# The Carbon cycle

Atmosphere, terrestrial biosphere and ocean are constantly exchanging carbon

The oceans store much more carbon than the atmosphere and the terrestrial biosphere

The oceans essentially determine the atmospheric CO_2 content

Carbon Cycle
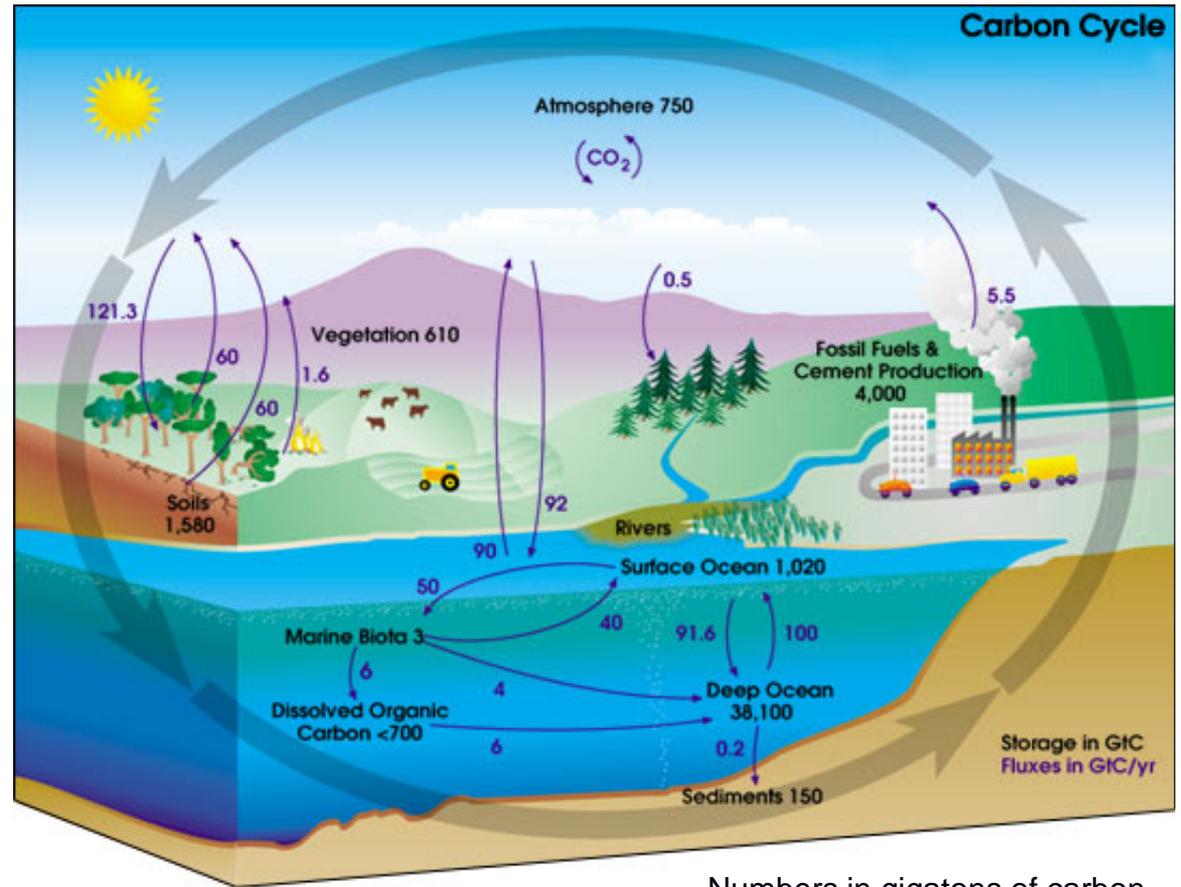
Numbers in gigatons of carbon
annual carbon fluxes in purple text

- $CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-$ (consumption of carbonate ions in seawater $\rightarrow$ acidification)
- $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$ (dissolution of calcium carbonate)
- $CO_2 + H_2O \rightarrow CH_2O + O_2$ (photosynthesis)

Atmospheric carbon dioxide

Atmospheric carbon reservoir is **small** but flux rates are high

CO_2 that enters the ocean reacts with seawater to form carbonic acid and its dissociation products:

$CO_2(g) + H_2O \Leftrightarrow H_2CO_3$

dissociation:

$H_2CO_3 \Leftrightarrow HCO_3^- + H^+$

$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$

Atmospheric Carbon Dioxide
Measured at Manua Loa, Hawaii

Annual Cycle

$= ml/m^3$
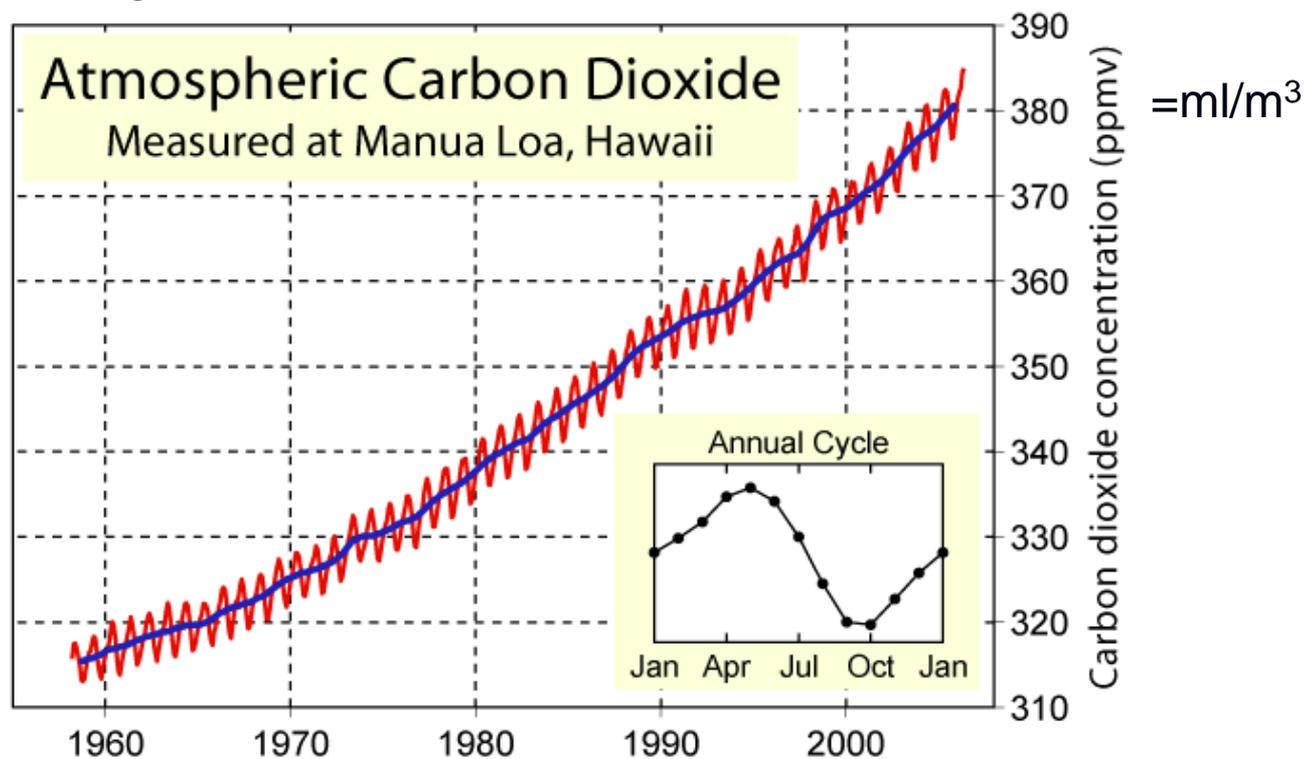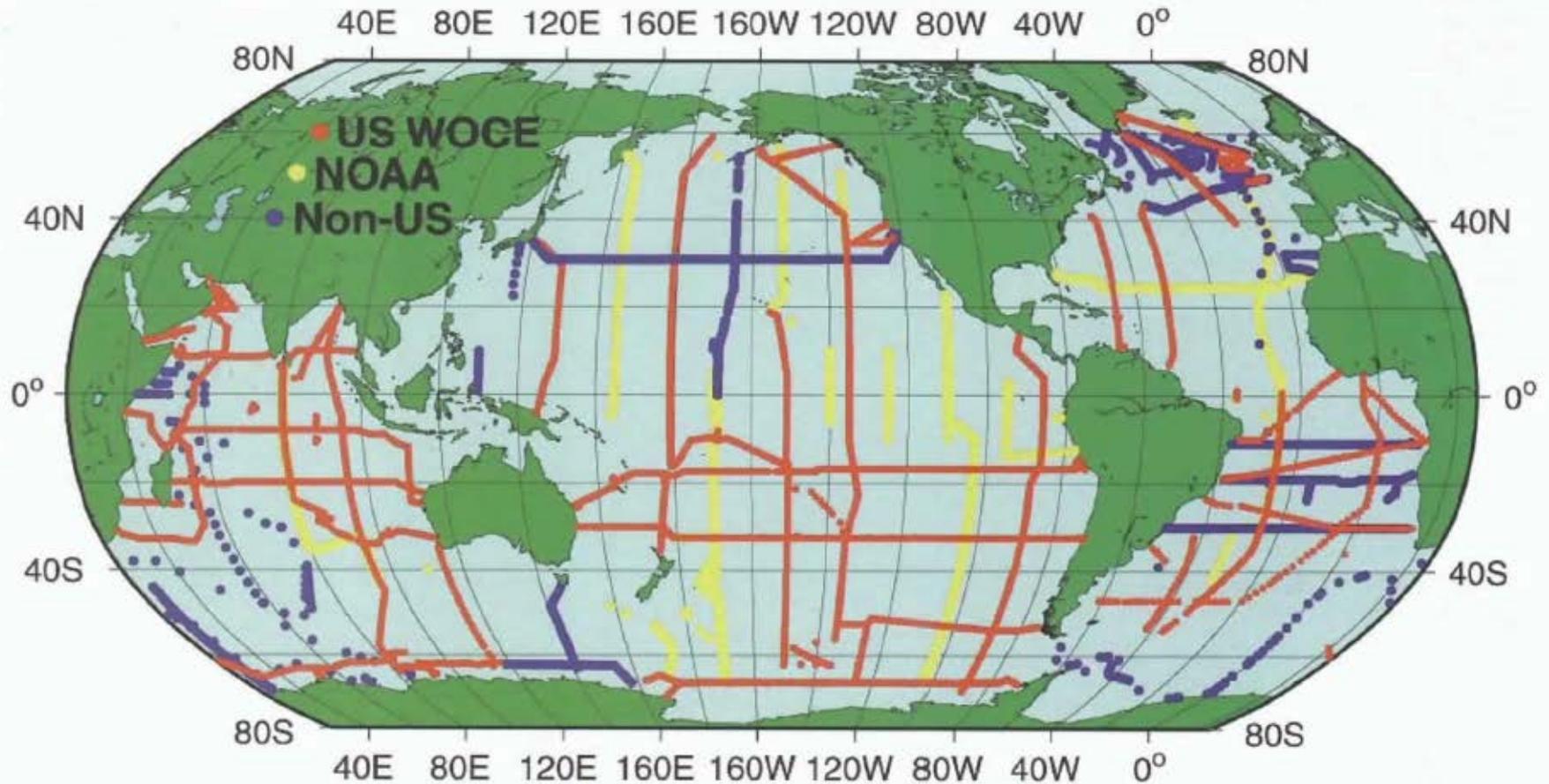
CO$_2$ in seawater

Figure 2. The Global Survey of CO$_2$ in the Ocean: cruise tracks and stations occupied between 1991 and 1998.

Feely et al. (2001): Oceanography 14

Dissolved carbon dioxide in seawater

Three major reservoirs for CO_2 exchange:

- Atmosphere

- terrestrial biosphere

- Oceans

Oceans contain 60 times as much carbon as atmosphere

Distribution of CO$_2$ and ^{13}C in seawater
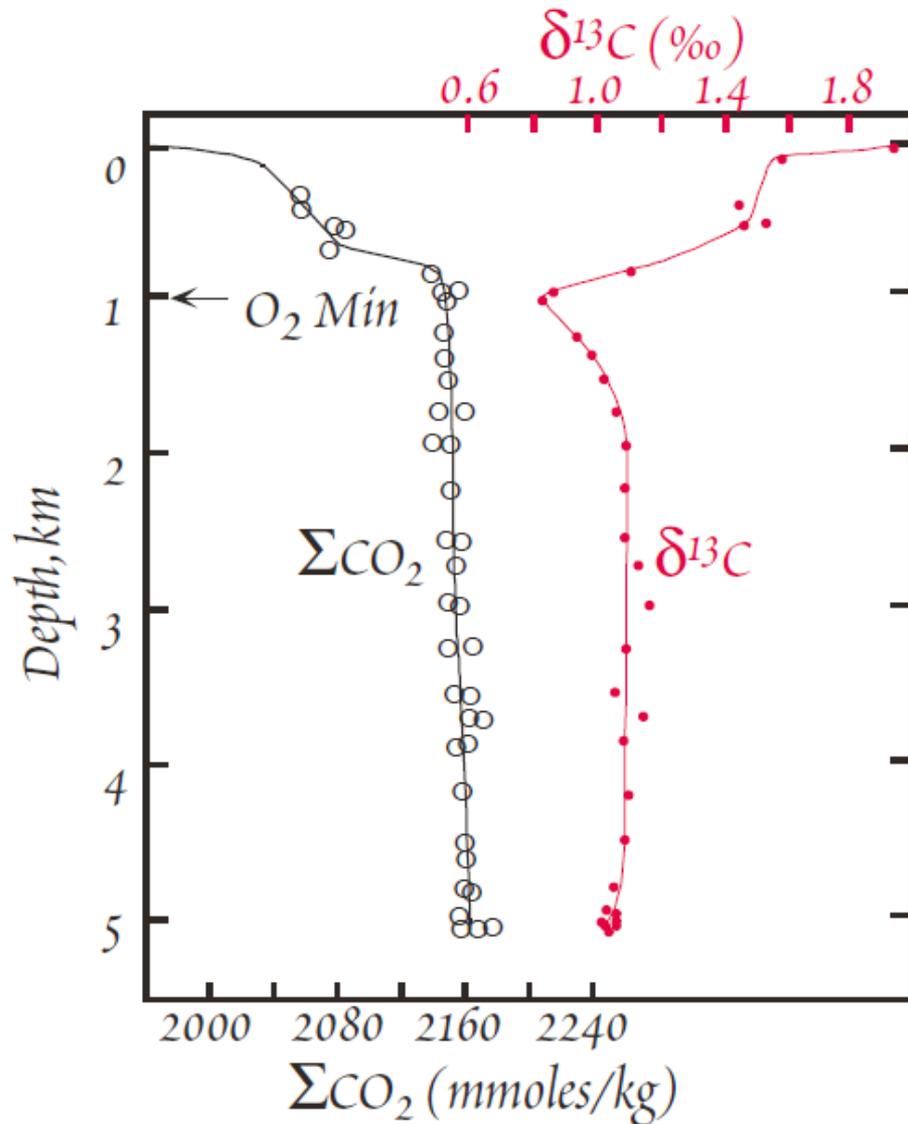
Vertical CO$_2$ variations in oceans due to biological activity

Photosynthesis converts CO$_2$ to organic matter in the surface water depleting it in CO$_2$

Respiration converts organic matter back into dissolved CO$_2$ and only a very small fraction of the organic matter is buried in the sediment

$$CO_2 + H_2O \underset{\text{respiration}}{\overset{\text{photosynthesis}}{\rightleftharpoons}} CH_2O + O_2$$

W. White: Geochemistry
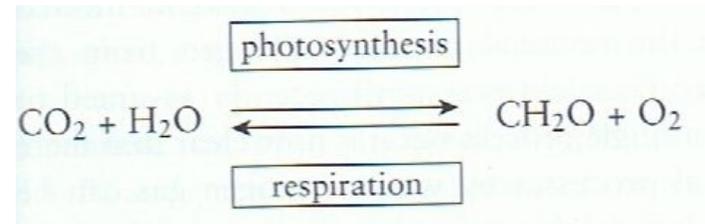
Effects on carbon isotopic composition

^{12}C TAKEN UP BY PHOTOSYNTHESIS: SHELLS ($CaCO_3$) ENRICHED IN ^{13}C

PHOTOSYNTHESIS
$H_2O + CO_2 \rightarrow CH_2O + O_2$

• ZOOPLANKTON
• PHYTOPLANKTON

$\delta^{13}C$, $^o/_{oo}$

ROTTING/RESPIRATION
$CH_2O + O_2 \rightarrow H_2O + CO_2$

^{12}C INTO DISSOLVED CO_2 AFTER ROTTING OF BENTHOS ORGANIC MATTER
($\delta^{13}C$ in $CH_2O \sim -23$ $^o/_{oo}$):
SHELLS ($CaCO_3$) ENRICHED IN ^{12}C
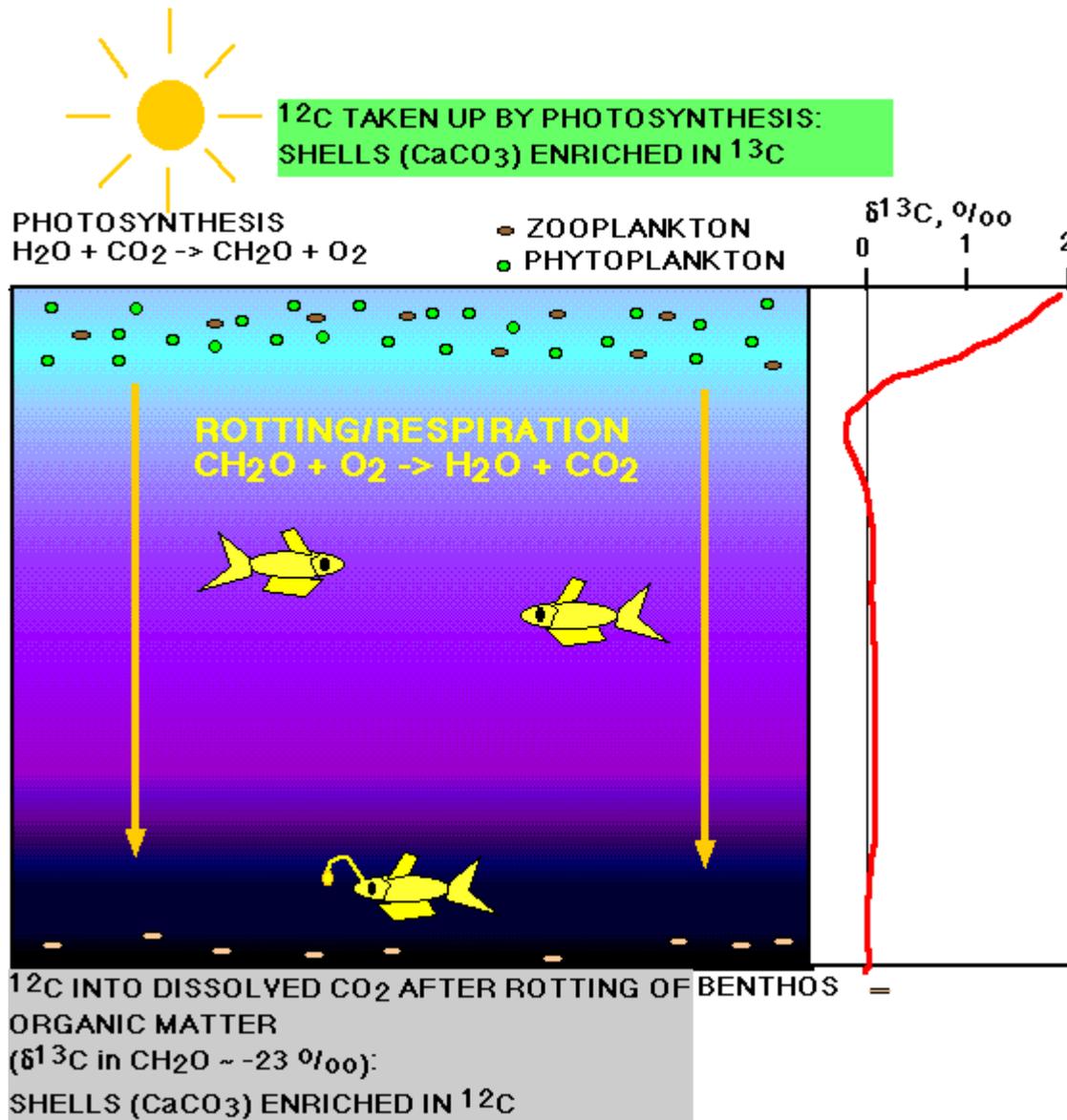
Planktonic organisms of the photic zone, forming calcareous tests from dissolved inorganic carbon (largely HCO_3^-) in these surface layers, use carbon that is enriched in ^{13}C

Carbon isotopic composition of DIC in Atlantic and Pacific Oceans

PACIFIC OCEAN   ATLANTIC OCEAN

"OLD" WATER: "YOUNG" WATER:
POOR IN O_2 RICH IN O_2
RICH IN CO_2 POOR IN CO_2
LOW $\delta^{13}C$ HIGH $\delta^{13}C$

$\delta^{13}C$, ‰
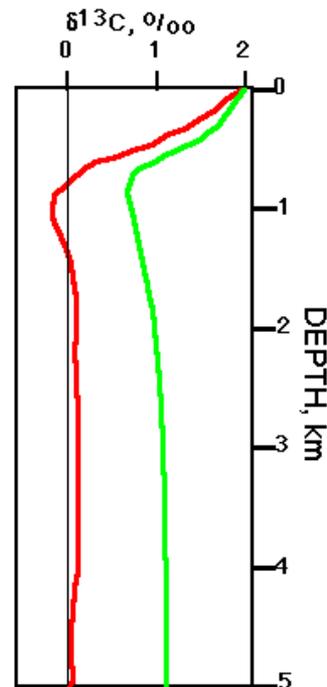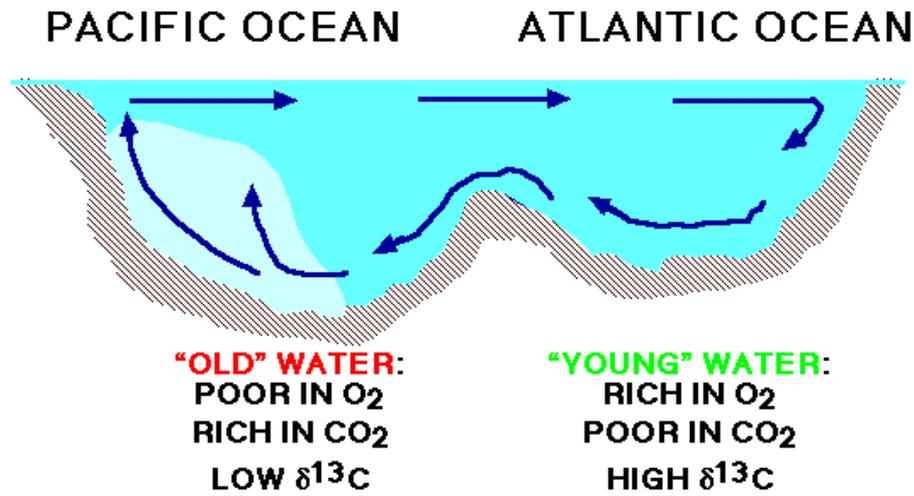
waters that have been out of contact with the surface ocean for a long time, have accumulated much carbon derived from oxidation of organic material, thus their total dissolved inorganic carbon is isotopically light.

http://condor.wesleyan.edu/ethomas/ees123/359caox.htm

Alkalinity

Total concentration of weak acid anions in water (anions that neutralize acidity, H^+)
measure of acid-neutralizing capacity

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + [NO_3^-] + [OH^-] - [H^+]$$

Carbonate alkalinity: $CAlk = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4] + [OH^-] - [H^+]$

Alkalinity is not conservative
largely influenced by carbonate precipitation and dissolution

DOC, TCO$_2$ and TA

DOC = Dissolved organic carbon: organic molecules of varied origin and composition within seawater

TCO$_2$ = Total inorganic carbon: $\sum CO_2$ = cCO$_2$ + cH$_2$CO$_3$ + cHCO$_3$ + cCO$_3$

DIC dissolved inorganic carbon

TA = Total alkalinity = [HCO$_3^-$] + 2[CO$_3^{2-}$] + [B(OH)$_4$] + [OH$^-$] − [H+]

Alkalinity (continental waters)

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}$$

$$HCO^-_{3(aq)} \rightleftharpoons H^+_{(aq)} + CO^{2-}_{3(aq)}$$
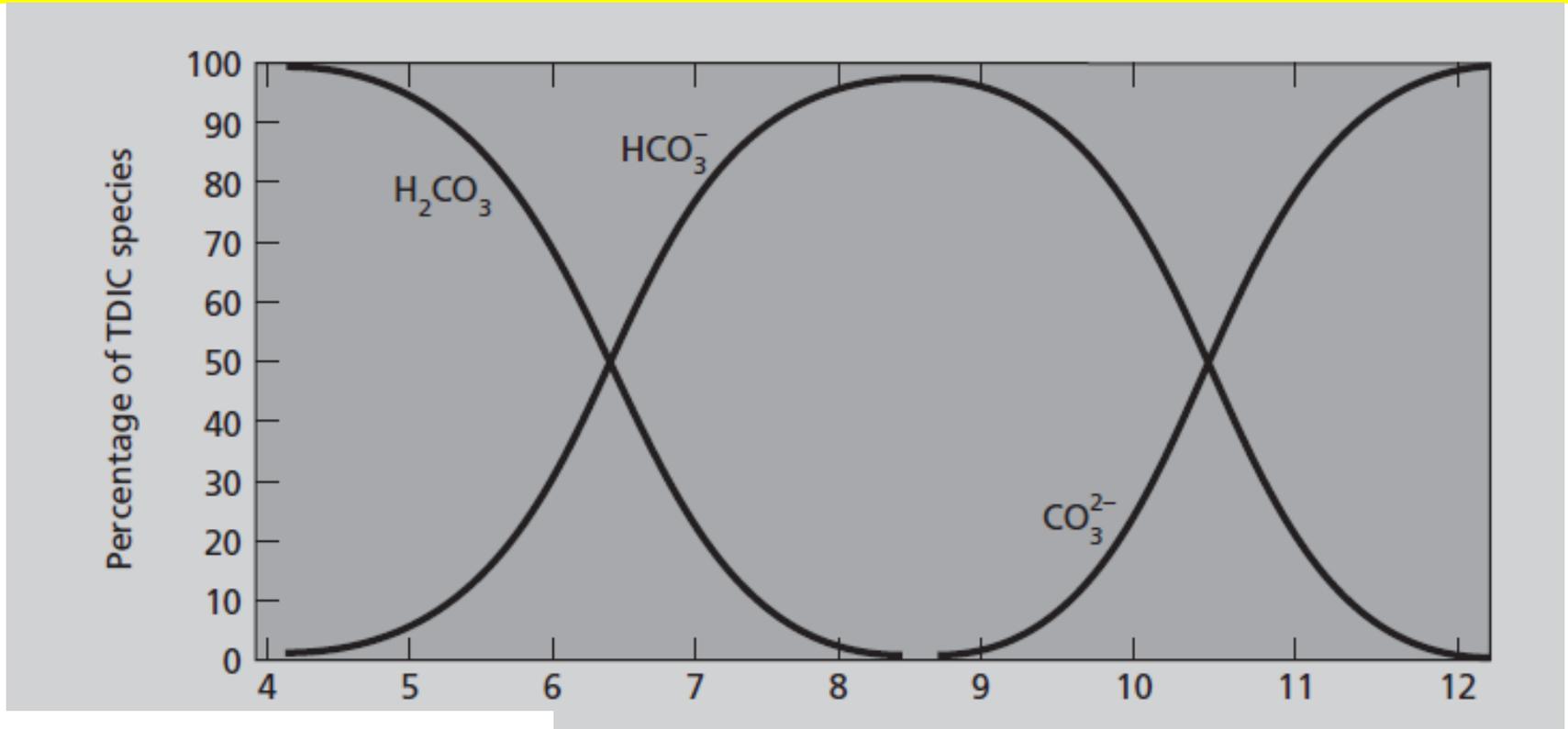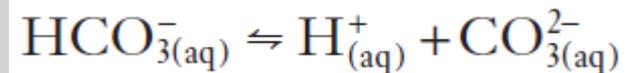
$$K_1 = \frac{aH^+ \cdot aHCO^-_3}{aH_2CO_3} = 10^{-6.4}$$

$$K_2 = \frac{aH^+ \cdot aCO^{2-}_3}{aHCO^-_3} = 10^{-10.3}$$

$$aHCO^-_3 = \frac{10^{-8} \cdot aCO^{2-}_3}{10^{-10.3}} = \frac{1 \times 10^{-8} \cdot aCO^{2-}_3}{5 \times 10^{-11}} = 200\, aCO^{2-}_3$$

The carbonate system

$$CO_2 : HCO_3^- : CO_3^{2-} = 1 : 100 : 10$$
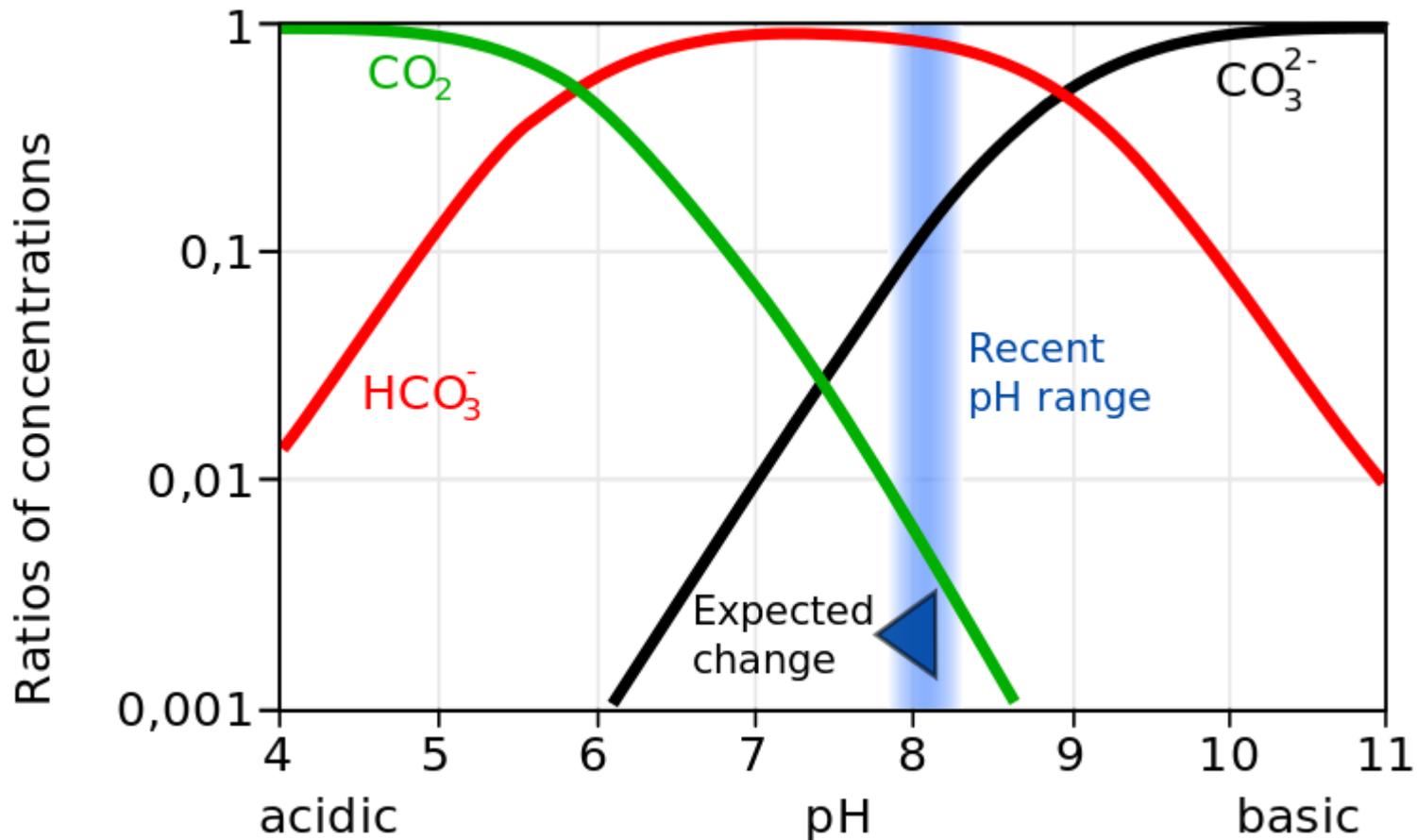
pH and alkalinity

bog = Moor

on the limestone the acidic water reacts with calcite to release Ca^{2+} + HCO_3^- ions:

$$CaCO_{3(s)} + H_2CO_{3(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)}$$

Bog source   Stream flow

Siliceous mudrock   Limestone

pH

Ca^{2+} (mmol l^{-1})

● pH
○ Ca^{2+}

Alkalinity (meq l^{-1})
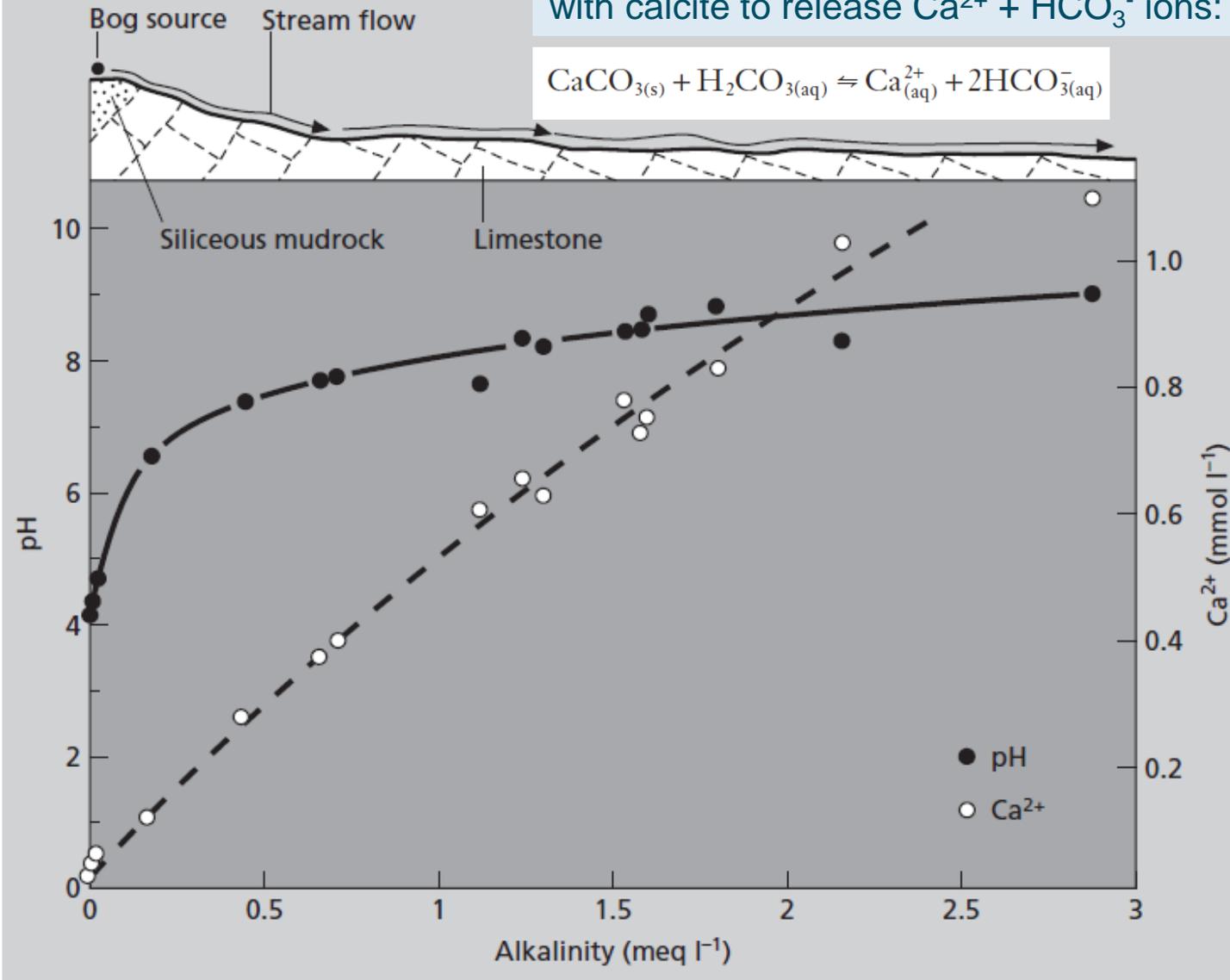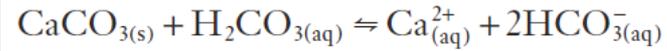
Dissolution - precipitation reactions

CO_2 exchange across air-sea interface:
$$CO_{2(g)} = CO_{2(aq)}$$

Dissolution of CO_2:
$$CO_2 + H_2O = H^+ + HCO_3^- \text{ (bicarbonate ion, K1)}$$

Dissolution of CO_2:
$$HCO_3^- = H^+ + CO_3^{2-} \text{ (carbonate ion, K2)}$$

Solubility product of calcium carbonate:
$$Ca^{2+} + CO_3^{2-} = CaCO_3$$

Precipitation of calcium carbonate (decreases pH):
$$Ca^{2+} + 2HCO_3^- = CaCO_3 + H_2O + CO_2$$
$$CO_2 + H_2O = H^+ + HCO_3^-$$
$$Ca^{2+} + HCO_3^- = CaCO_3 + H^+$$
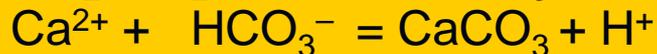
Dissolution of calcium carbonate (increases alkalinity, utilizes/consumes CO_2):
$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$$
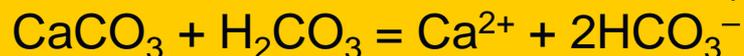
pH-variation in seawater

pH variation due to biological activity:
► **removal** of dissolved CO_2 by photosynthesis increases pH
► **release** of CO_2 by respiration decreases pH

bicarbonate is the predominant carbonate species in seawater:

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$$

Photosynthesis → reaction driven to the left, consuming H^+

Respiration → reaction driven to the right, producing H^+.

pH of the ocean decreases with depth due to respiration.

W. White: Geochemistry
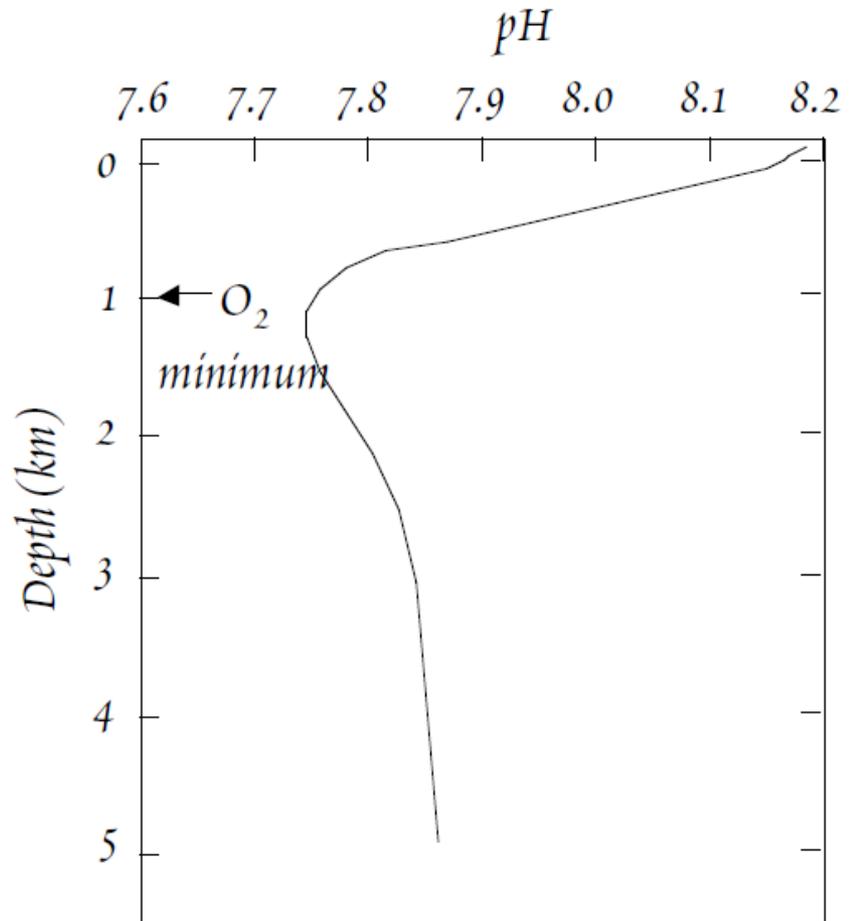
pH and total carbon dioxide (TCO$_2$) profiles: North Atlantic vs. North Pacific Ocean

seawater in North Pacific Ocean more acidic (lower in pH) than in North Atlantic Ocean
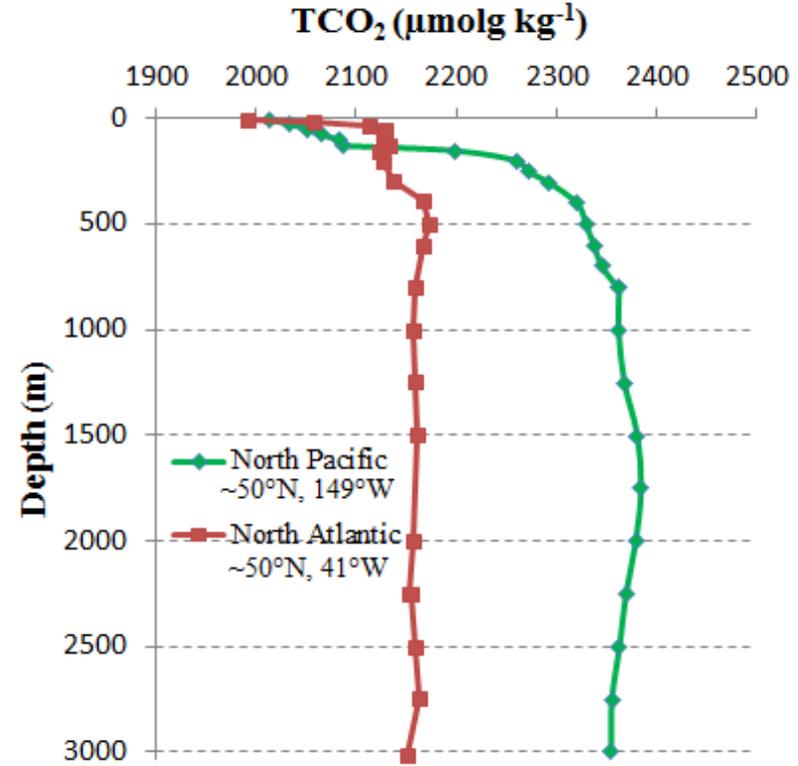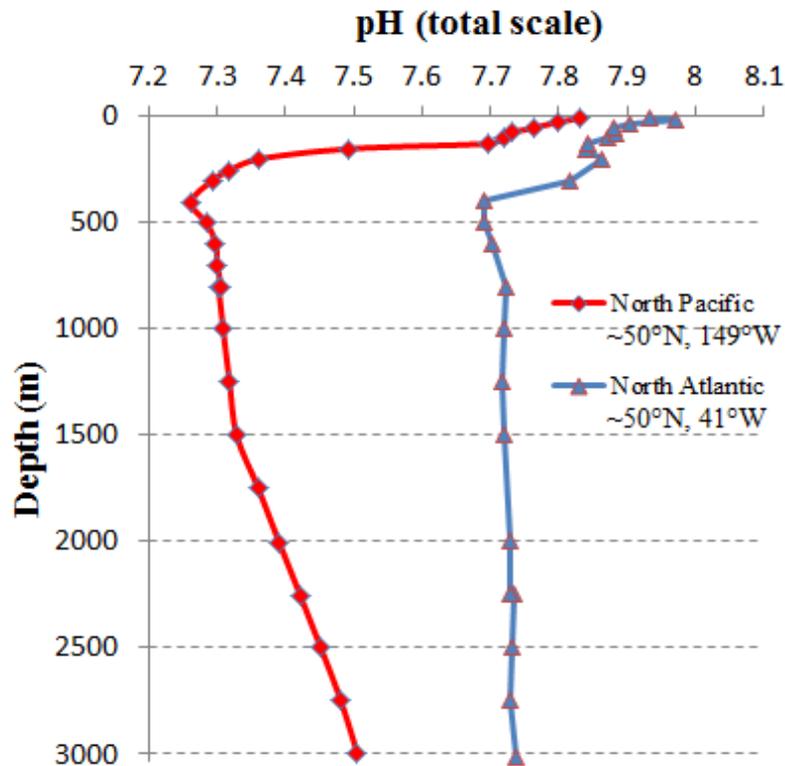
profound differences in seawater chemistry between the two oceans.
aragonite compensation depth in the North Pacific shallower than the North Atlantic

http://funwithkrill.blogspot.de/2012/09/seawater-chemistry-north-atlantic-vs.html

PACIFIC OCEAN   ATLANTIC OCEAN

"OLD" WATER: "YOUNG" WATER:
POOR IN O_2 RICH IN O_2
RICH IN CO_2 POOR IN CO_2
LOW $\delta^{13}C$ HIGH $\delta^{13}C$

$\delta^{13}C$, $^o/_{oo}$
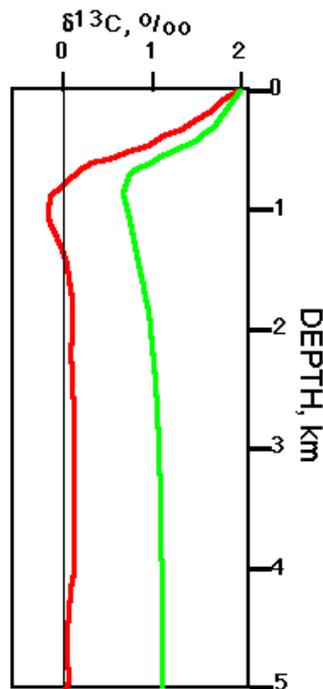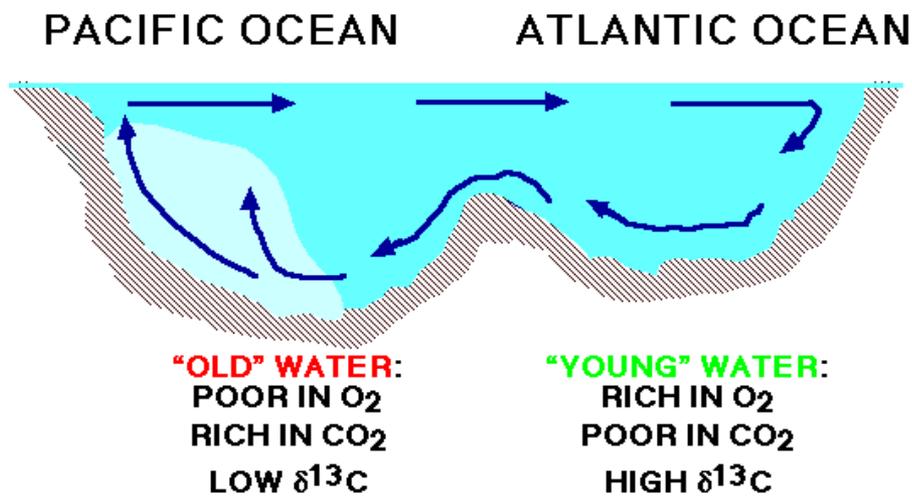
What about TA?

TA higher in older waters of the N'Pacific ocean

http://condor.wesleyan.edu/ethomas/ees123/359caox.htm

Calcite and opal compensation depth
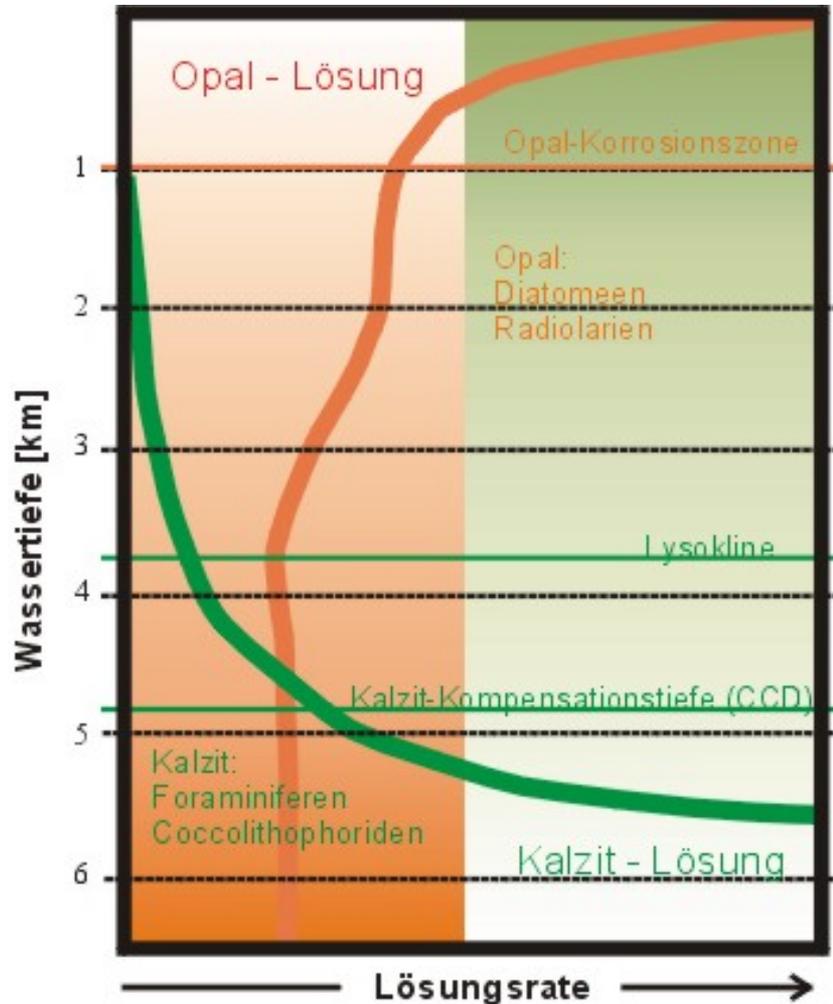
Solubility of SiO_2 decreases with increasing pressure and decreasing temperature – opposite as for calcium

Quelle: http://www.meeresgeo-online.de/

CO_2 is more than twice as soluble in cold polar waters than in warm equatorial waters. The high-latitude zones are also regions where intermediate and bottom waters are formed. As these waters cool, they become denser and sink into the ocean interior, taking with them the CO_2 accumulated at the surface.

Surface ocean CO$_2$

Net Flux (moles CO$_2$ m^{-2} year^{-1})

source: IPCC
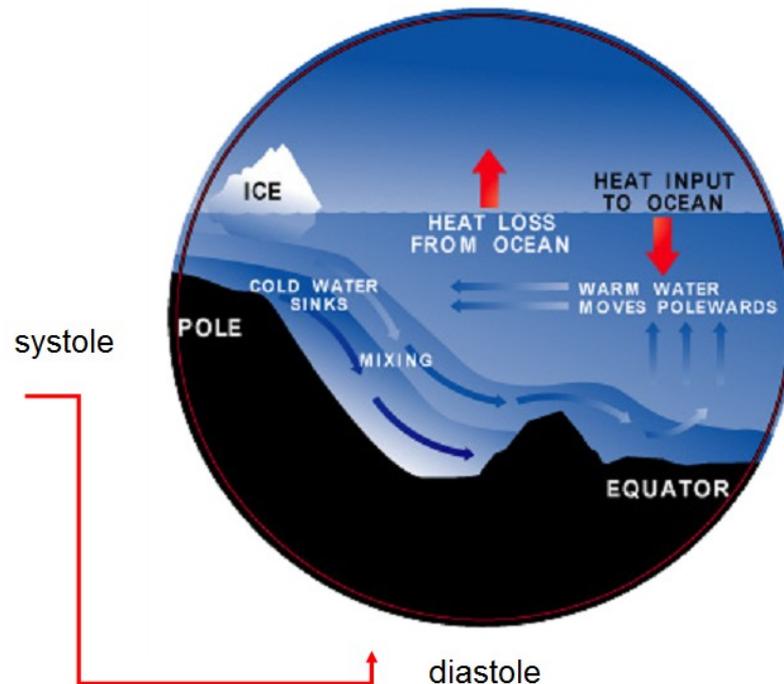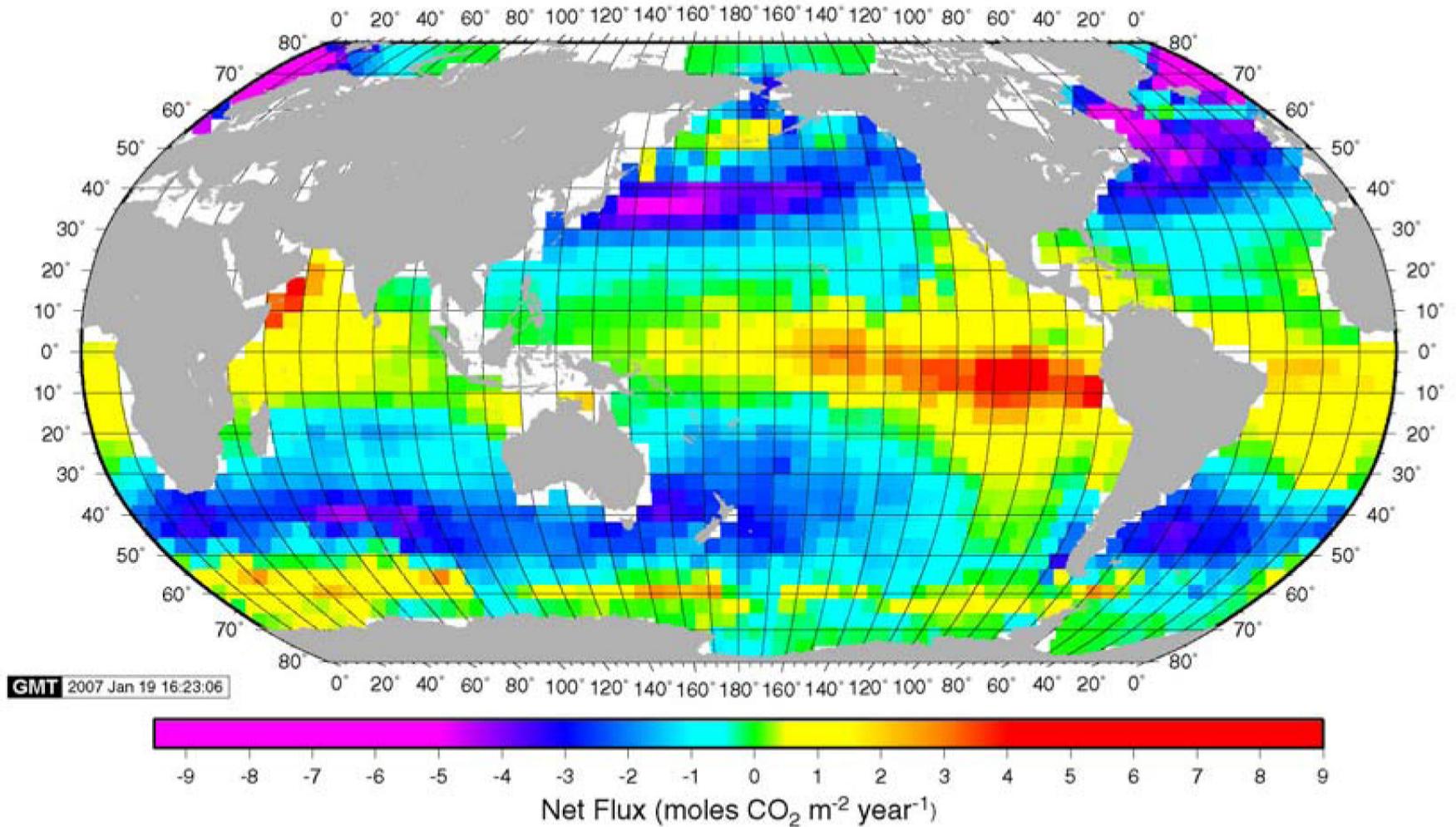
The biological pump

Transport of CO_2 from surface to deep water as organic matter and biogenic carbonate
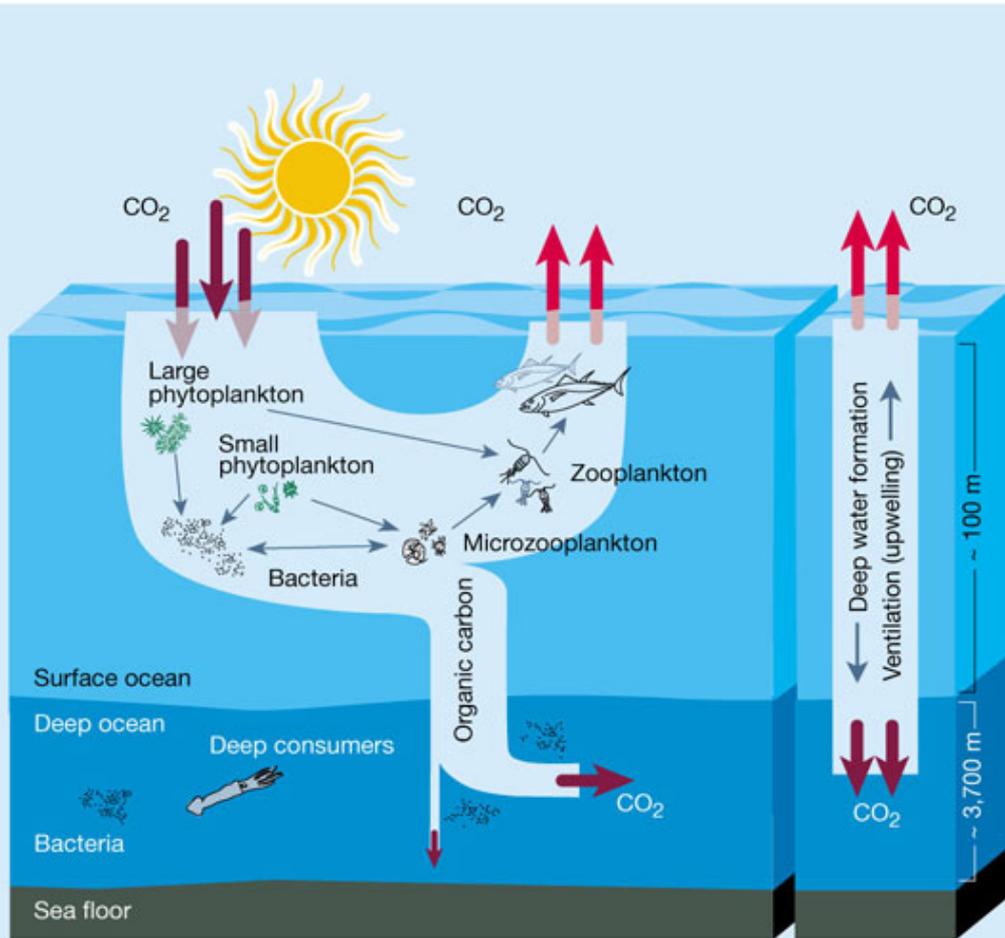
Seawater supersaturated with respect to CO_2 in upwelling zones

Undersaturated by photosynthesis

Highly undersaturated in polar regions

The CO_2 pumps
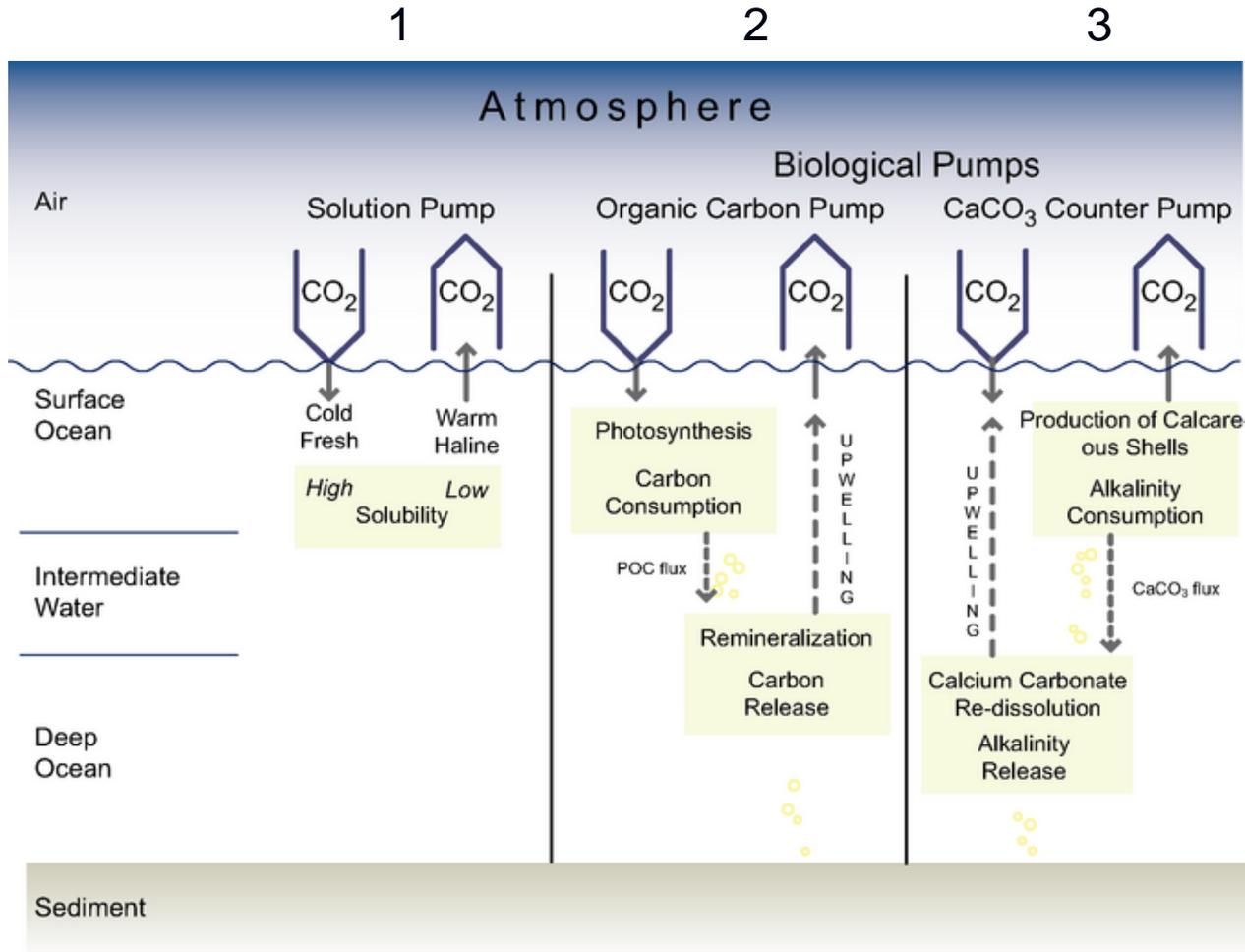
(1) absorption or release of CO_2 due to changes in solubility of gaseous CO_2

(2) changes in carbon fixation in surface waters by photosynthesis and export of this carbon through sinking of organic particles out of the surface layer

(3) changes in the release of CO_2 in surface waters during formation of $CaCO_3$ shell material

Heinze et al. (1991)

Revelle factor (R)

Revelle factor (or buffer factor) R

$$R = (\Delta[pCO_2] / [pCO_2]) / (\Delta[TCO_2] / [TCO_2])$$

Fractional change of seawater pCO_2 to the fractional change in TCO_2 at equilibrium after a perturbation of the CO_2 system

The buffering reaction determines how much additional CO_2 can be dissolved in surface water in response to a pCO_2 increase in the atmosphere

In the present-day ocean, R varies between 8 and 13

CO$_2$ system in seawater

$CO_2(g)$

Gas Exchange

$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$
Carbonic acid

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
Bicarbonate

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$
Carbonate

Atmosphere

Surface ocean

	1XCO$_2$	2XCO$_2$	
	280	560	[ppm]
	8	15	[μmol kg^{-1}]
	1617	1850	
	268	176	
	1893	2040	DIC
	8.15	7.91	pH

Feely et al. (2001): Oceanography 14
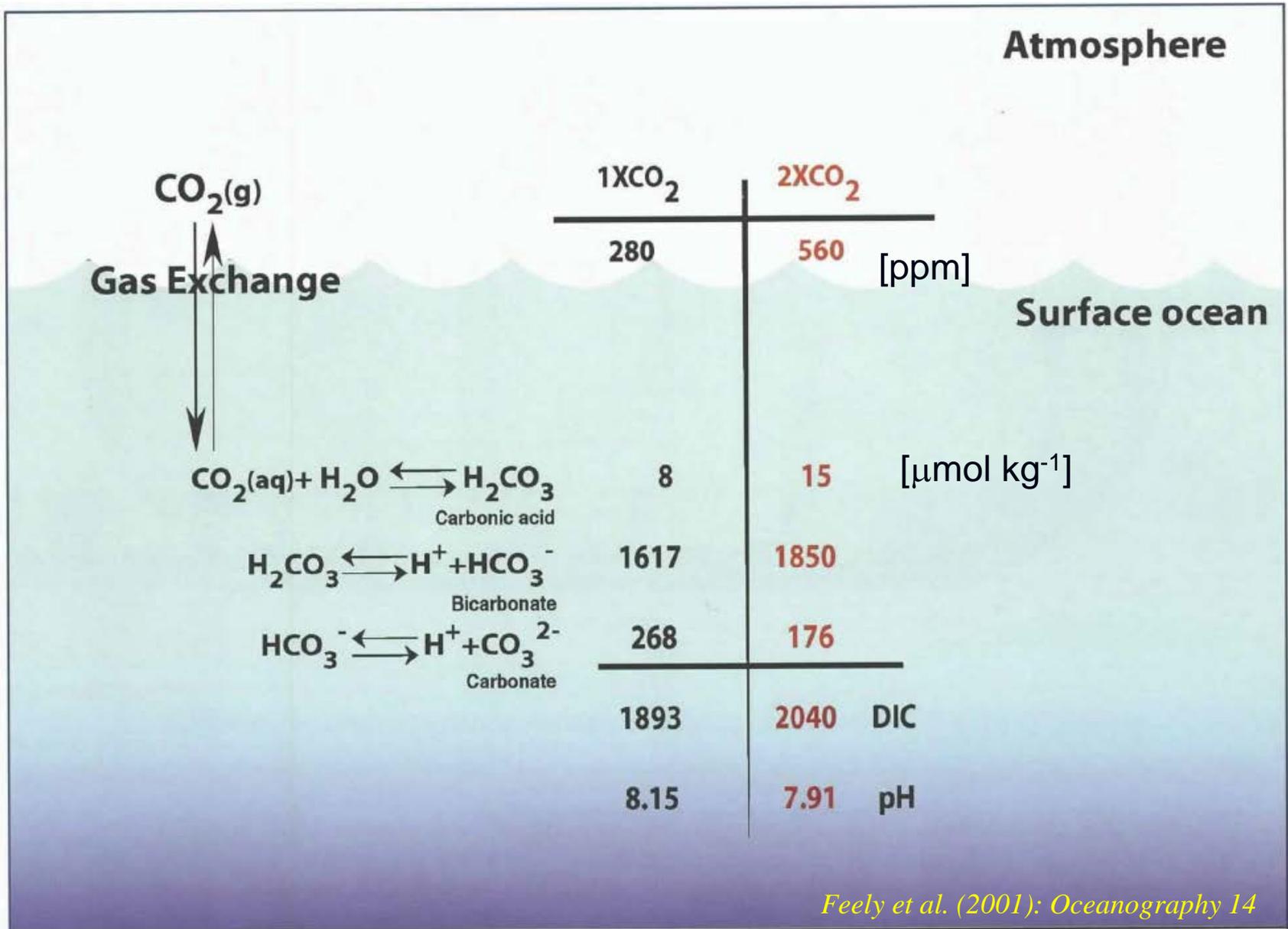
Pre-industrial vs anthropogenic CO_2 in the oceans
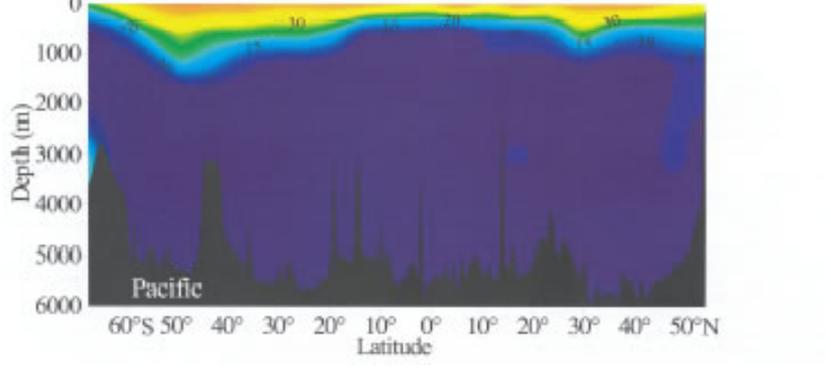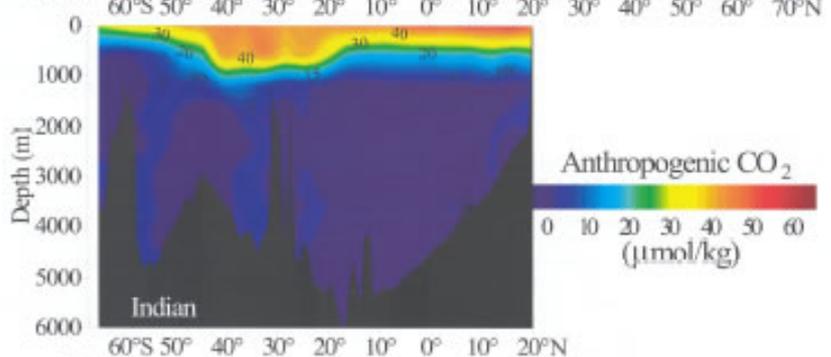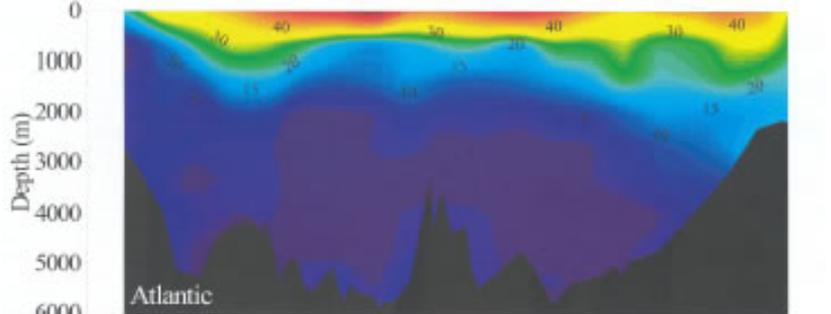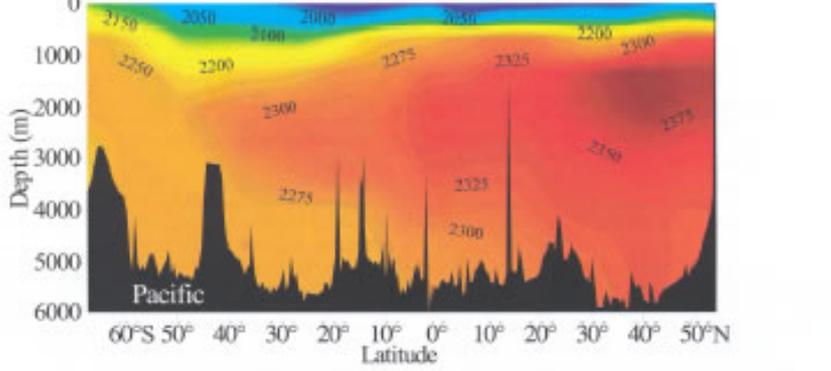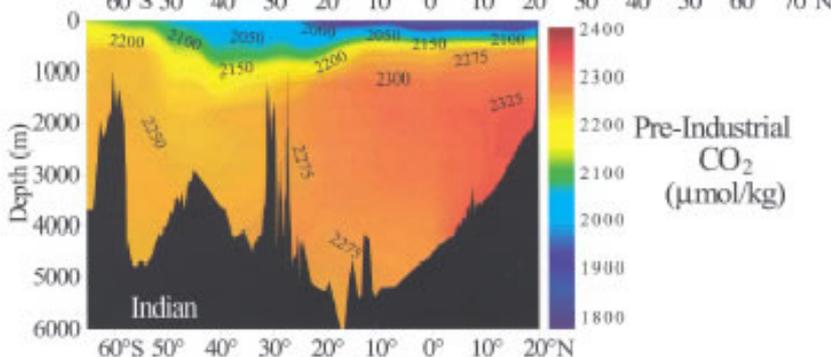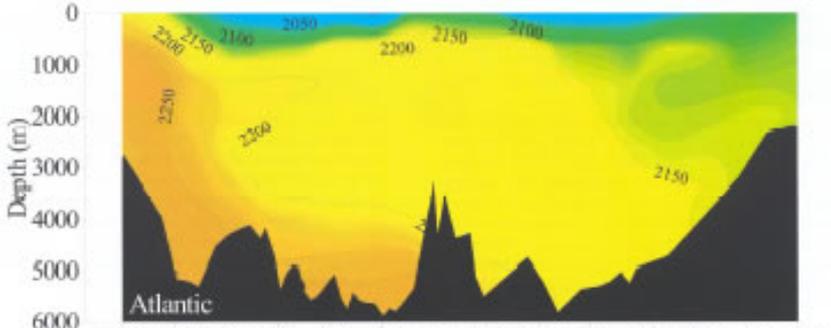
Feely et al. (2001) Oceanography 14

Carbonate dissolution and CCD

At *carbonate compensation depth* (CCD) or *carbonate snow line*: rate of carbonate accumulation equals the rate of carbonate dissolution.

$CaCO_3$ more prone to dissolve in deeper ocean because:

► lower temperature
► greater pressure
► higher acidity (more CO_2)
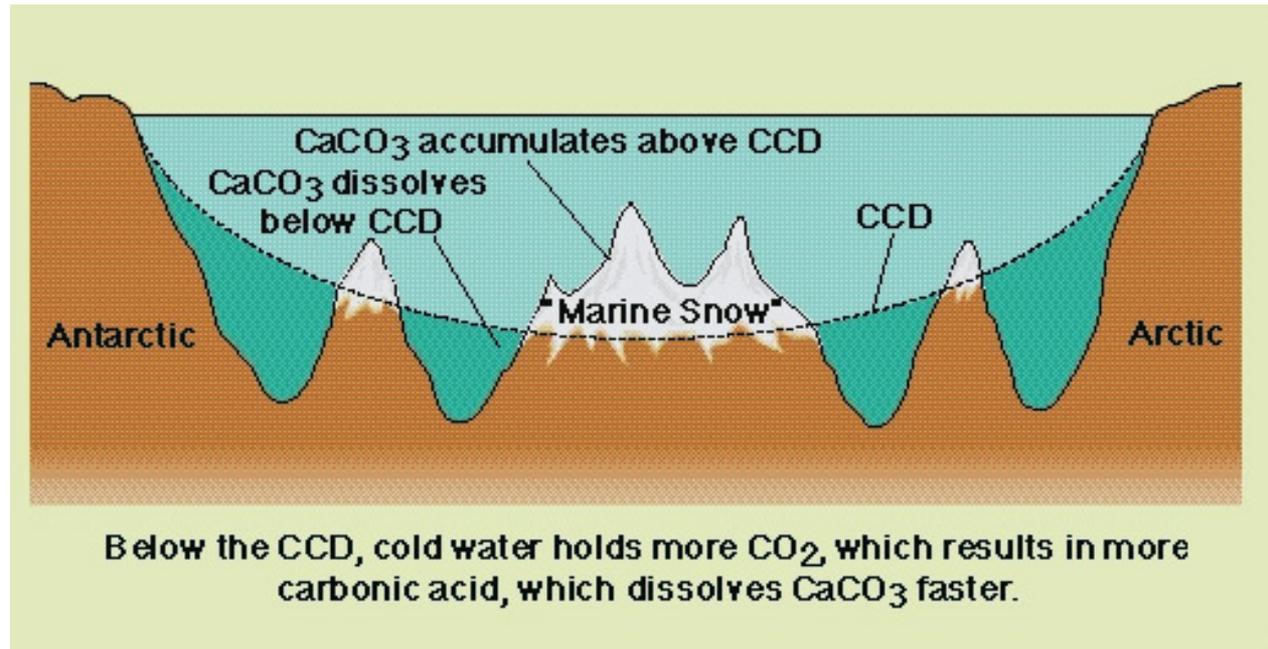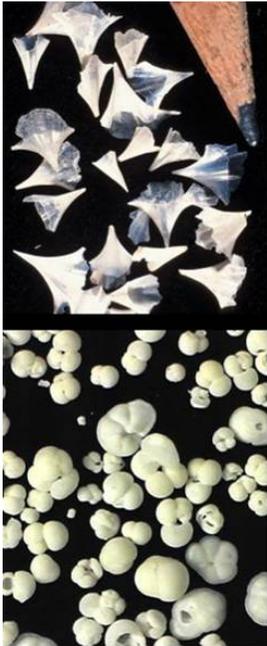
Dissolution rate of calcite as a function of depth in the Pacific at 19°N 156°W

Peterson (1966) experiment

Dissolution starts where undersaturation is reached

W. White: Geochemistry

W. White: Geochemistry

Carbonate dissolution and CCD

CaCO3 accumulates above CCD
CaCO3 dissolves below CCD
CCD
Antarctic
"Marine Snow"
Arctic

Below the CCD, cold water holds more CO_2, which results in more carbonic acid, which dissolves $CaCO_3$ faster.

— seafloor deeper than CCD will be devoid of carbonate sediments
— Depth of CCD varies; higher in the Pacific because deep water in the Pacific has more CO_2 (more acidic)
— Lysocline: 500-1000 m above CCD at this depth shells begin to dissolve

(1) $H_2O + CO_2 = H_2CO_3$
(2) $CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$

$CaCO_3$ = calcite (hexagonal) or aragonite (orthorhombic)
H_2CO_3 = carbonic acid (eq.2)
HCO_3^- = bicarbonate

Carbonate dissolution and CCD
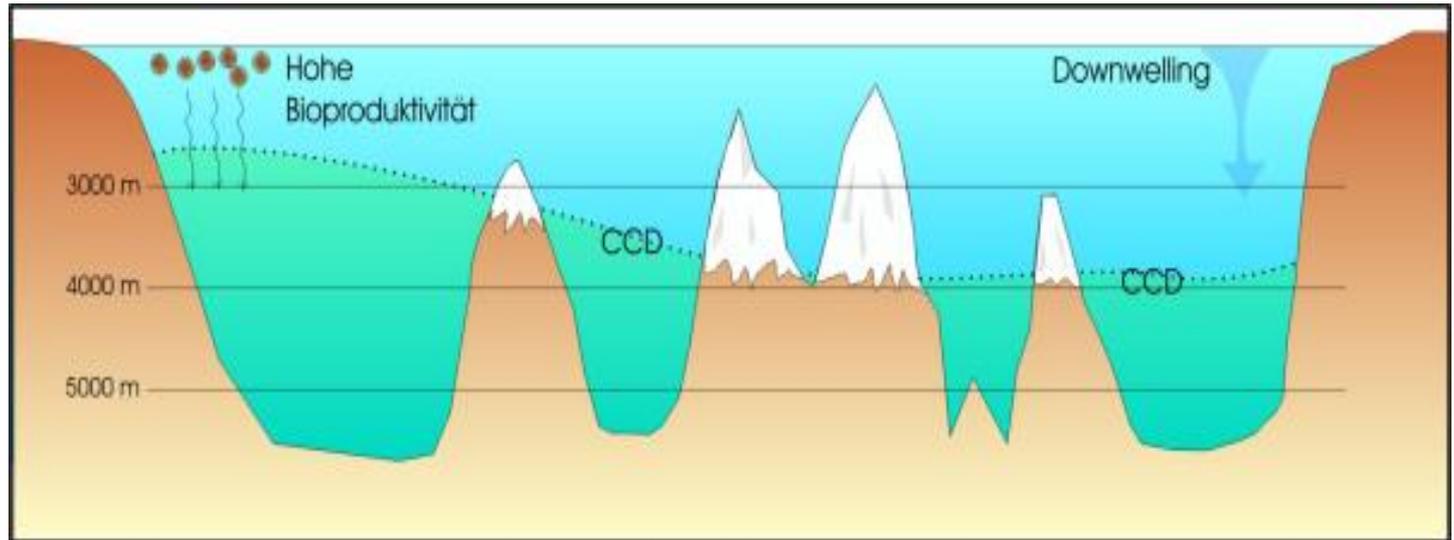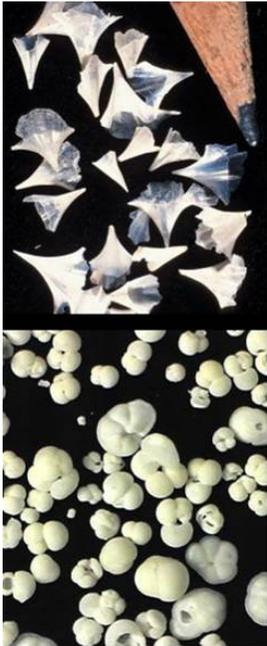
- seafloor deeper than CCD will be devoid of carbonate sediments
- Depth of CCD varies; higher in the Pacific because deep water in the Pacific has more CO_2 (more acidic)
- Lysocline: 500-1000 m above CCD at this depth shells begin to dissolve

consequence: *c.* 90% of calcite particles produced in the upper ocean waters and sinking below the CCD will be dissolved

Carbonate dissolution and CCD
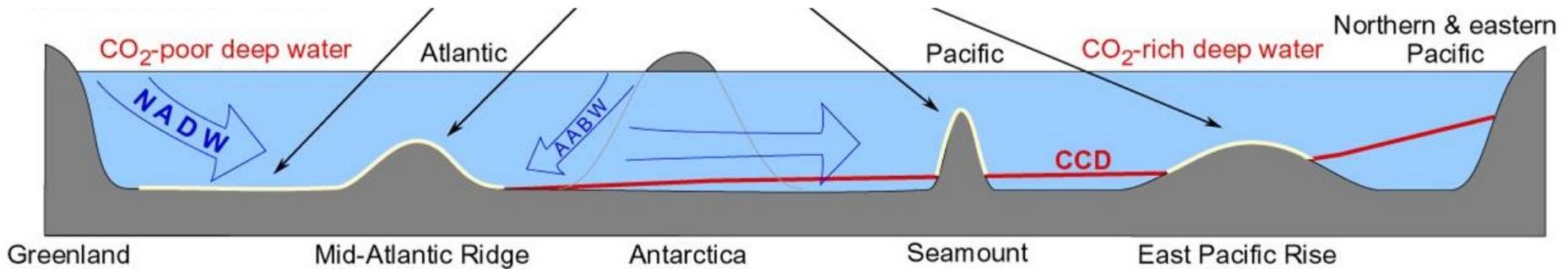
Depth of Lysocline depends on:

- temperature
- pressure
- biological activity ($CH_2O + O_2 \leftrightarrow CO_2 + H_2O$)
- CO_2-concentration

Nutrients in seawater
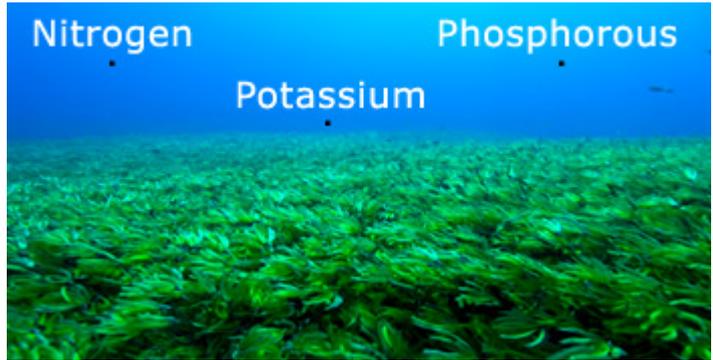
Biolimiting or nutrient elements

limiting factor in the upper euphotic zone is nutrient availability

limiting N or P availability seawater can limit algal blooms
If N and P are available productivity can remain low because of the lack of Fe
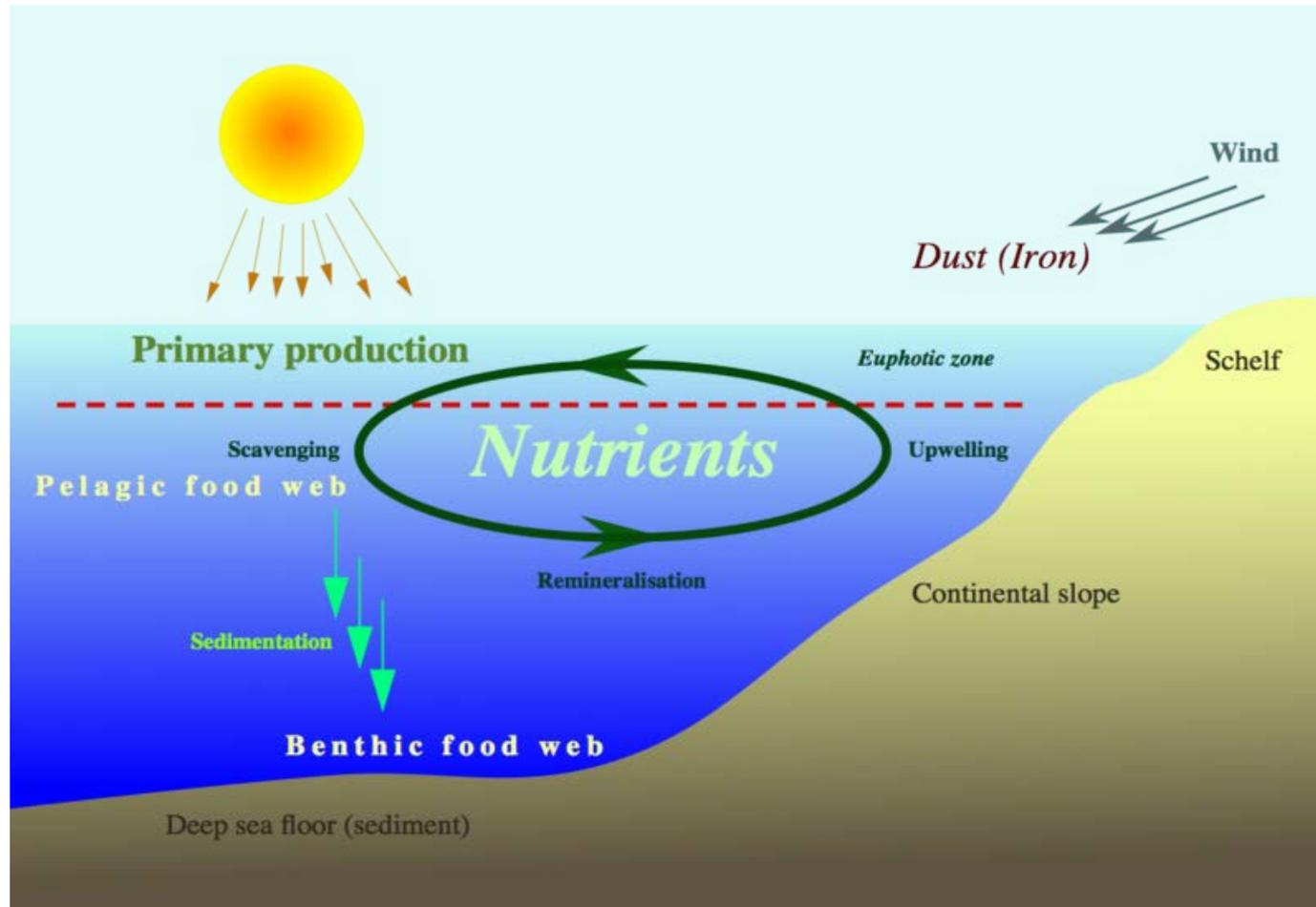
Phytoplankton
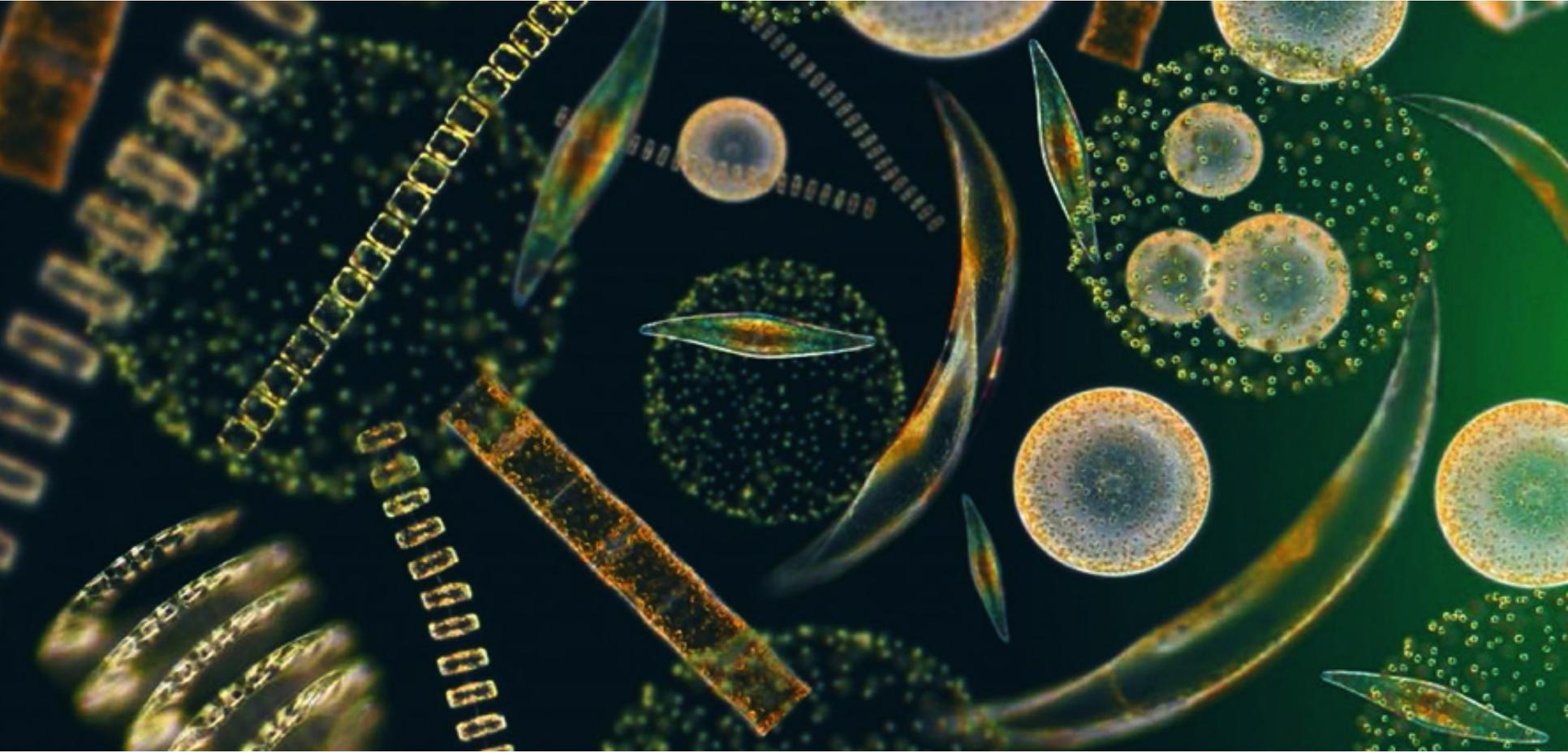
Phytoplankton
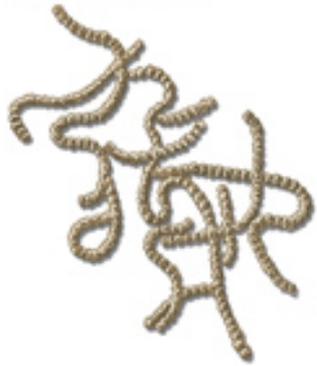
cyanobacteria   diatom   dinoflagellate   green algae   coccolithophore

Ocean primary production of phytoplankton
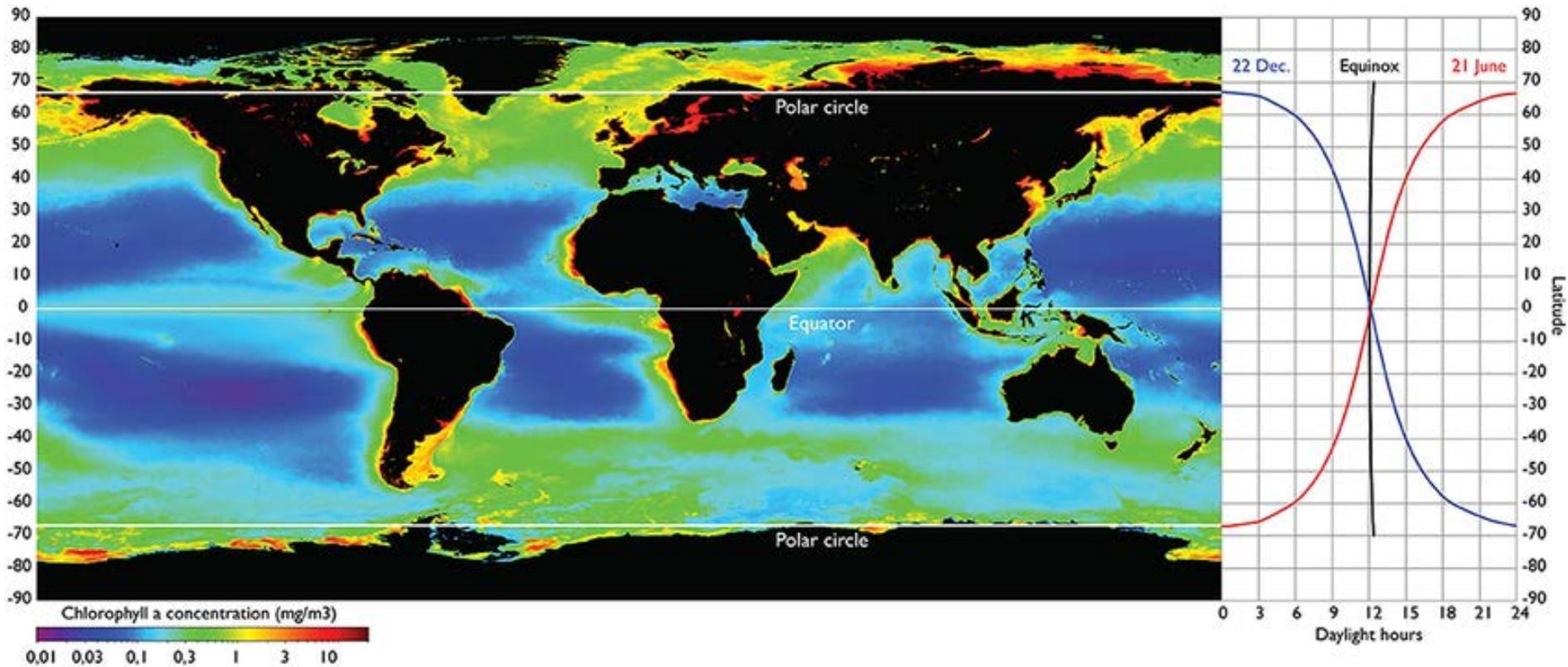
Seasonal Cycle of Phytoplankton
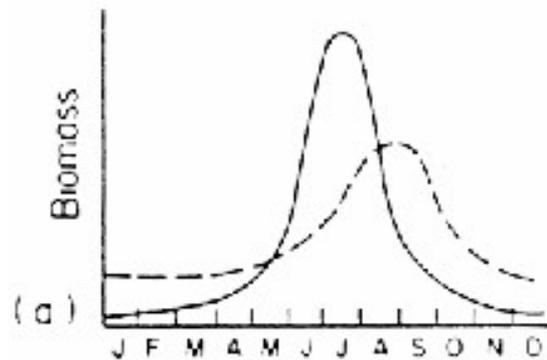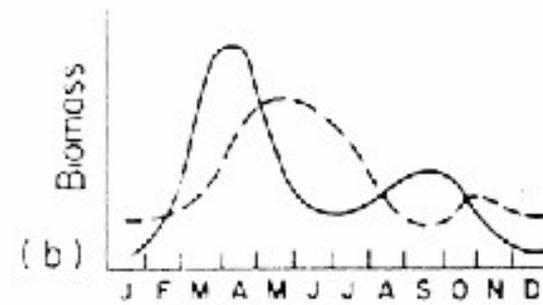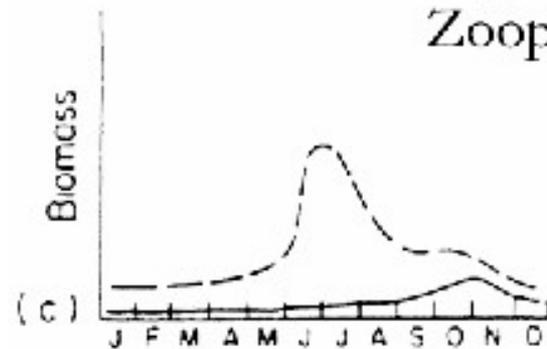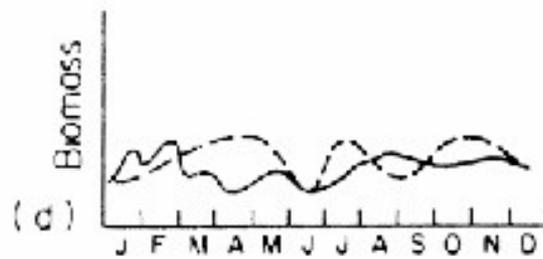
# Redfield ratio

Relationship between nitrate and phosphate in seawater
C:N:P in most phytoplankton is 106:16:1

Gruber & Deutsch 2014 Nat. Geosci.

Nutrient elements


W. White: Geochemistry

Nutrient elements

W. White: Geochemistry
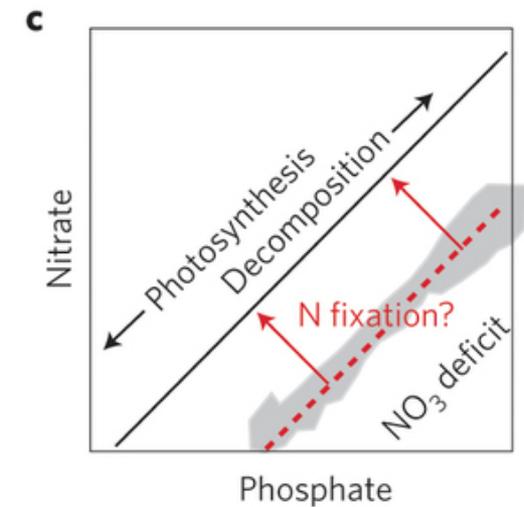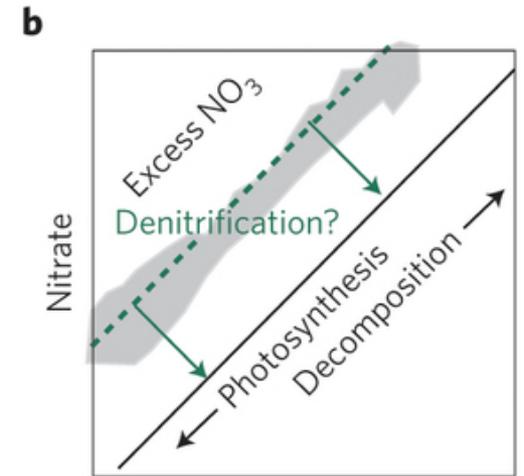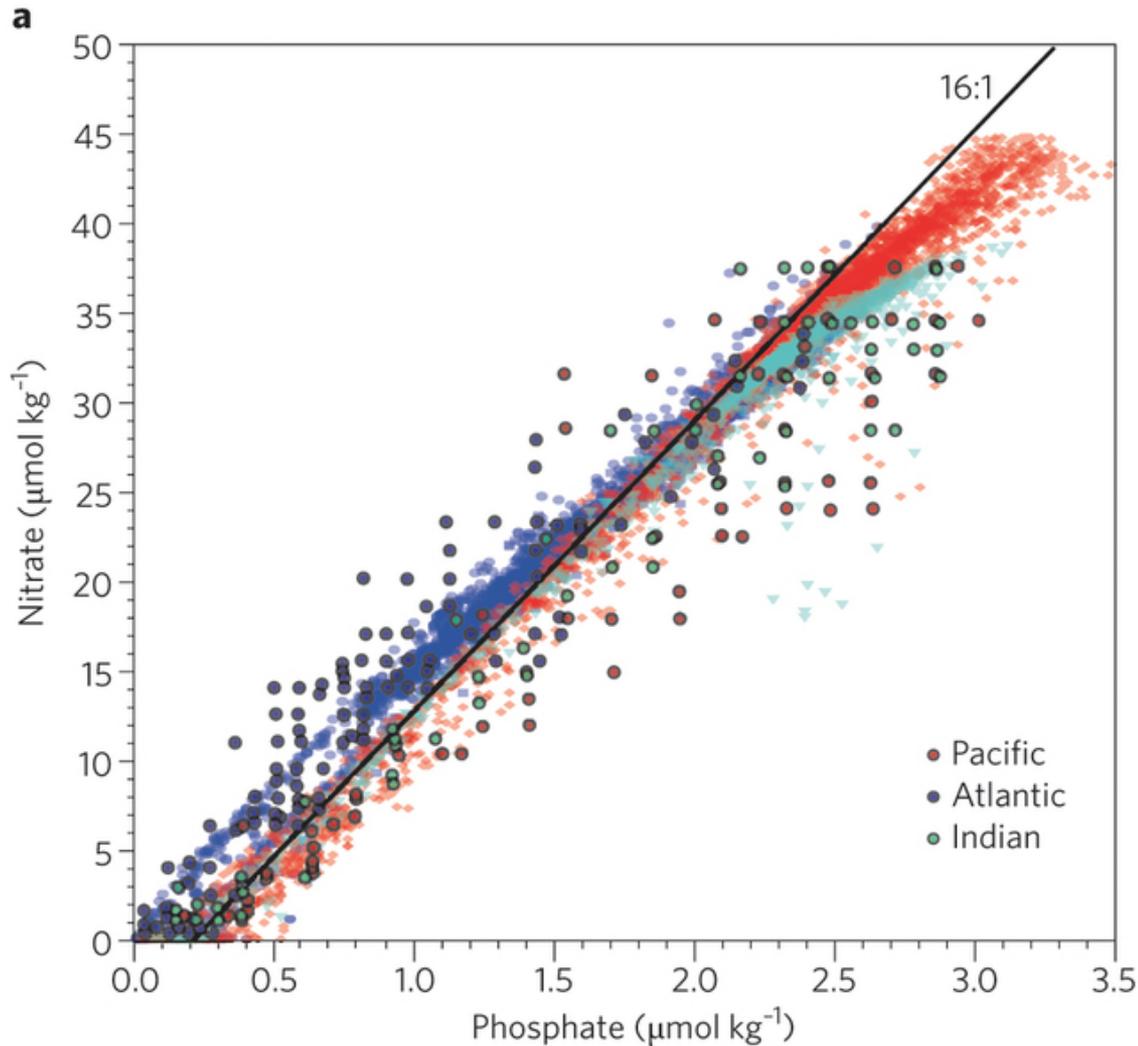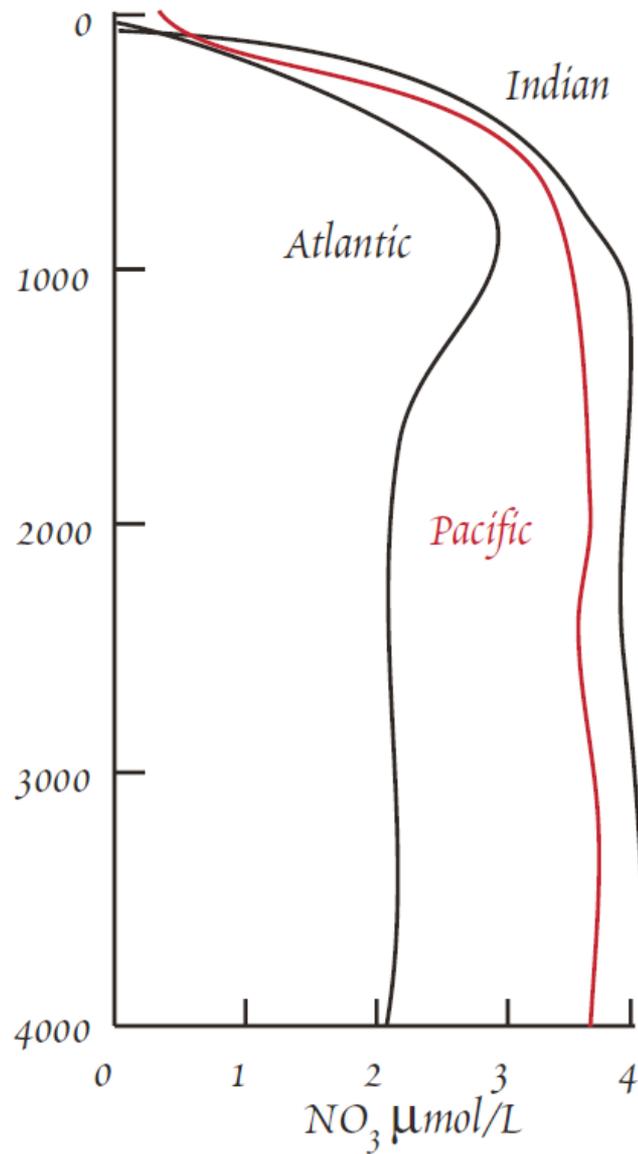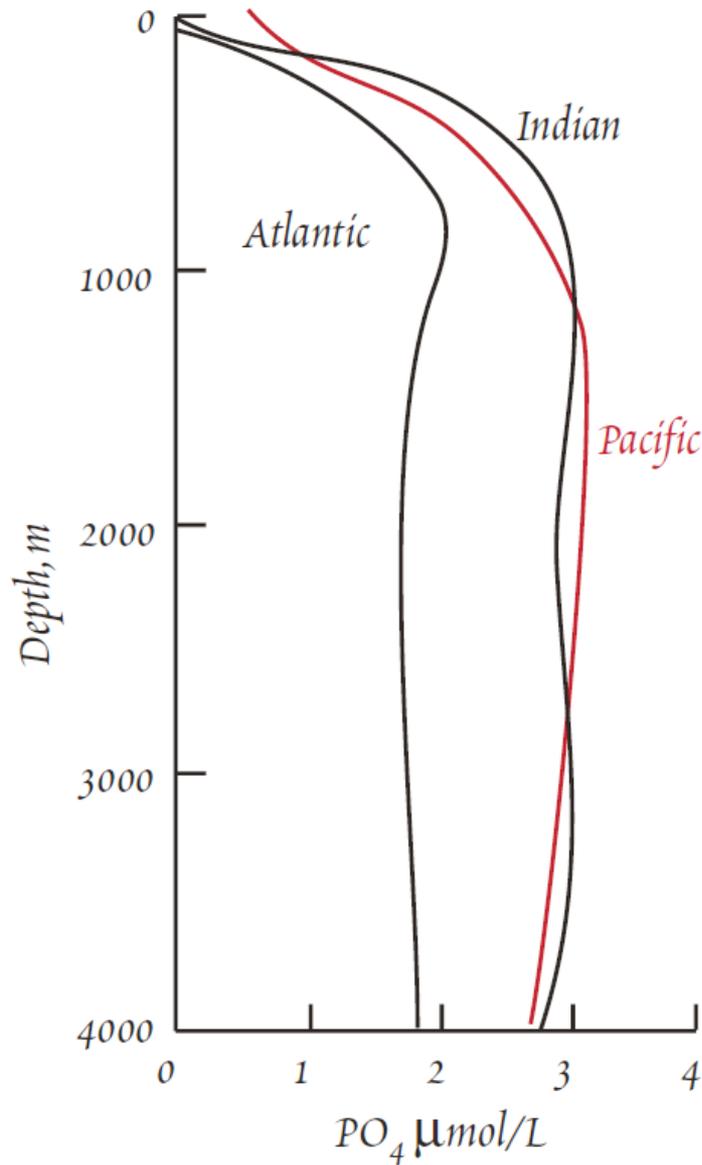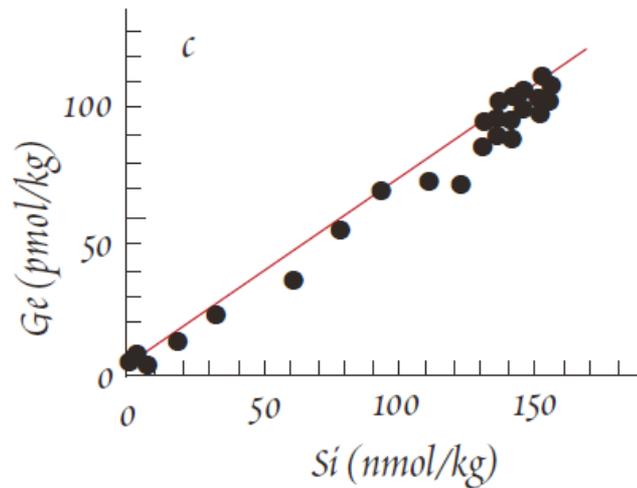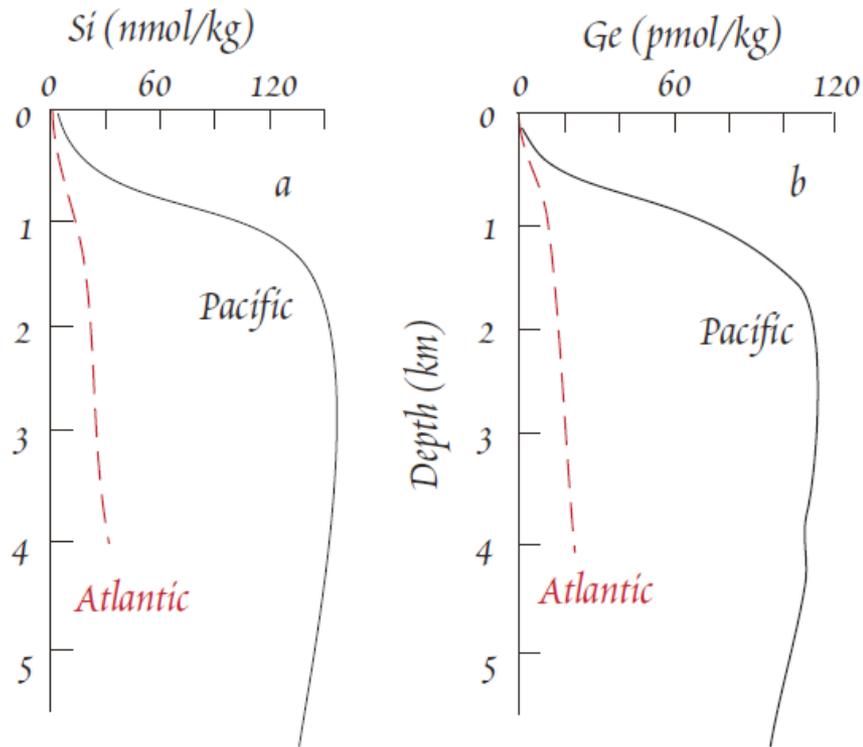
Nutrient elements

Left: concentration profiles of two labile nutrients (Cd: points and phosphate: curves)

Right: concentration profiles of two refractory nutrients (Zn: points and silicate: curves)
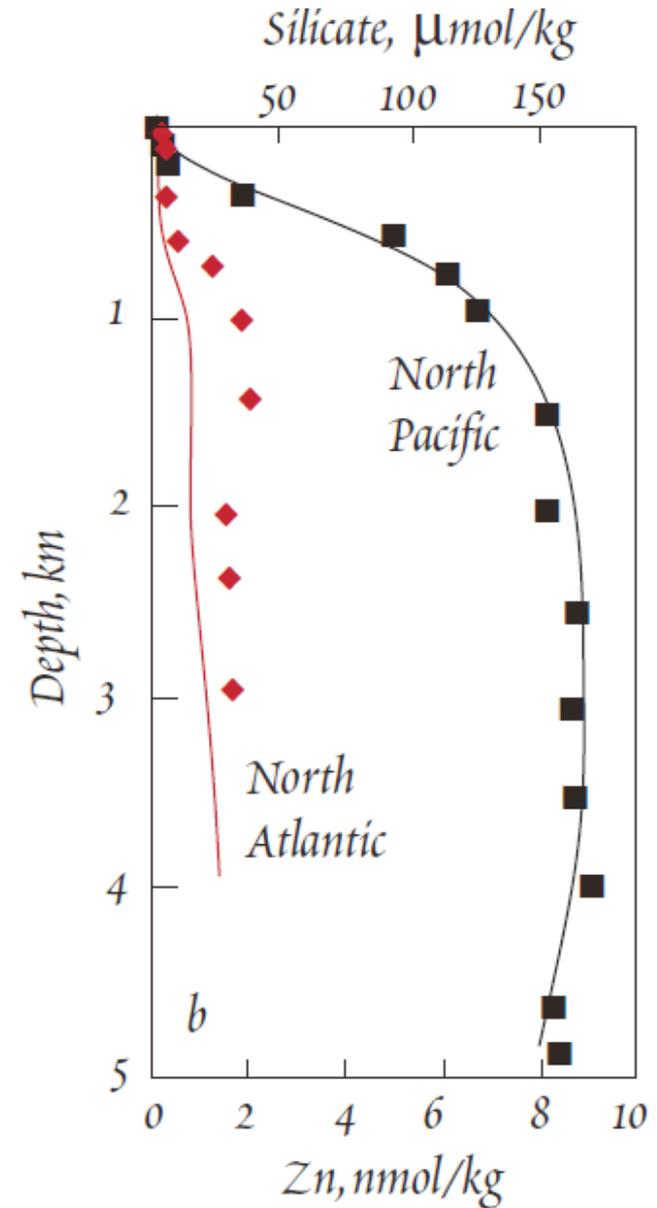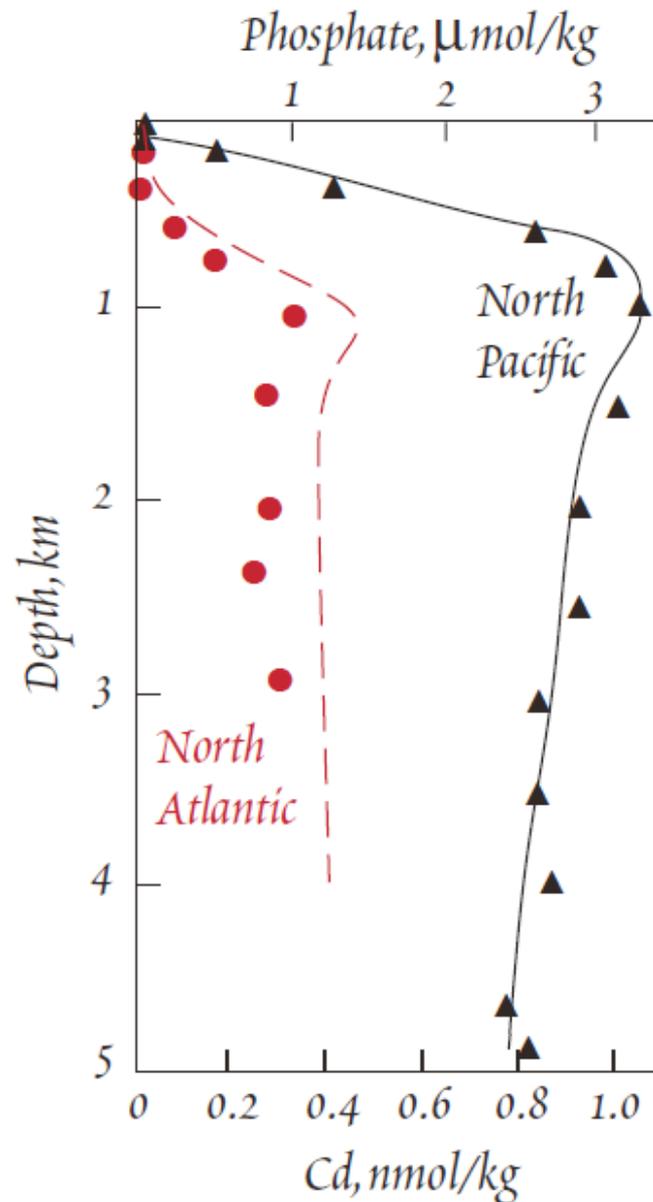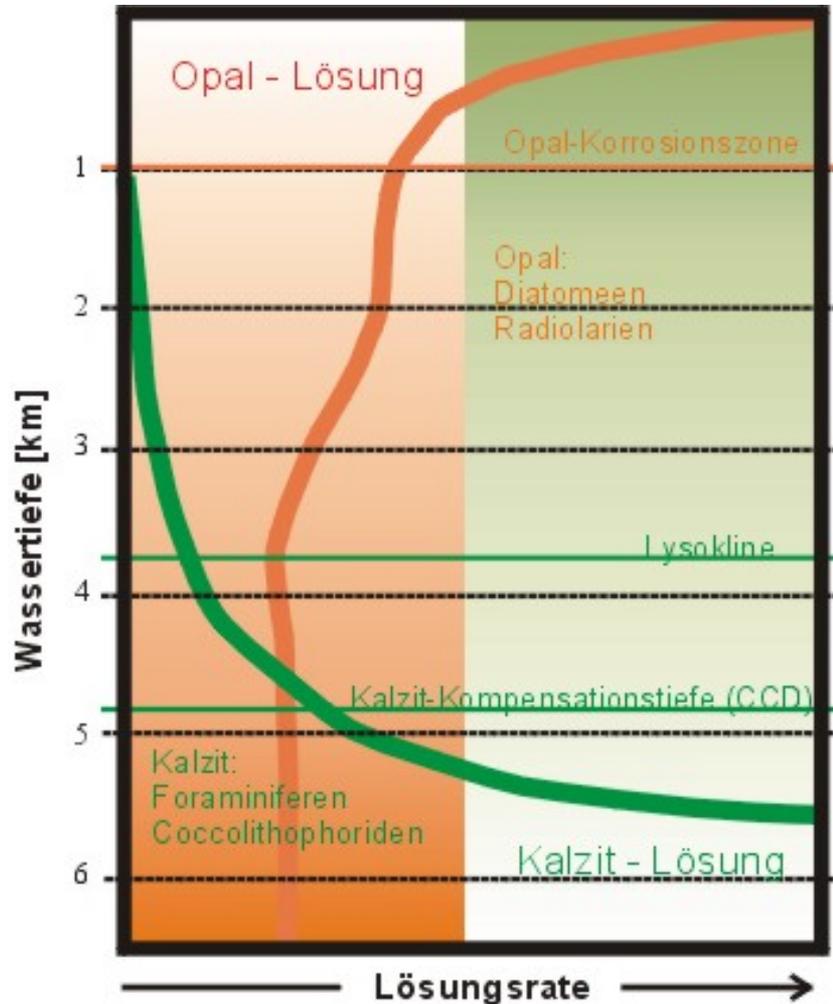
W. White: Geochemistry

Quelle: http://www.meeresgeo-online.de/

Solubility of SiO_2 decreases with increasing pressure and decreasing temperature – opposite as for calcium

nitrogen

$$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$$
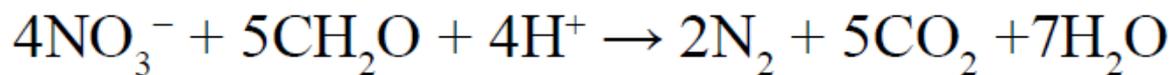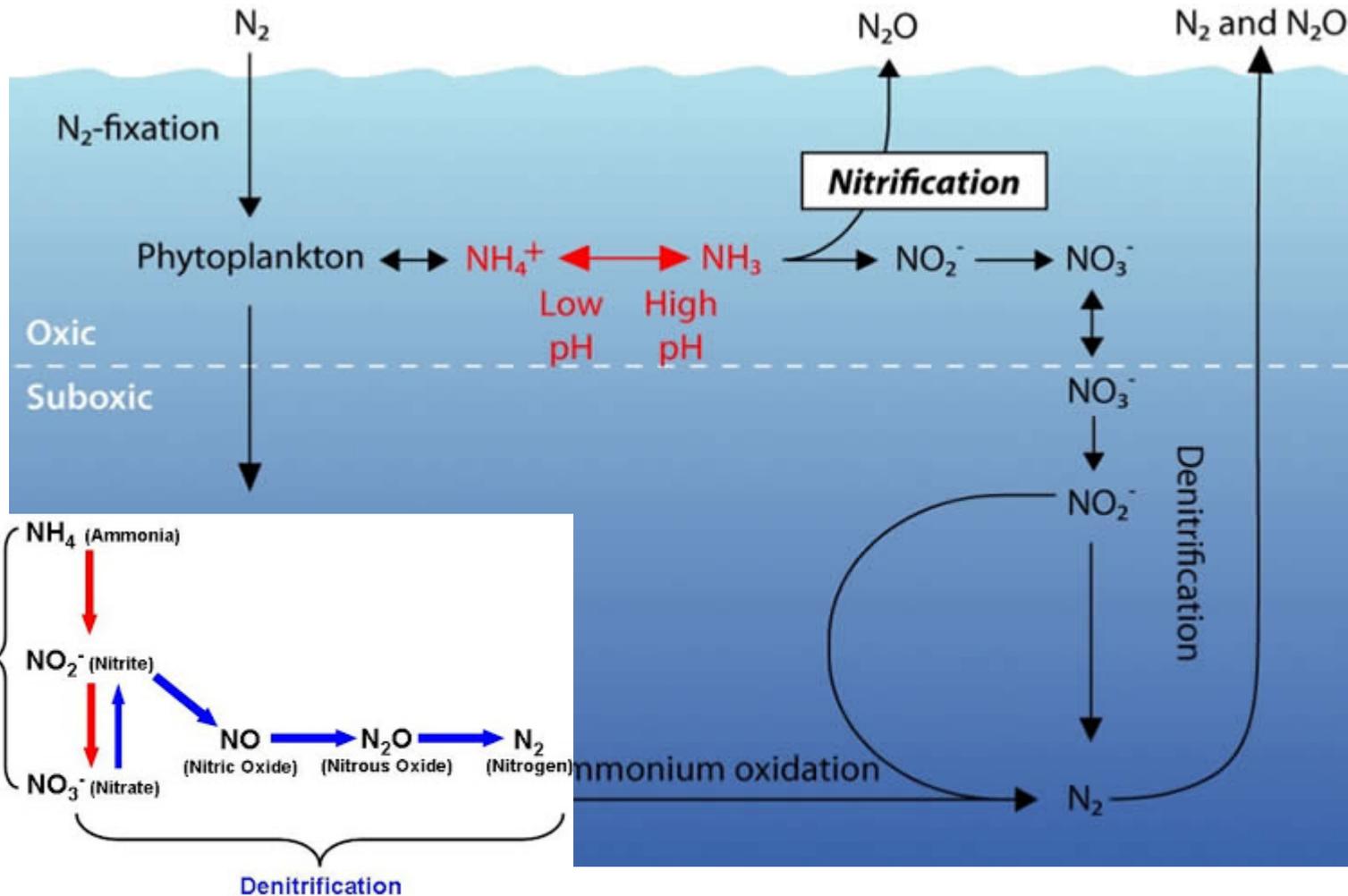
*Beman et al. (2011)*

Ocean acidification
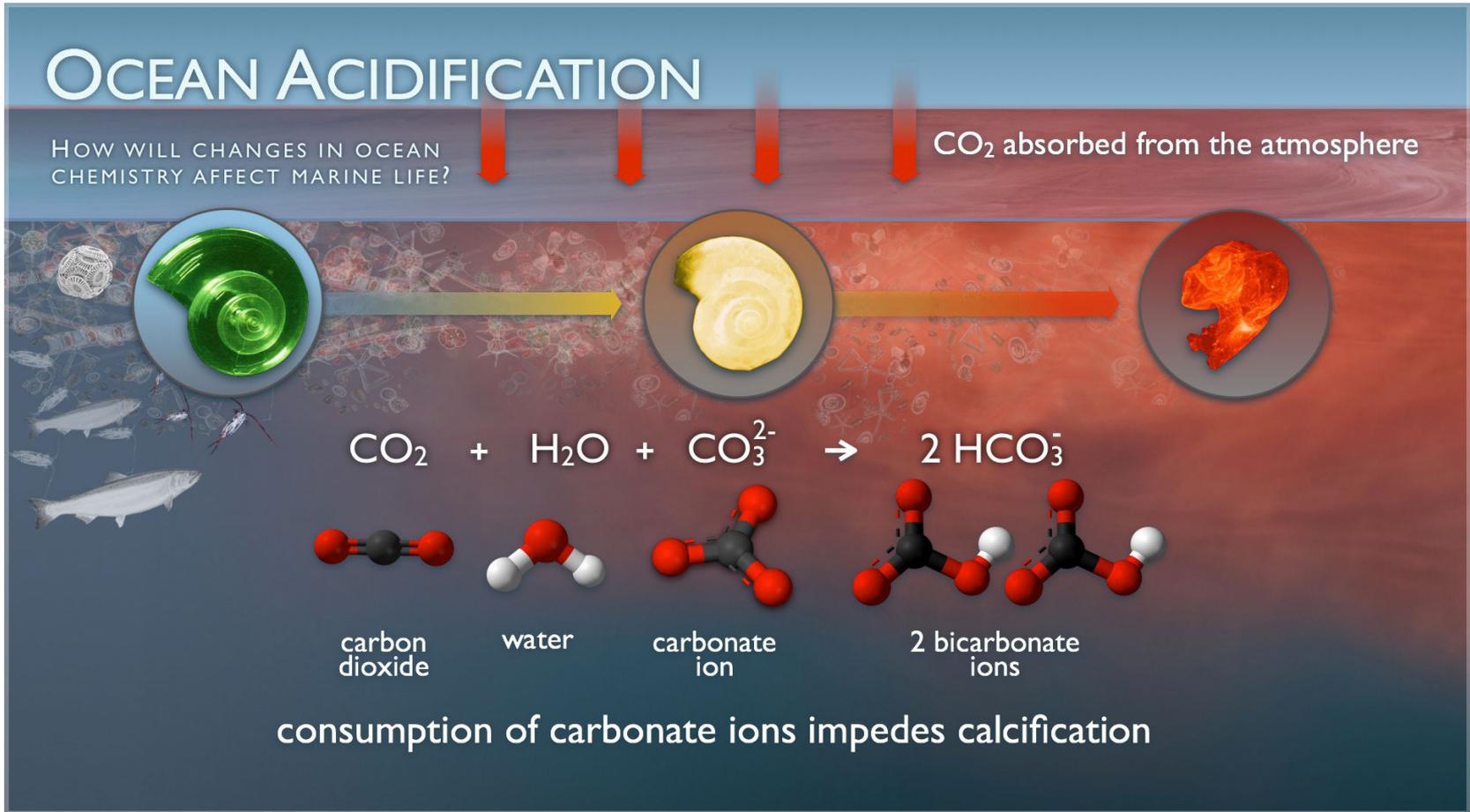
Oceans absorb CO_2 from the atmosphere. CO_2 dissolves in seawater and forms carbonic acid. The pH decreases. Oceans reach a less alkaline and therefore more acidic state.

Ocean acidification

Benthic coral reef calcium carbonate dissolution in an acidifying ocean

*Eyre et al (2014) Nature Climate Change 4*
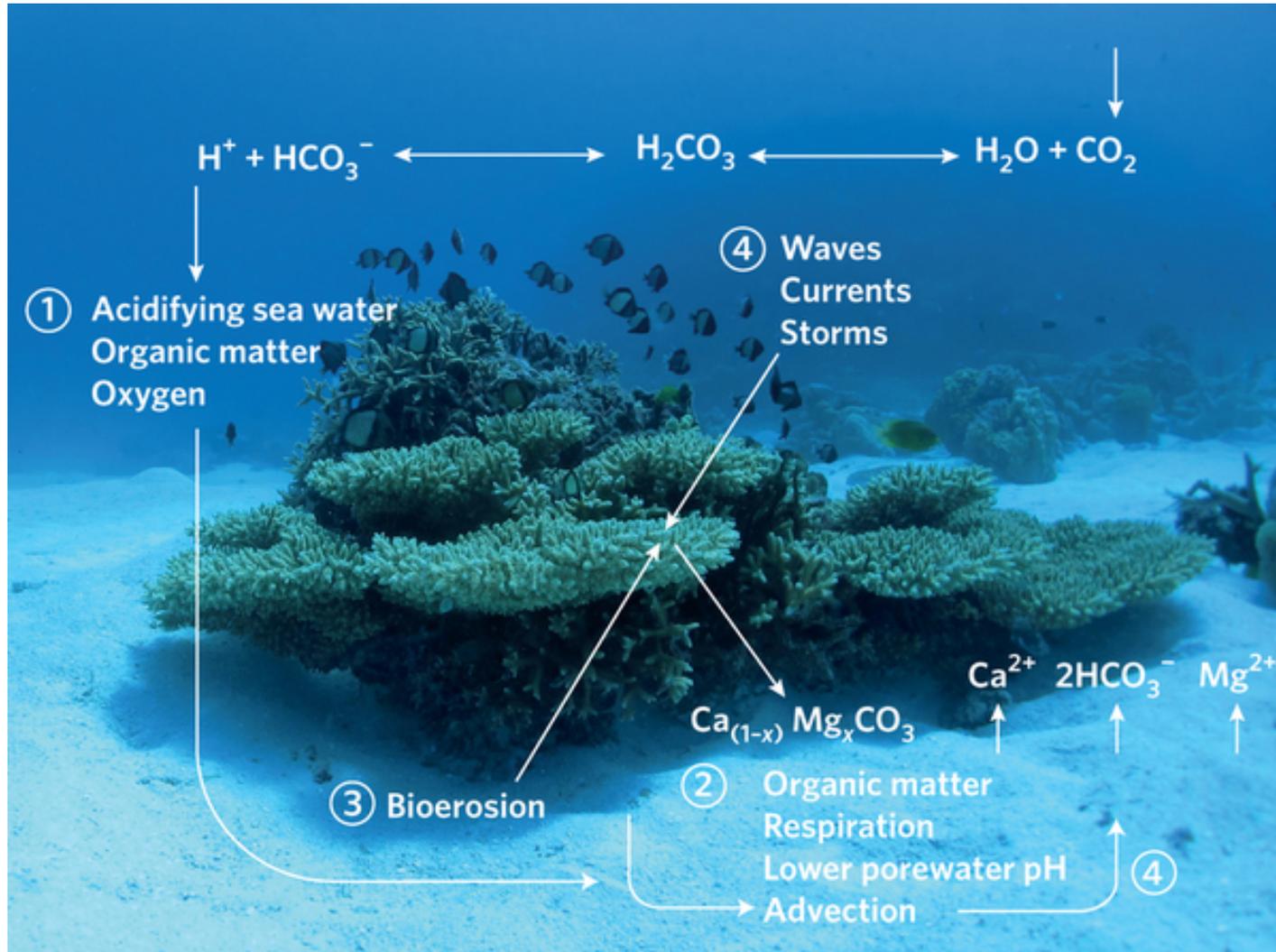
Fertilizing the ocean with iron

reducing atmospheric CO_2 concentrations by storage in marine organisms (sequestration)

algal growth in all of these regions can be stimulated by fertilizing the water with iron

plants assimilate carbon, carbon dioxide from the atmosphere is thus converted to biomass

Fertilizing the ocean with iron

1 Oceans naturally absorb CO2

CO_2

2 Iron sulphate added to ocean

3 Availability of iron prompts phytoplankton bloom which use CO2 to grow

CO_2

4 Phytoplankton die and fall to the ocean floor where the CO2 is held for centuries
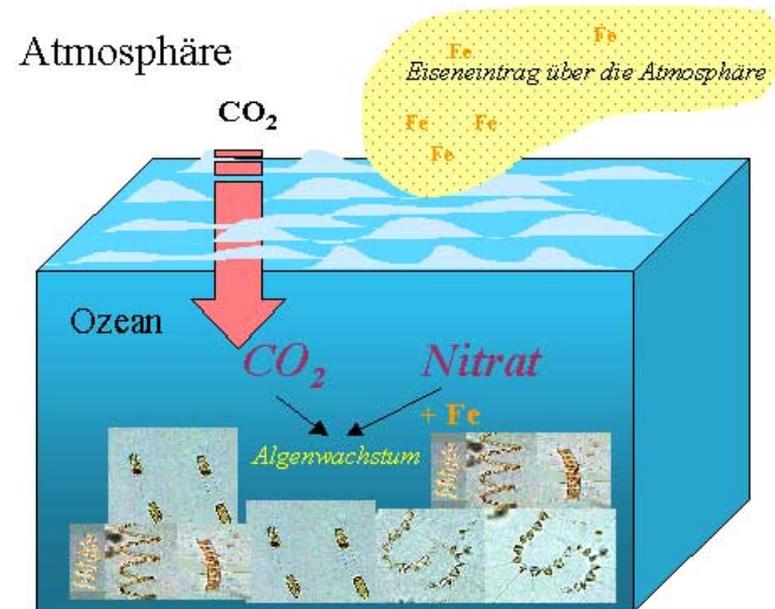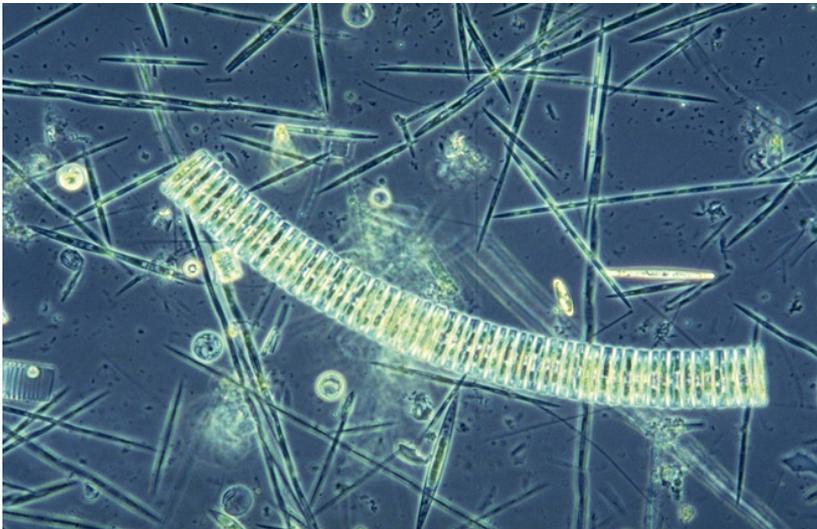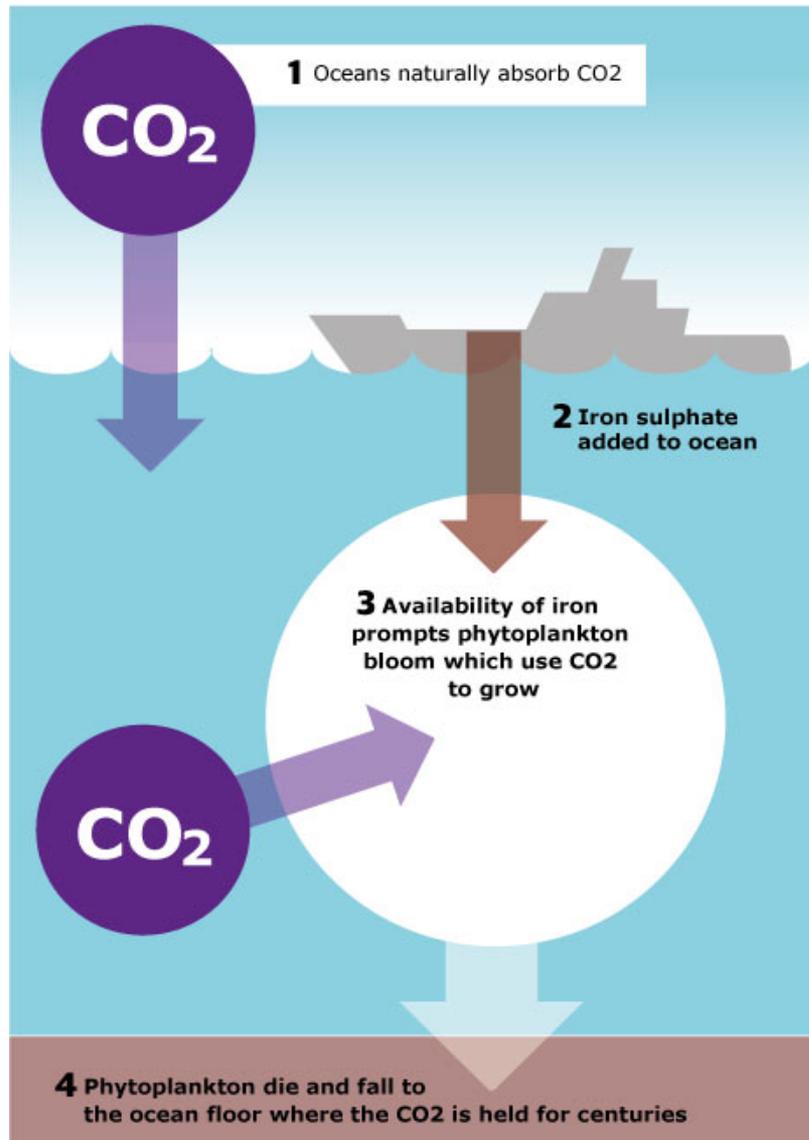
when the algae die and sink to the bottom and are digested by animals or broken down by microorganisms, the carbon dioxide is released again.

if breakdown occurs at great depths, the CO_2 will be released into the atmosphere within a few hundred to thousand years because of global ocean circulation.

iron fertilization could have undesirable side effects: disturbs nutrient budget in other regions.

could contribute to local ocean acidification due to the increased decay of organic material and thus greater carbon dioxide input into the deeper water layers.

decay of additional biomass created by iron fertilization would consume more oxygen

deep ocean as a major source of dissolved iron
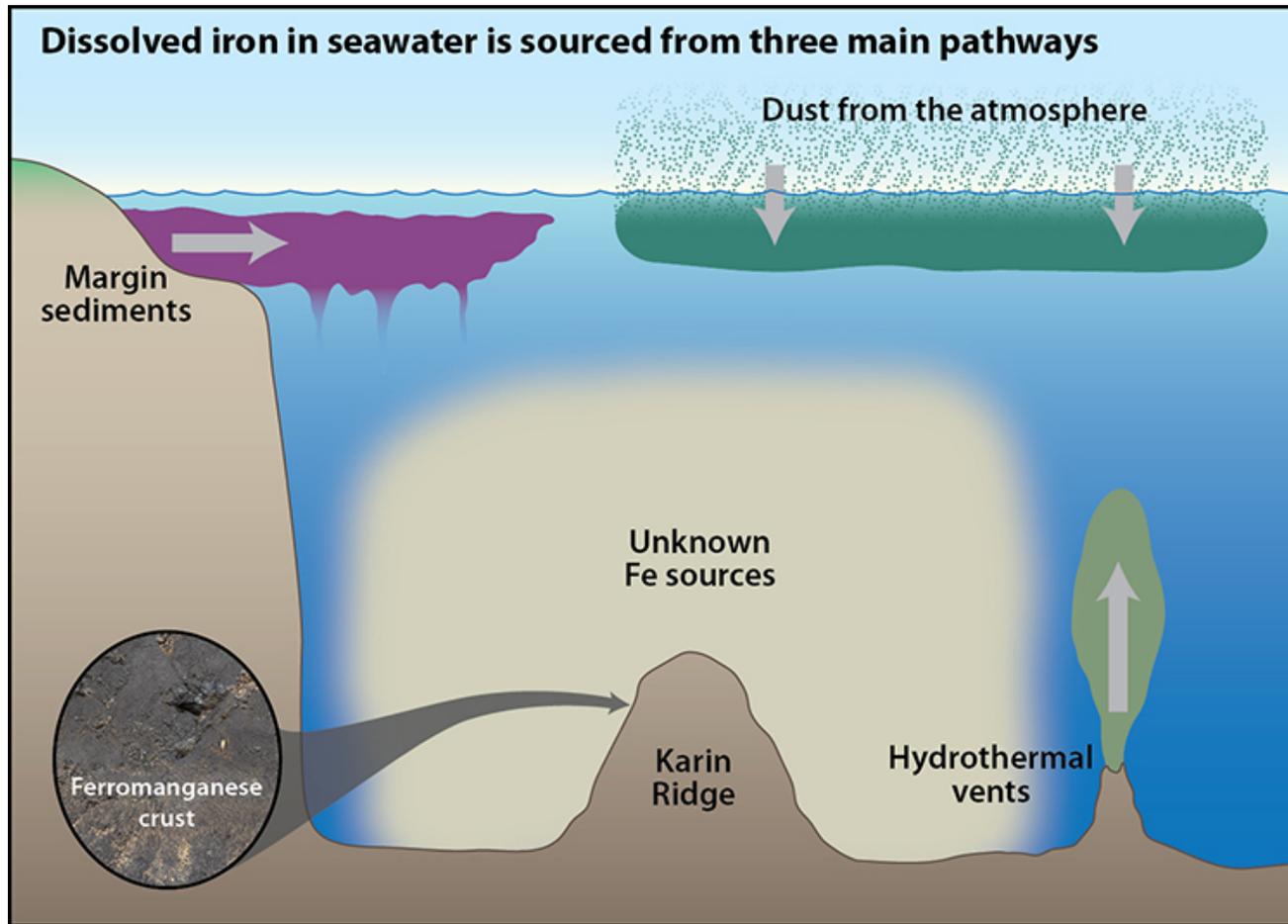
Horner et al. (2015) *Proceedings of the National Academy of Sciences*