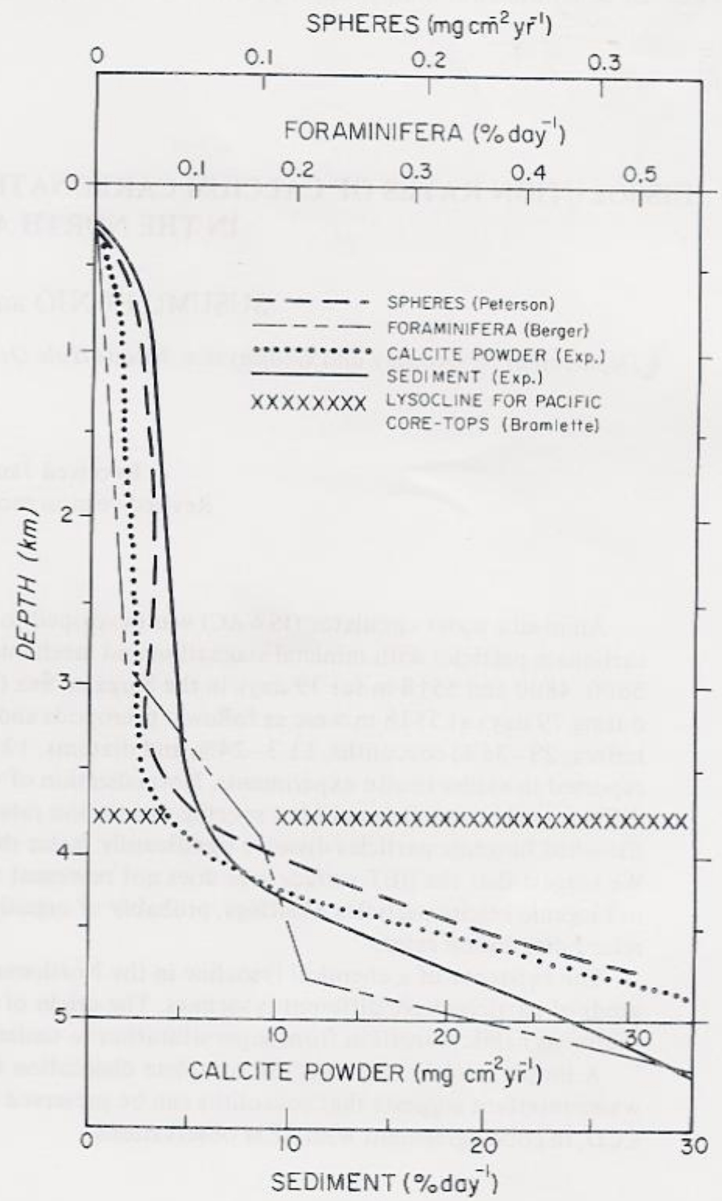
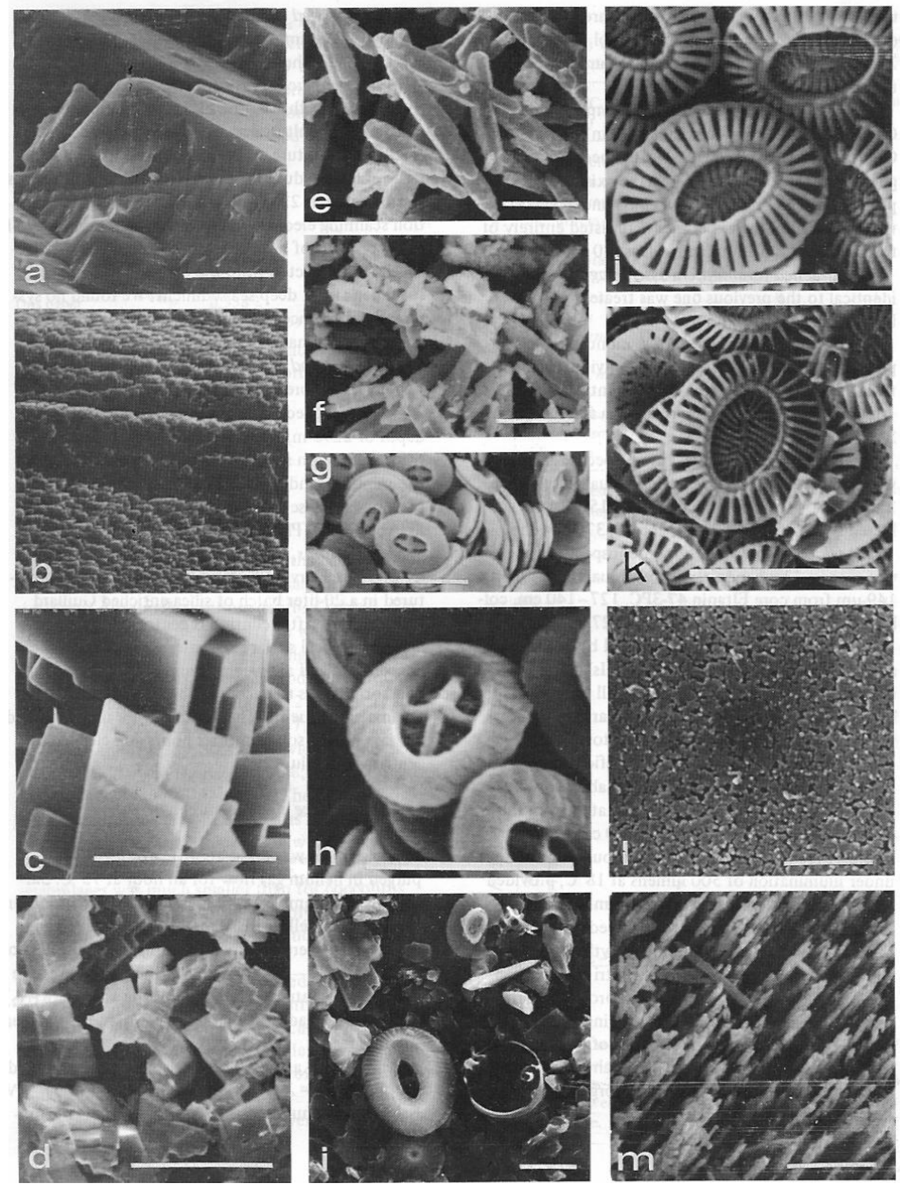
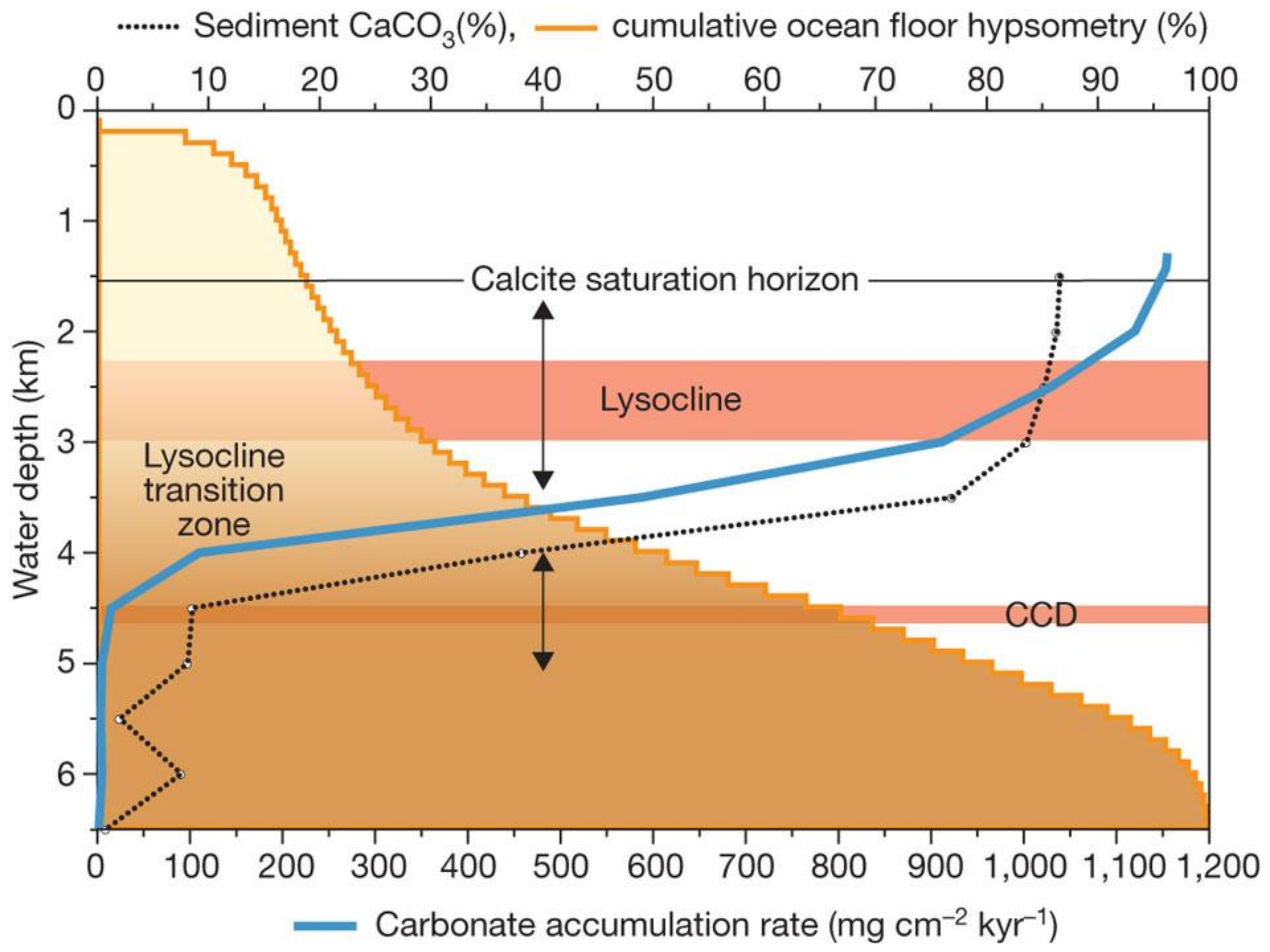


Fig. 1. After Morse and Berner [17]. Peterson [18] and Berger [19] in-situ experiments versus laboratory experiments of Morse and Berner [17]. Note the orders of magnitude difference in the absolute dissolution rates.





Sediment $CaCO_3$(%), cumulative ocean floor hypsometry (%)
0
10
20
30
40
50
60
70
80
90
100
Water depth (km)
0
1
2
3
4
5
6
Calcite saturation horizon
Lysocline
Lysocline transition zone
CCD
0
100
200
300
400
500
600
700
800
900
1,000
1,100
1,200
Carbonate accumulation rate (mg cm^{-2} kyr^{-1})

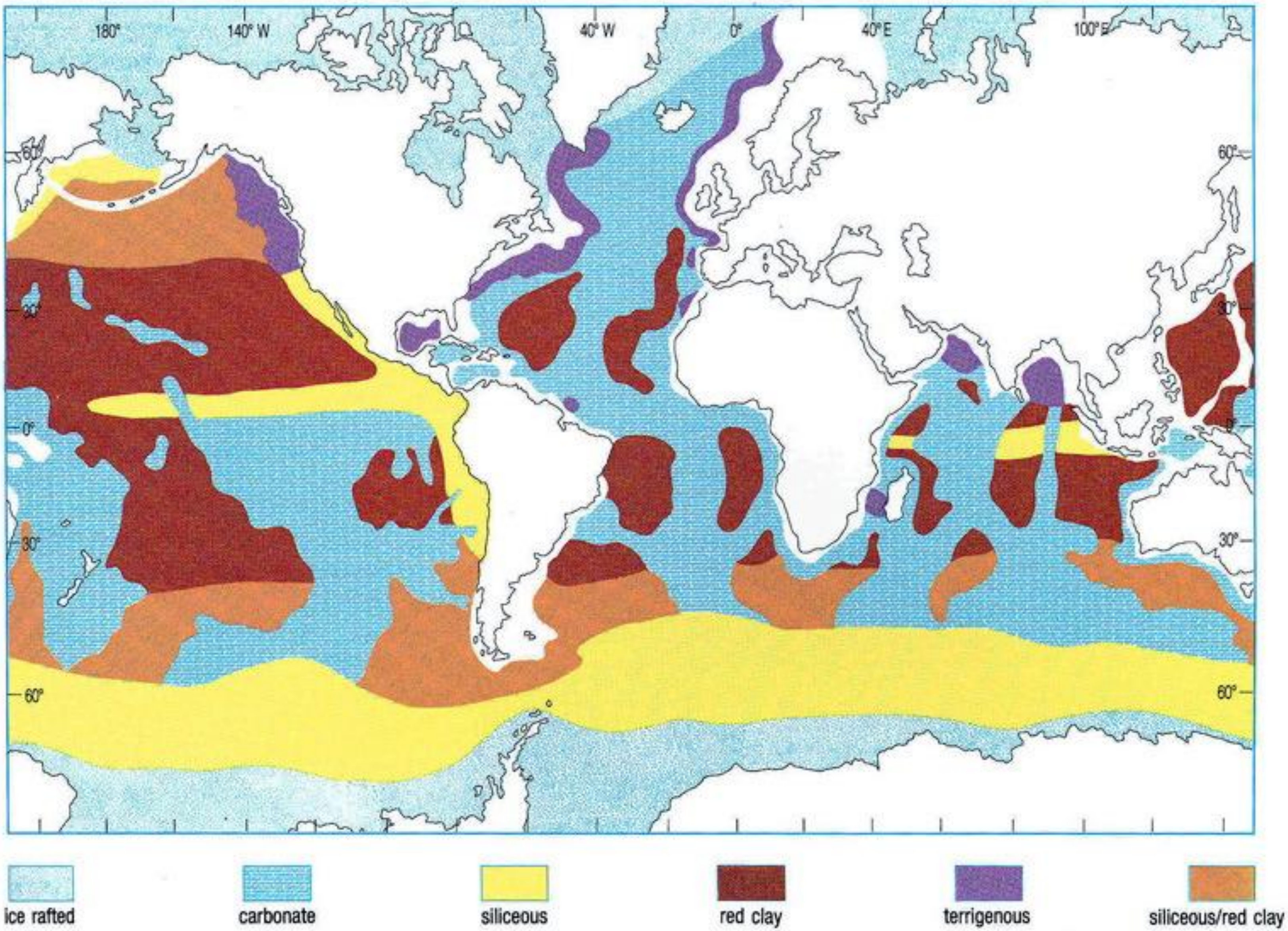


Figure 1.4 Distribution of dominant sediment types on the floor of the present-day oceans. Note that red clays are also terrigenous sediments.

End of third lecture