Buffer capacity

pH is an intensity factor, not to be confused with the capacity of a solution to give or accept a proton (acidity, alkalinity), also to be distinguished from the buffer capacity of the solution.

The buffer capacity of a solution is a measure of its ability to resist changes of pH upon the addition of a strong acid or base. The buffer capacity is defined as:

$$\beta = dC_B/dpH = -dC_A/dpH \approx 2.303 \ \Sigma \ \lambda_i^2 \ [X_i]$$

where C_A (or C_B) is an infinitesimal addition of strong acid (or base), λ is the neutralizing capacity of species i and [X] is the concentration of compounds capable of neutralizing a proton or OH^-.

The pH of seawater is relatively constant (~7.8 to 8.3) and buffered by the carbonate system:

$$CO_3^{2-} \ \underset{OH^-}{\overset{H^+}{\rightleftarrows}} \ HCO_3^- \ \underset{OH^-}{\overset{H^+}{\rightleftarrows}} \ H_2CO_3 \ \rightleftarrows \ CO_2\uparrow + H_2O$$
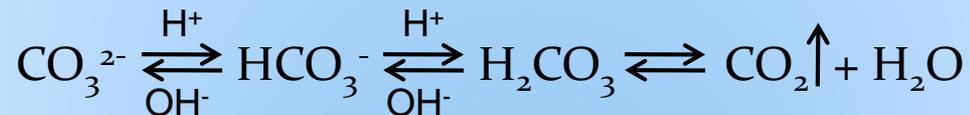
Buffer capacity of seawater

If a parcel of water to which the acid was added is in contact with the atmosphere, the excess CO_2 produced by the sequential protonation of CO_3^{2-} and HCO_3^- will be able to escape to the atmosphere further reducing the increase in pH.

$$\beta = 2.303 \left([HCO_3^-] + 4[CO_3^{2-}] + [H^+] + [OH^-] \right)$$

However, if the parcel of water is isolated from the atmosphere and cannot rid itself of the generated CO_2, its buffering mechanism is diminished.

$$\beta = 2.303 \left([H_2CO_3^*] + [CO_3^{2-}] + [H^+] + [OH^-] \right)$$

Consequently, at pH ≈ 8, the buffer capacity of the carbonate system in equilibrium with a gas phase is roughly 100 times greater than that of an isolated aqueous phase.

On the other hand, the buffer capacity of the system would be greatly increased by the presence of solid $CaCO_3$, since acid added to the system would readily react with the solid:
$$CaCO_3 + H^+ \longleftrightarrow Ca^{2+} + HCO_3^-$$

in which case, if the system is open to the atmosphere:

$$\beta = 2.303 \left(4[Ca^{2+}] + [HCO_3^-] + 4[CO_3^{2-}] + [H^+] + [OH^-] \right)$$

Buffer capacity provided by the carbonic acid system in aqueous solutions

$$\beta_{H2O} = 2.303\ ([H^+] + [OH^-])$$
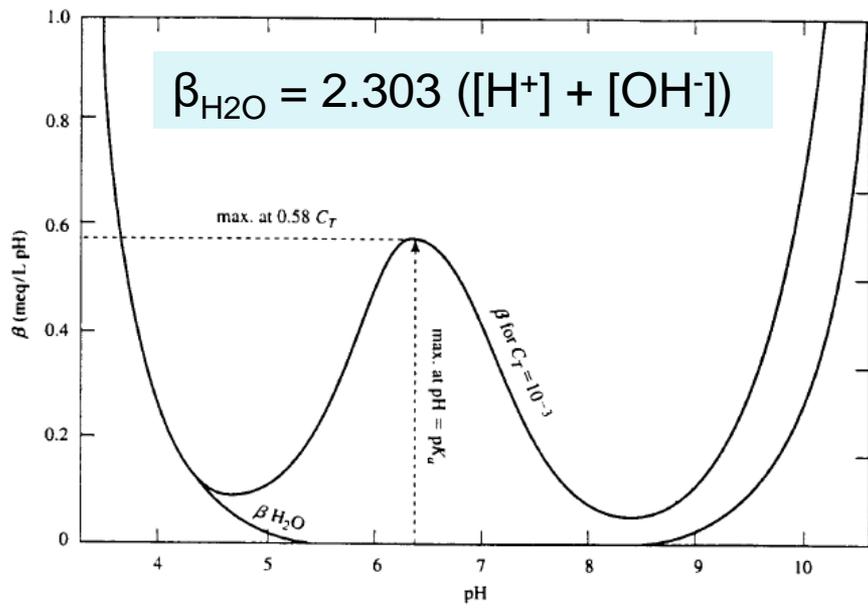
Figure 5.10 A linear plot of the buffer capacity of carbonic acid species as a function of pH for $C_T = 10^{-3.0}$ M showing that the maximum buffer capacity equals $0.58\ C_T$, and occurs at pH = $pK_1(H_2CO_3^o)$ = 6.35. The lower curve is the buffer capacity of water, β_{H_2O}.
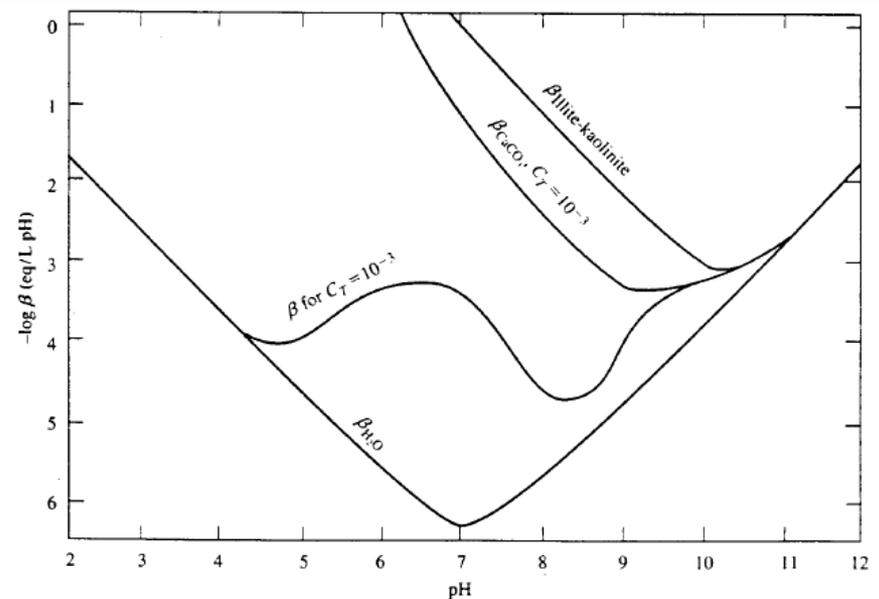
Figure 5.11 A log plot of the buffer capacity due to carbonic acid species for $C_T = 10^{-3.0}$ M (see Fig. 5.10); at saturation with respect to calcite for $C_T = 10^{-3.0}$ M; and for equilibrium between the clays illite and kaolinite. The lower curve is β_{H_2O}.

Buffer capacity of seawater

On short time scales, the pH of the ocean is buffered by the carbonic acid system and, to a lesser extent, by the boric acid-borate equilibrium.

On geological time scales, it has been proposed that the pH of the ocean is regulated by reactions involving suspended clay minerals, such as between kaolinite and K-mica:

$$1.5 \ Al_2Si_2O_5(OH)_4(s) + K^+ \longleftrightarrow KAl_3Si_3O_{10}(OH)_2 \ (s) + 1.5 \ H_2O + H^+$$

Assuming that we are dealing with pure phases, the equilibrium constant for this reaction is given by:

$$K^* = [H^+]/[K^+] \approx 10^{-6.4} \text{ in pure water} , 10^{-6.2} \text{ in seawater}$$

Since $[K^+]_{sw} = 0.01021$ mol/kg, the equilibrium $[H^+]_{sw} = 6.4 \times 10^{-9}$ (or pH = 8.19)

pH variations in the oceans

The pH in surface waters is mostly affected by CO_2 uptake by photosynthesizing organisms and solubility (f(T,S)) and may vary on the order of 0.5-0.7 pH units. At depth, in the vicinity of the O_2 minimum, pH is affected by the release of CO_2 through the degradation of organic matter sinking through the water column.

$$CO_2 + H_2O \xrightleftharpoons[\text{respiration}]{\text{photosynthesis}} \text{"CH}_2\text{O"} + O_2$$
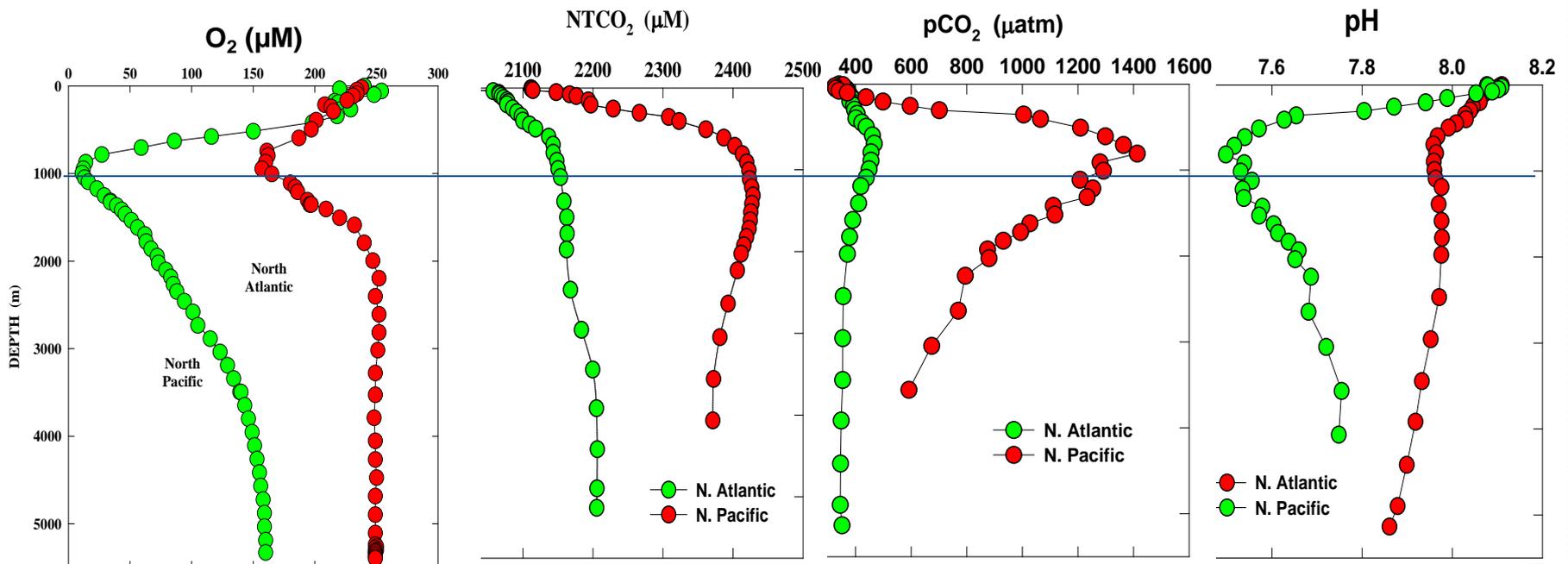
Recent measurements of pH$_t$ in the St-Lawrence Estuary
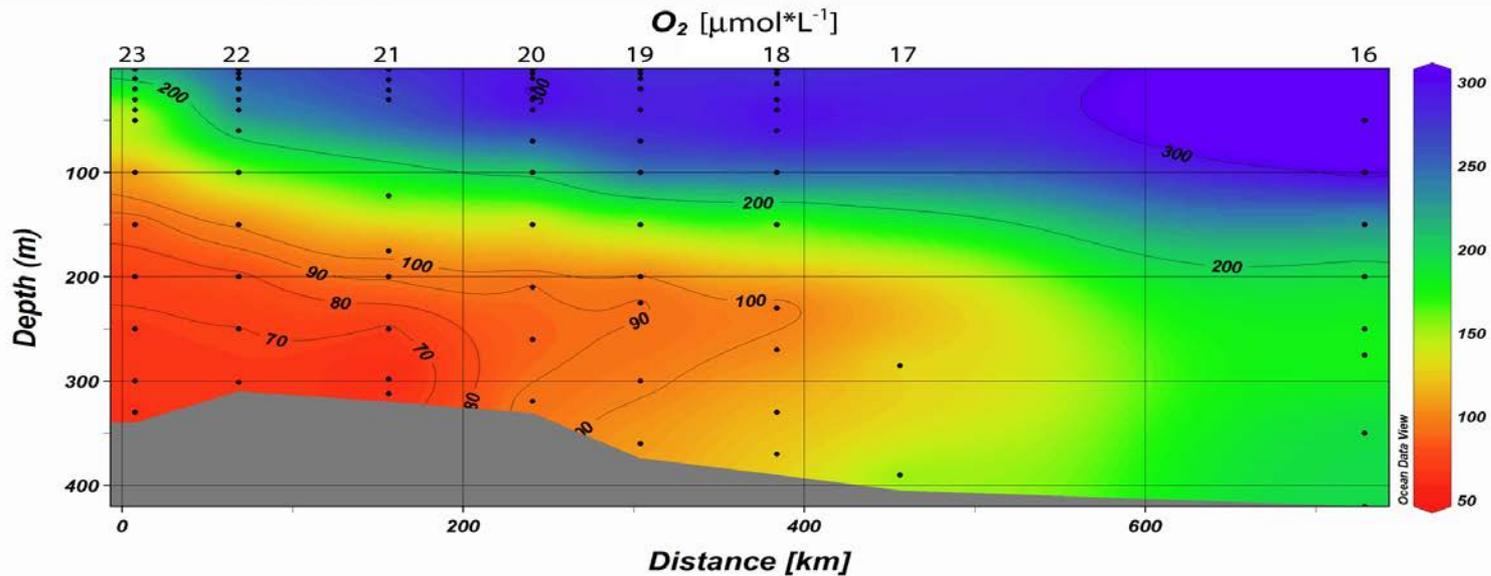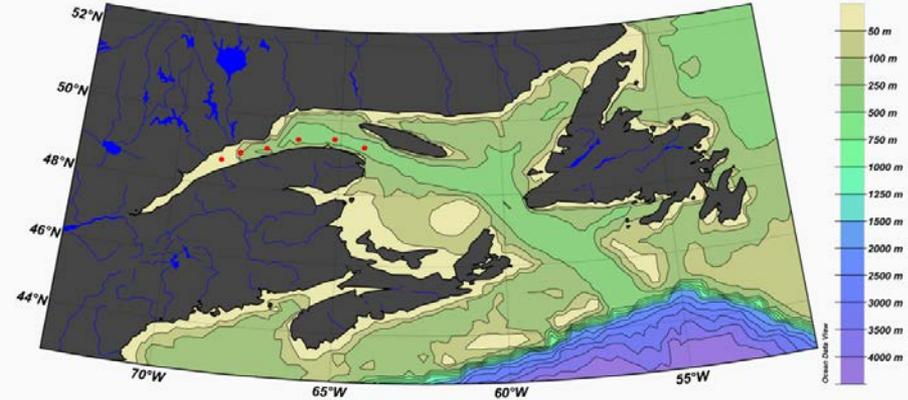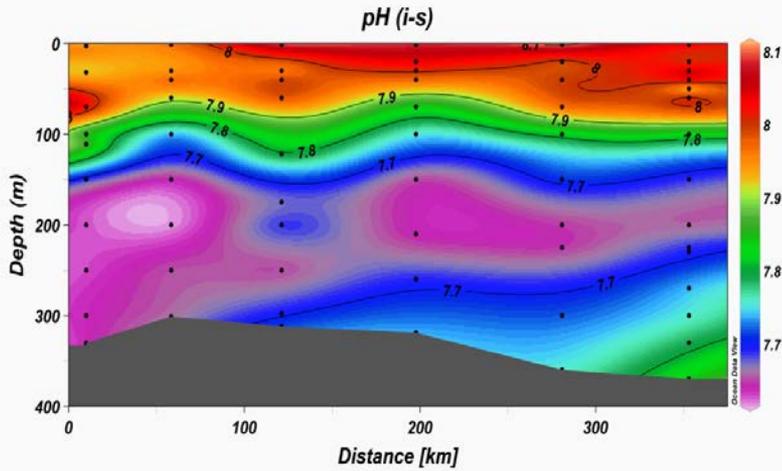
Carbonate Reactions

Carbon dioxide dissolved in water produces carbonic acid which, in turn, dissociates into bicarbonate and carbonate ions, releasing H^+ to the solution.

$$CO_{2(g)} \longleftrightarrow CO_{2(aq)} \qquad (1)$$
$$H_2O + CO_{2(aq)} \longleftrightarrow H_2CO_3 \quad (2) \quad slow$$
$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \quad (3) \quad fast$$
$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-} \quad (4) \quad fast$$
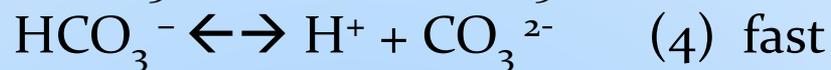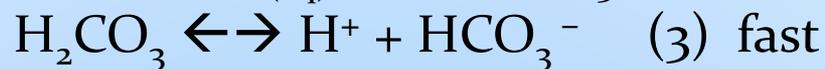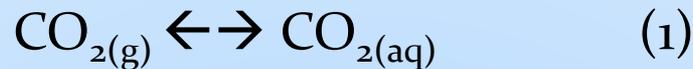
$$K_o^* = [H_2CO_3^*]/pCO_2$$

$$K_1^{'} = [HCO_3^-] \, a(H^+)/ [H_2CO_3^*]$$
$$or \ K_1^* = [HCO_3^-] \, [H^+]/ [H_2CO_3^*]$$

$$K_2^{'} = [CO_3^{2-}] \, a(H^+)/ [HCO_3^-]$$
$$or \ K_2^* = [CO_3^{2-}] \, [H^+]/ [HCO_3^-]$$

Characterization of the carbonate system

Measurable parameters:

- $pCO_2 = CO_2$ partial pressure in equilibrium with the solution.

- $pH = \log (H^+) \sim -\log [H^+]$

- ΣCO_2 or TCO_2 or $DIC = [H_2CO_3{*}] + [HCO_3^-] + [CO_3^{2-}]$
total dissolved inorganic carbon concentration

- $A_c = [HCO_3^-] + 2 [CO_3^{2-}] =$ carbonate alkalinity

The carbonate alkalinity is derived from the titration alkalinity.

For a simple CO_2-H_2O system: $A_t = [HCO_3^-] + 2 [CO_3^{2-}] + [OH^-] - [H^+]$

For a complex electrolyte solutions such as seawater:

$A_t = [HCO_3^-] + 2 [CO_3^{2-}] + [OH^-] + [B(OH)_4^-] + [H_3SiO_4^-] + [HS^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] - [H^+]$

A_t = equivalent sum of the bases that are titratable with a strong acid

pCO$_2$ shower-head equilibrator chamber
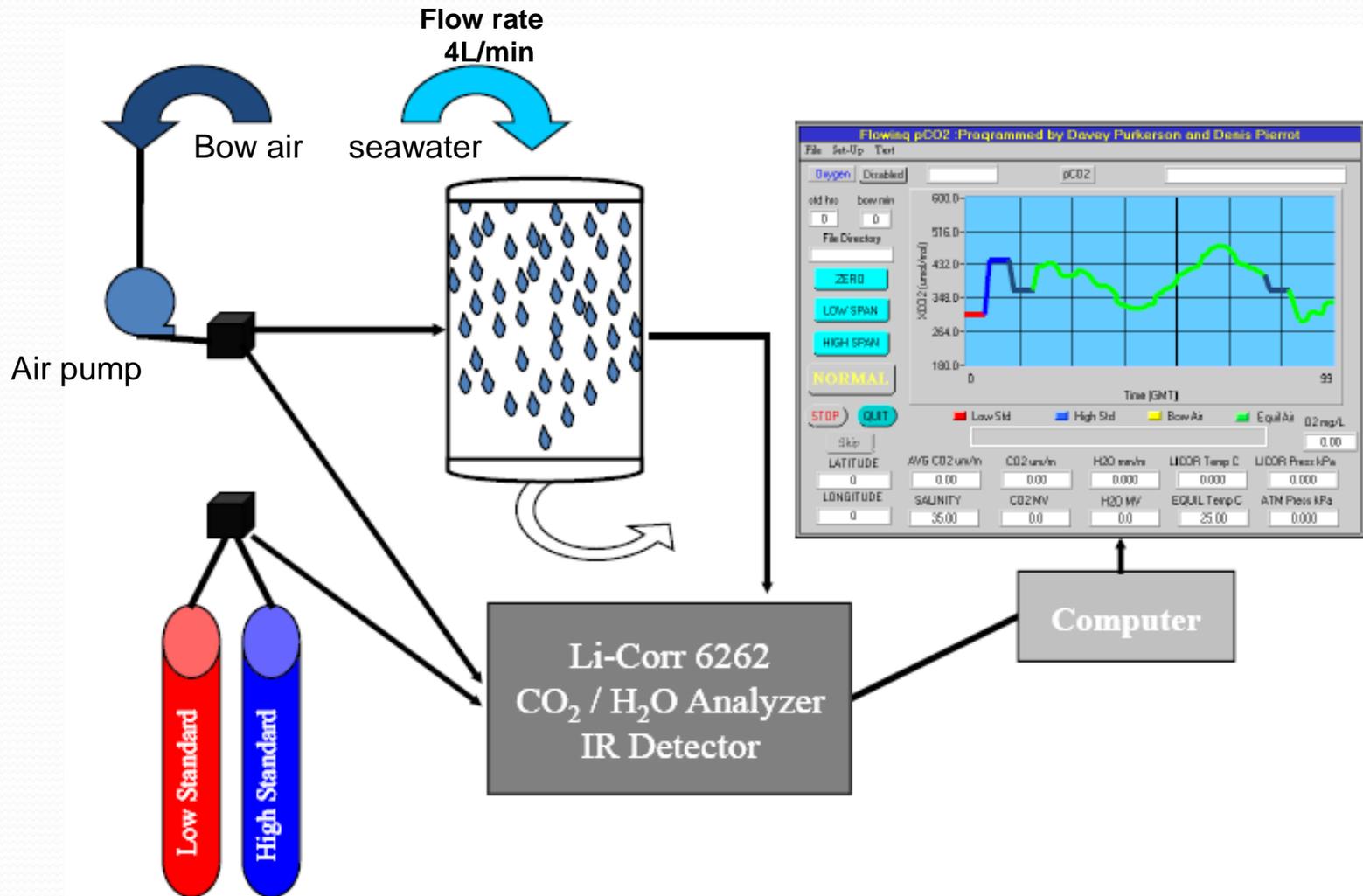
Semi-impermeable gas membrane with I.R. detection
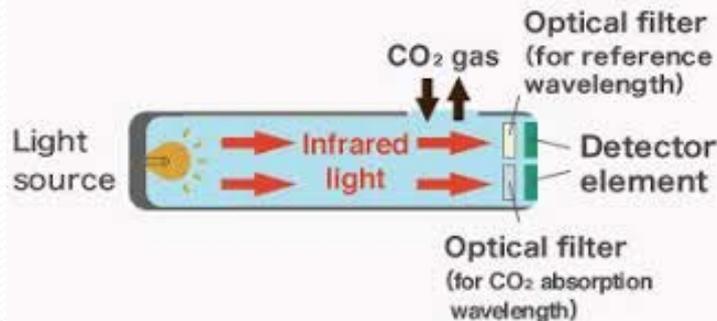
Potentiometric pH measurements
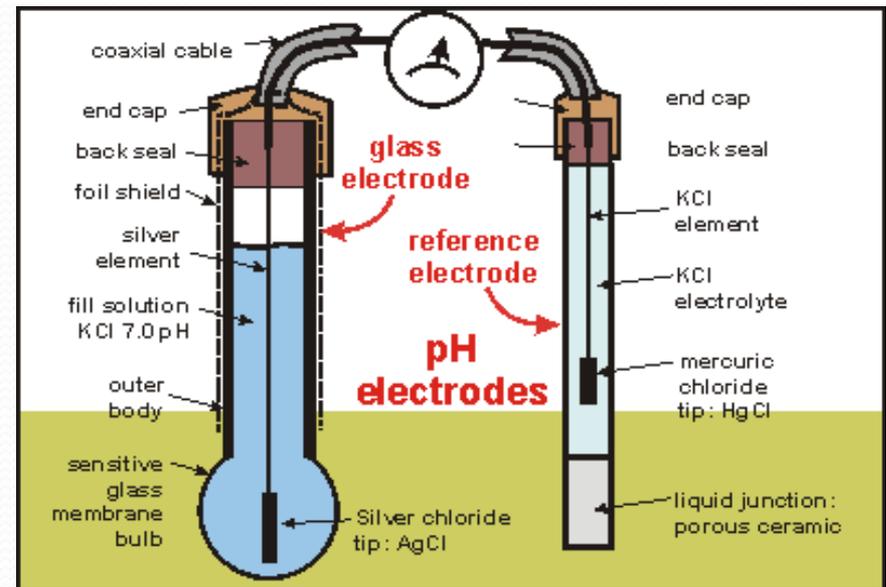
Spectrophotometric pH measurements
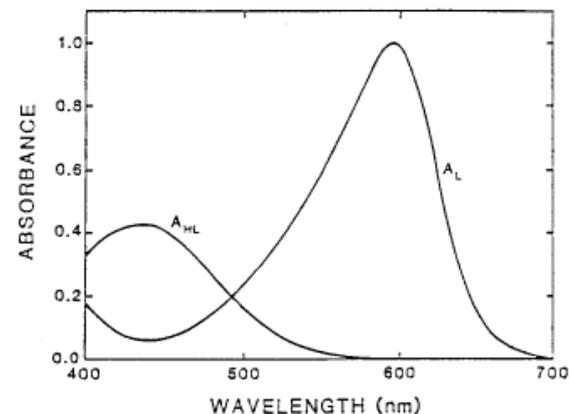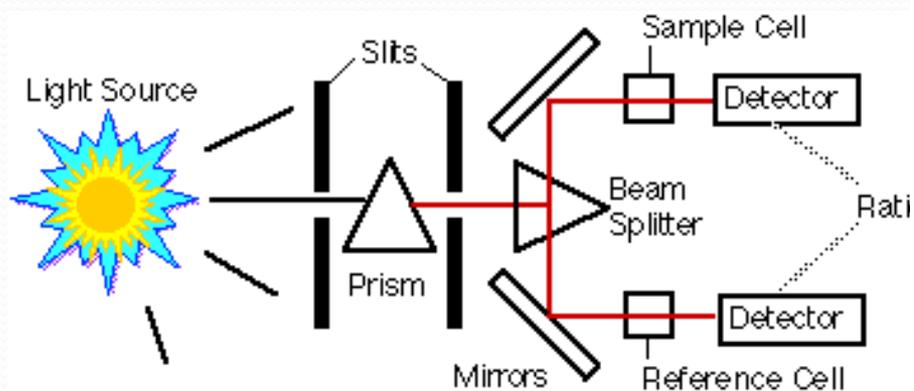
Figure 1. Relative molar absorbances of L^{2-} and HL^- are shown for the pH indicator thymol blue at 25.0 °C. A_L and A_{HL} were obtained at pH $\simeq 12$ and pH $\simeq 4$ at a constant total indicator concentration.
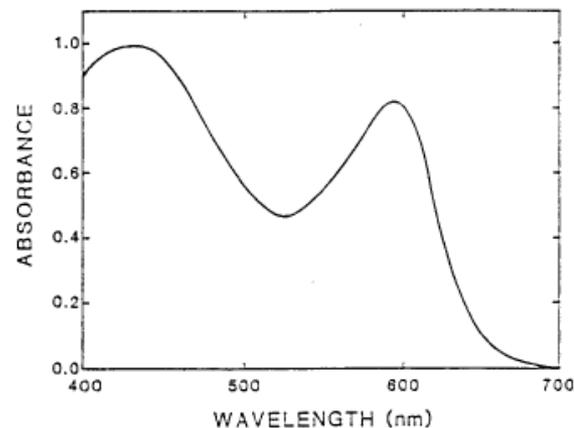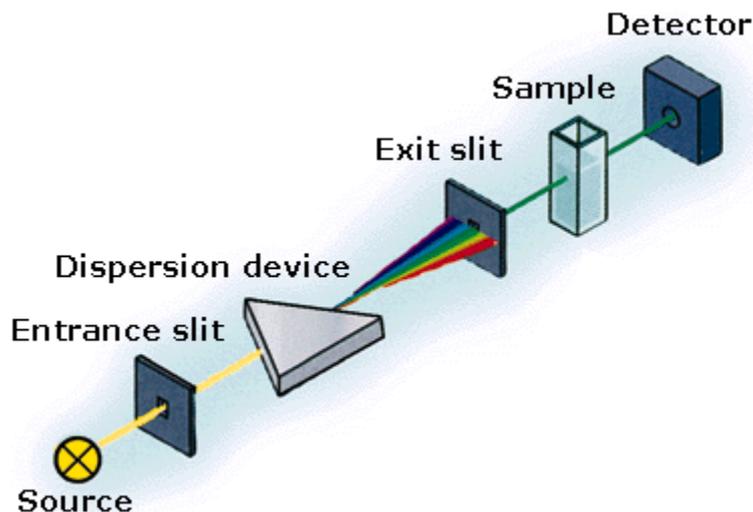
Figure 2. Absorbance of thymol blue is shown in Tris seawater buffer at pH 8.201 (35‰, 25 °C).

Coulometric determination of DIC (TCO$_2$, ΣCO$_2$)

Standard Electrolysis

$CO_2 + HO(CH_2)_2NH_2 \rightarrow O(CH_2)_2NHCOO^-$ (blue) $+ H^+$
At the cathode: $4\ H_2O + 4\acute{e} \rightarrow 2H_2(g) + 4OH^-$
At the anode: $4Ag^o + 4Cl^- \rightarrow 4AgCl + 4\acute{e}$
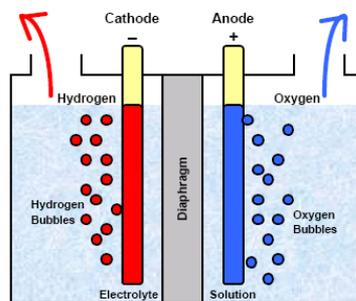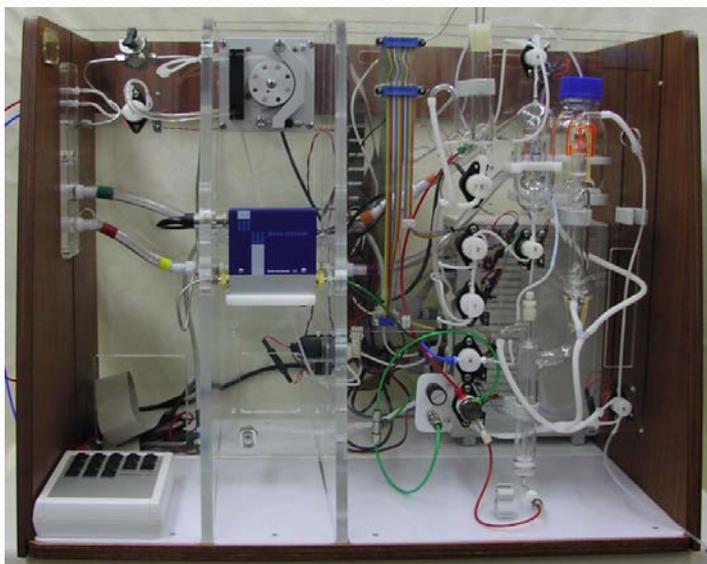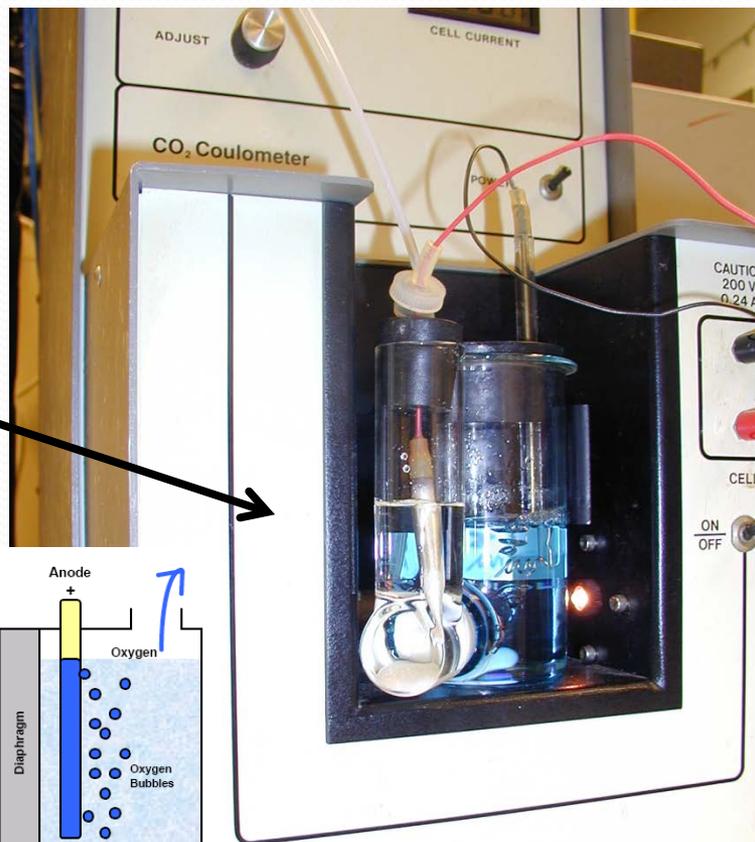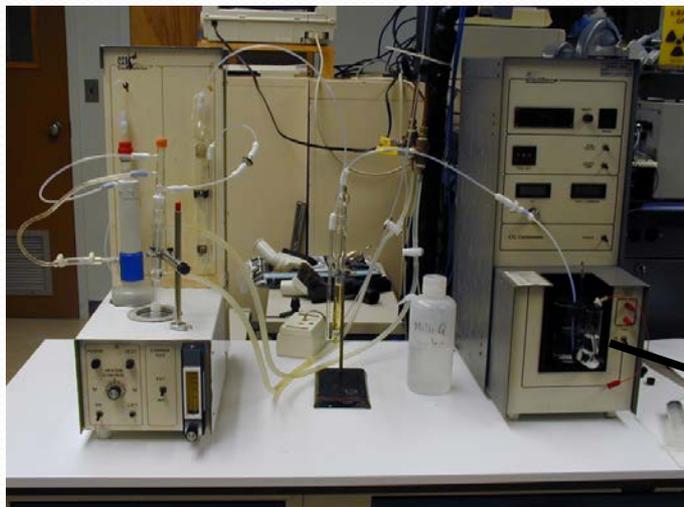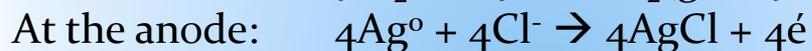
DIC infra-red analyzer

$$DIC + H_3PO_4 \rightarrow CO_2 \uparrow$$
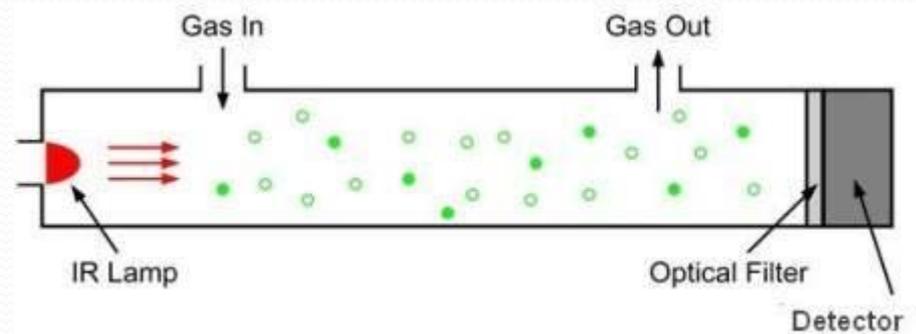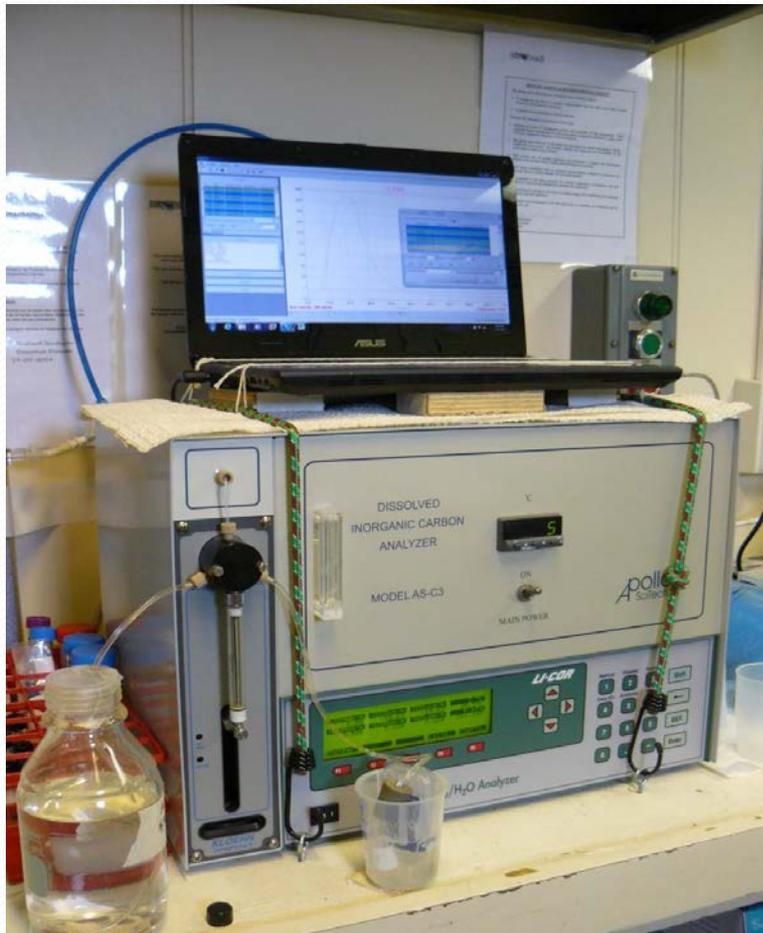
Potentiometric titrations of alkalinity

EMF

mL HCl

mL HCl
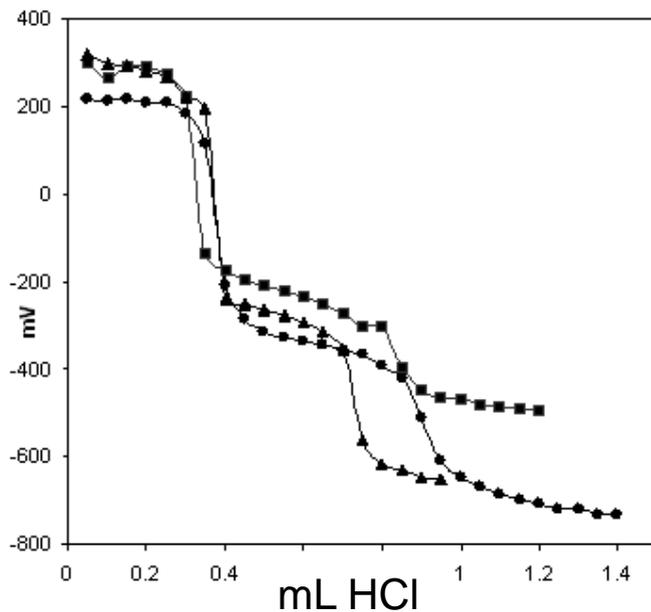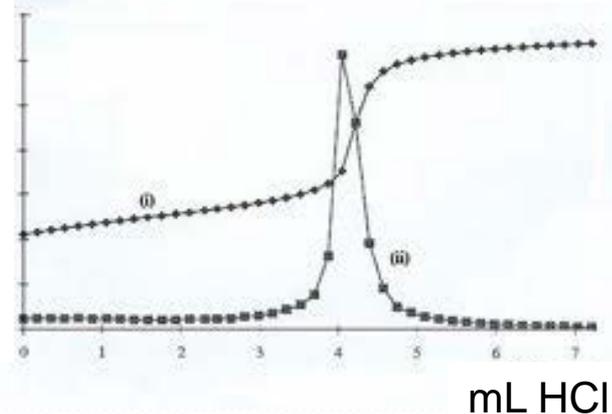
The concept of alkalinity

The concept of alkalinity is derived from the fundamental principle that solutions are electrically neutral (no net charge). In other words, the number of positive charges carried by cations is equal to the total number of charges carried by anions:

$$\Sigma[i]\ Z_i = 0$$

where [i] is the concentration of i and Z is the charge of the ith ion.

For the simple CO_2-H_2O system, the charge balance equation is:

$$[H^+] = [HCO_3^-] + 2\ [CO_3^{2-}] + [OH^-]$$

In a more complex aqueous system, such as seawater, the charge balance equation is extended to cover all dissolved ionic species:

$[Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + 2[Sr^{2+}] + \ldots + [H^+] =$
$[Cl^-] + 2[SO_4^{2-}] + [HCO_3^-] + 2\ [CO_3^{2-}] + [OH^-] + [B(OH)_4^-] + [H_3SiO_4^-] + [HS^-] +$
$[HPO_4^{2-}] + 2[PO_4^{3-}] + \Sigma[B_i]$

where $\Sigma[B_i]$ are all basic compounds (organic or inorganic) that can accept a proton.

The concept of alkalinity

Many of the ions that appear in the charge balance equation are "conservative" with respect to pH, their concentrations are not affected by changes in pH, pressure or temperature (as long as there is no precipitation or dissolution reactions). Separating these, we obtain:

Σ[conservative cations] – Σ[conservative anions] = $[HCO_3^-]$ + 2 $[CO_3^{2-}]$ + $[OH^-]$ + $[B(OH)_4^-]$ + $[H_3SiO_4^-]$ + $[HS^-]$ + $[HPO_4^{2-}]$ + 2$[PO_4^{3-}]$ + $\Sigma[B_i]$ – $[H^+]$ = A_t
= sum of all bases that are titratable with a strong acid to an equivalence point corresponding to the conversion of HCO_3^- to H_2CO_3.

Although the individual terms of the total alkalinity are not conservative with respect to pH, since their concentrations are dependent on pH and their respective dissociation constants (f(T,P,S)), the total alkalinity is a conservative quantity of the system.

In contrast, whereas ΣCO_2 is a conservative property in a closed system, it is not conservative in an open system to the atmosphere.

Seawater alkalinity

$A_t = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] + [B(OH)_4^-] + [H_3SiO_4^-] + [HS^-] + [HPO_4^{2-}] + 2[PO_4^{3-}]$
$\qquad + [OH-] + \Sigma[B_i] - [H^+]$

$\approx [HCO_3^-] + 2\,[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$

$\approx [HCO_3^-] + 2\,[CO_3^{2-}] + [B(OH)_4^-]$, in typical surface seawater

$\approx A_c + [B(OH)_4^-]$

$$B(OH)_3 + H_2O \longleftrightarrow B(OH)_4^- + H^+$$
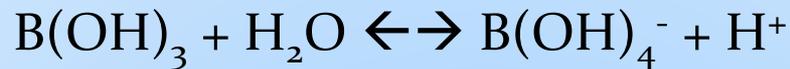
$$K_B^* = [H^+]\,[B(OH)_4^-]/[B(OH)_3] = f(T, P, S)$$

$$[B]_T = [B(OH)_3] + [B(OH)_4^-] = 1.174 \times 10^{-5} \text{ mole kg}^{-1} * S_p$$

$$[B(OH)_4^-] = K_B^*\,[B]_T/(K_B^* + [H^+])$$

$A_c = [HCO_3^-] + 2\,[CO_3^{2-}]\,(+ [OH^-] - [H^+]) \approx A_t - \{K_B^*\,[B]_T/(K_B^* + [H^+])\}$

Influence of pCO_2 on alkalinity? & how we determine the speciation of DIC in solution?

Distribution of CaCO$_3$-rich sediments
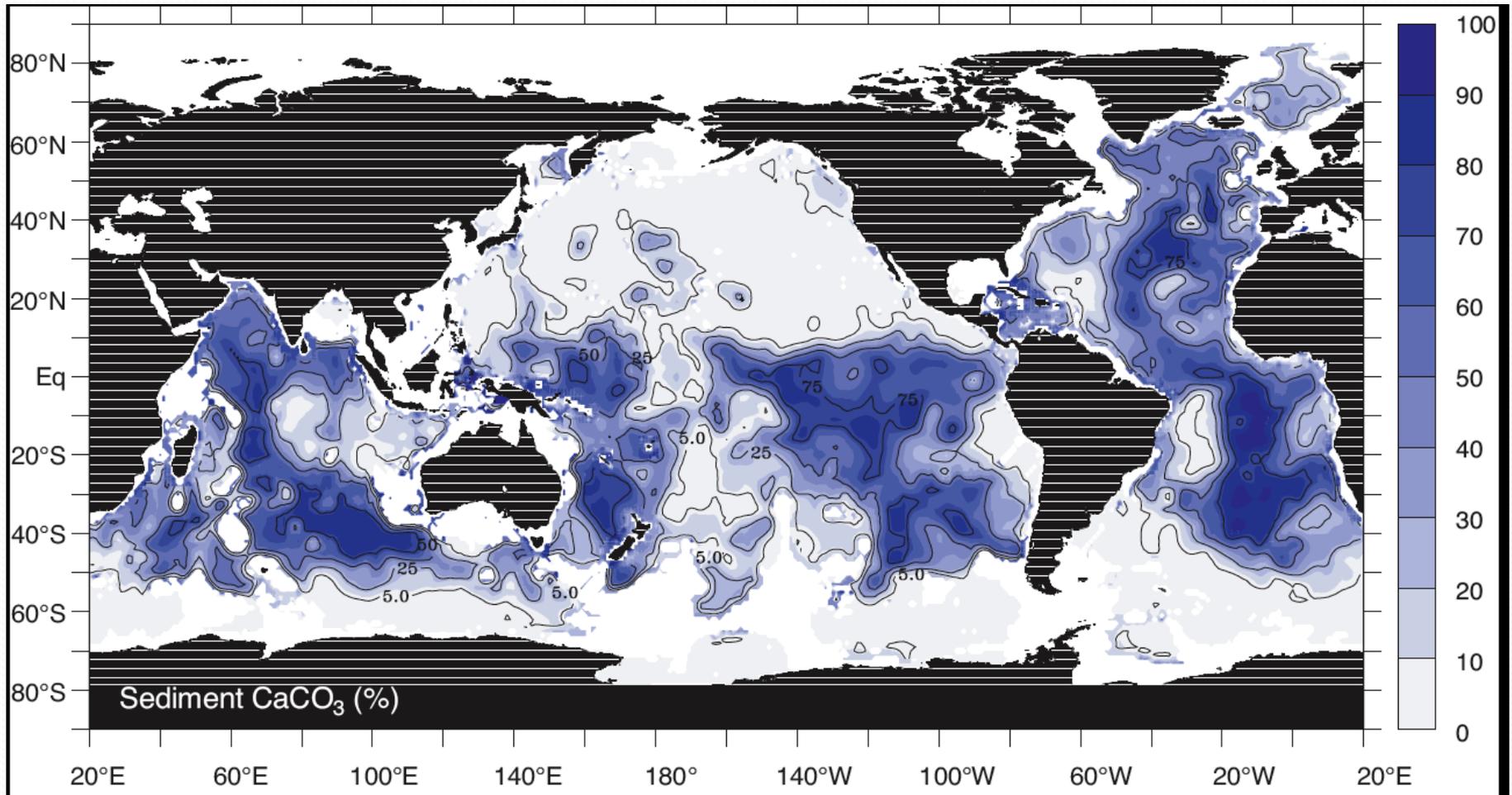
Sediment CaCO$_3$ (%)

Distribution of CaCO₃-rich sediments

>30% CaCO₃
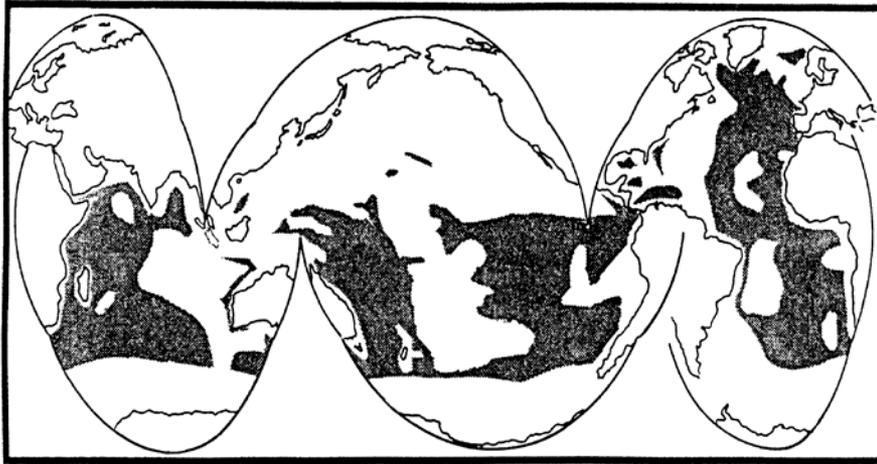
>70% CaCO₃
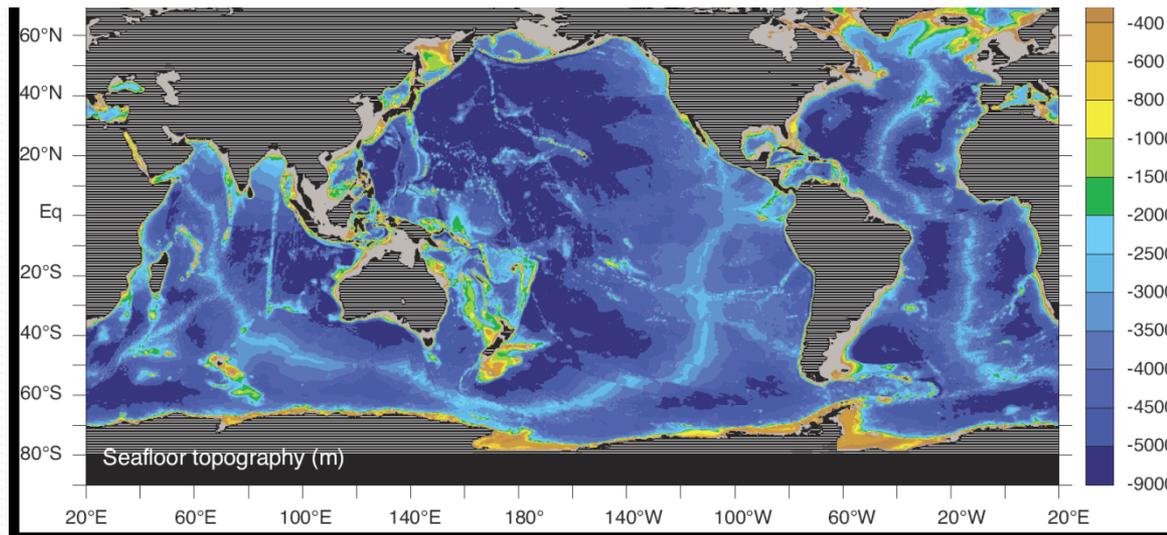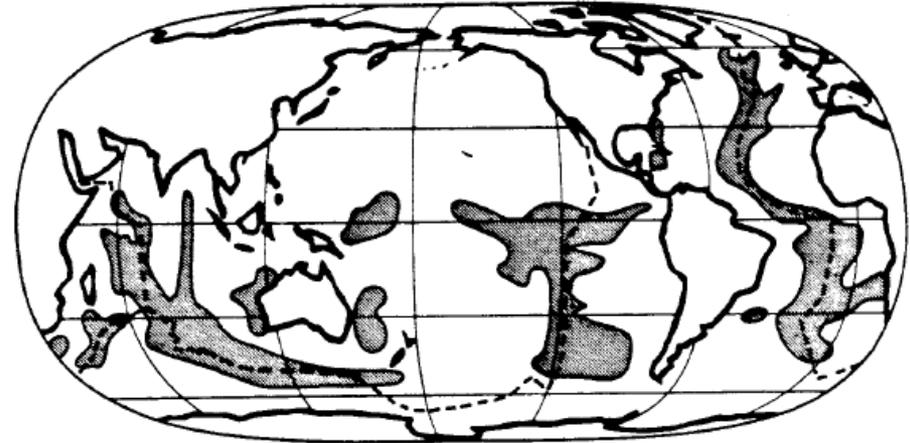
$CaCO_3$ in ocean sediments

The presence of $CaCO_3$ strongly buffers seawater pH and ultimately neutralizes the anthropogenic CO_2 absorbed by the oceans.

$$\beta = 2.303 \; (4[Ca^{2+}] + [HCO_3^-] + 4[CO_3^{2-}] + [H^+] + [OH^-])$$

$$H_2O + CO_2 \longleftrightarrow H_2CO_3$$
$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$
$$\underline{H^+ + CaCO_3 \longleftrightarrow Ca^{2+} + HCO_3^-}$$
$$H_2O + CO_2 + CaCO_3 \longleftrightarrow Ca^{2+} + 2HCO_3^-$$
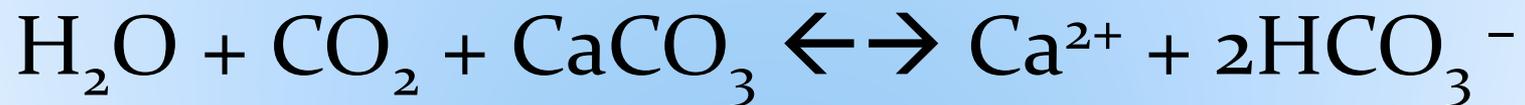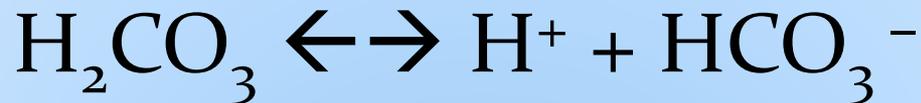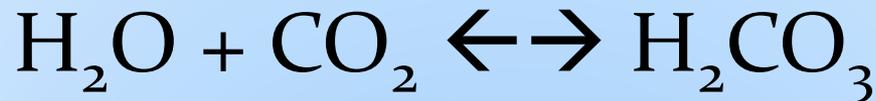
Calcite Microfossils
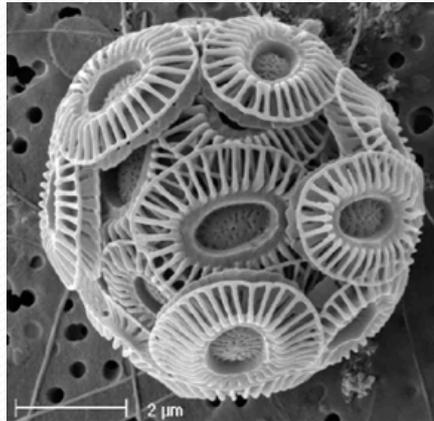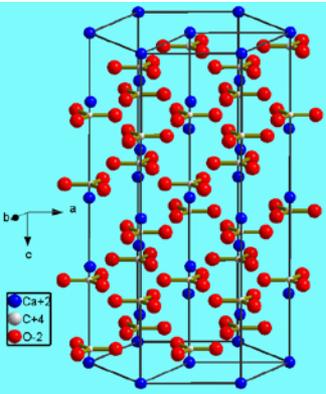
Coccolithophores
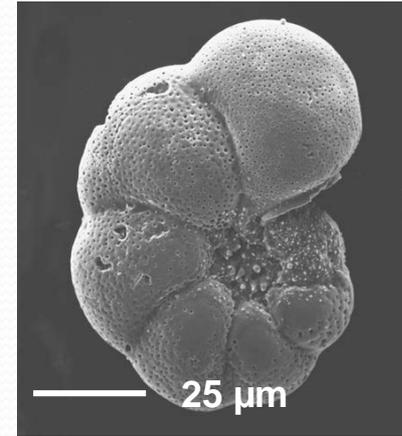
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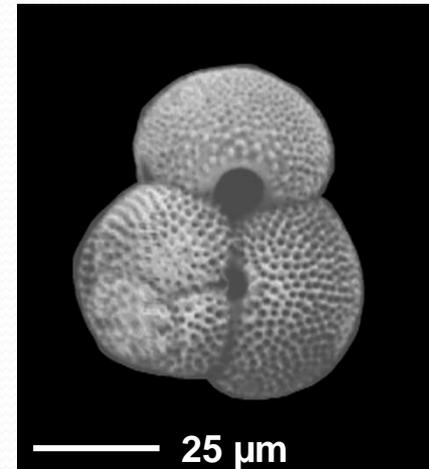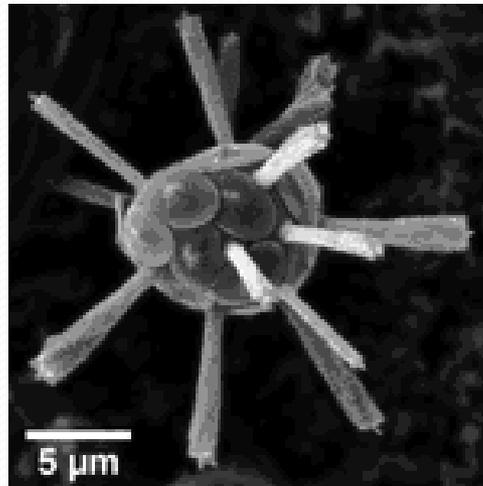
Pteropods

20/76

Coccolith blooms

SeaWiFS satellite image,
near Newfoundland, Canada

Landsat satellite image, south
of Cornwall (UK)

Acc.V Spot Magn Det WD   2 µm
5.00 kV 3.0 6500x SE 10.0   JRY 218
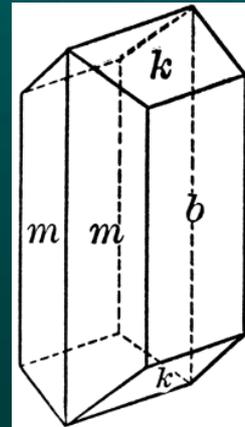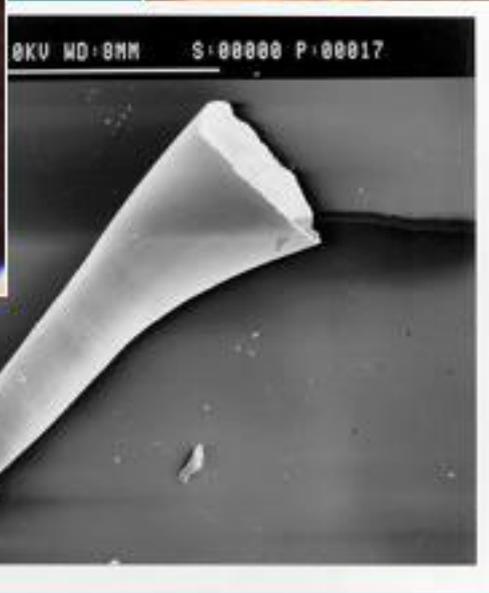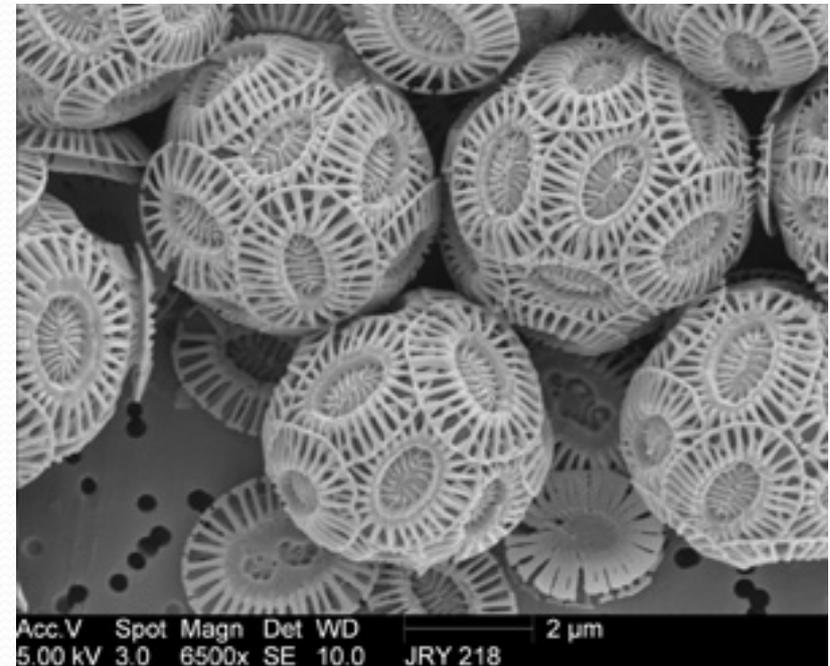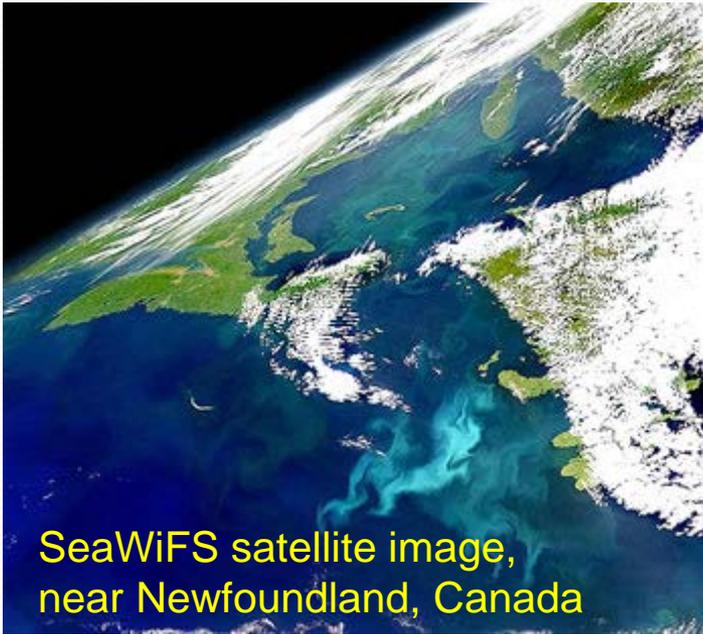
Emiliani huxleyi

CaCO$_3$ production and export

CaCO$_3$ export (mol m^{-2} y^{-1})
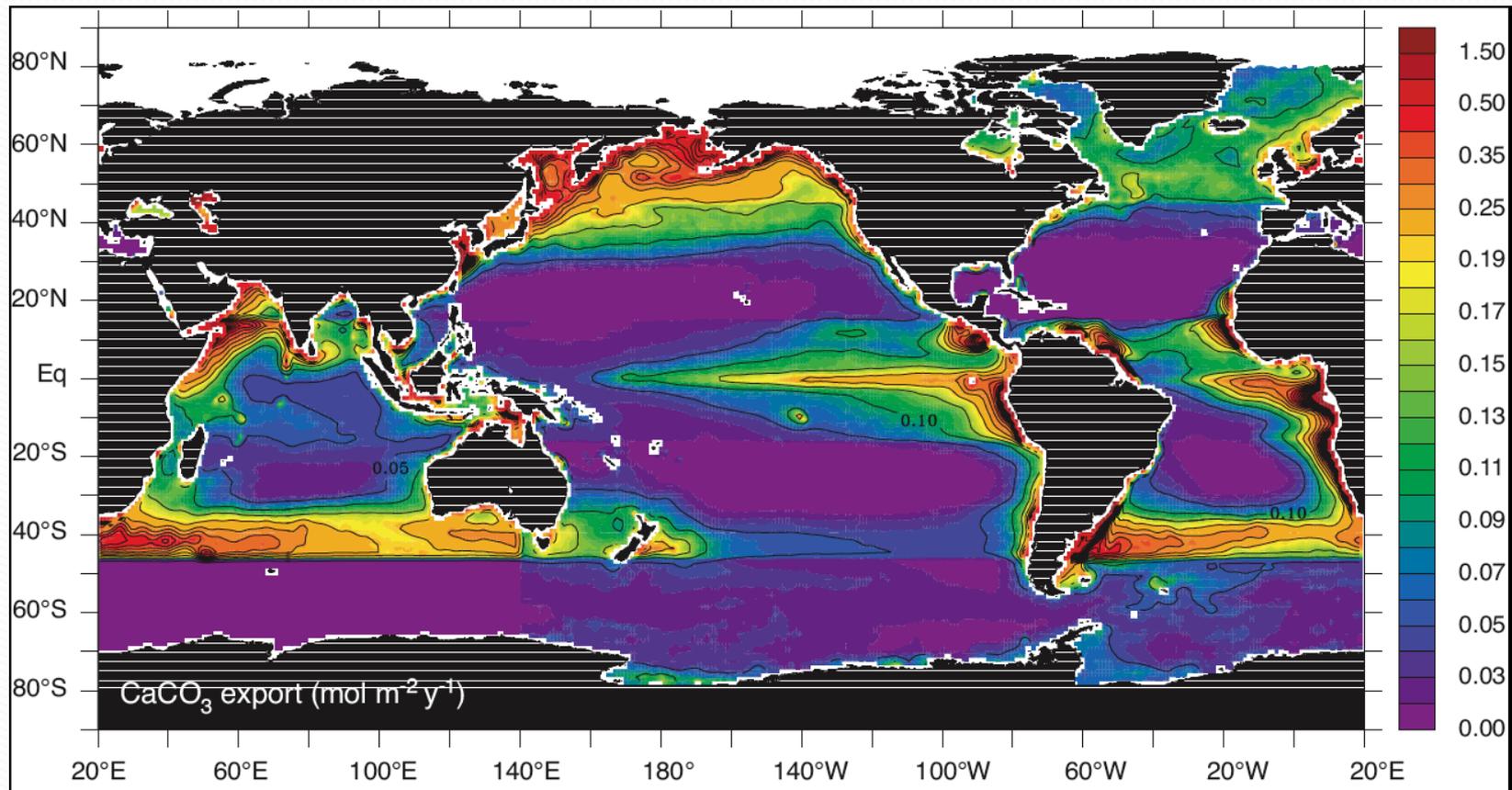
Saturation state of the oceanic water column
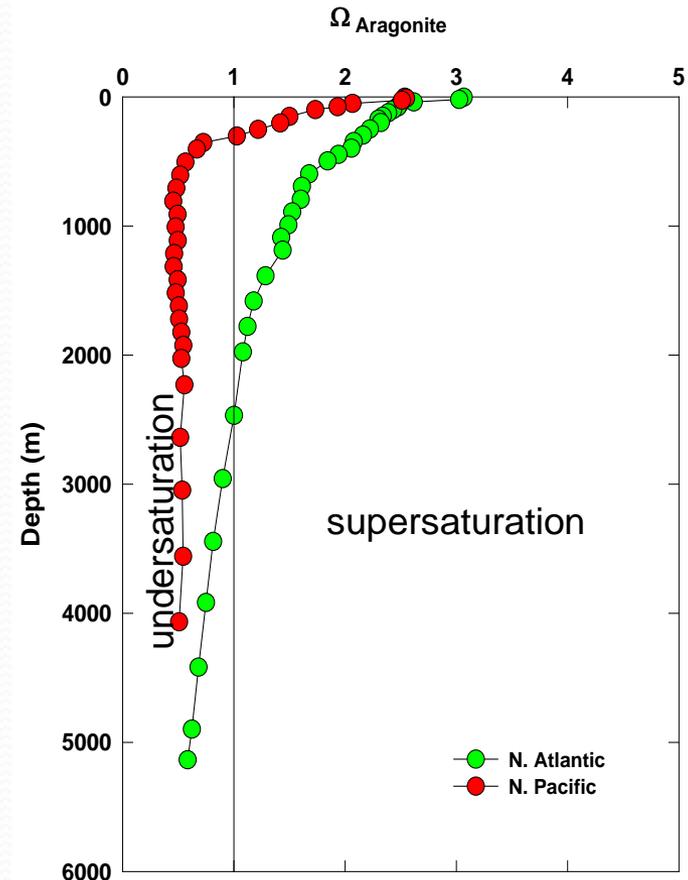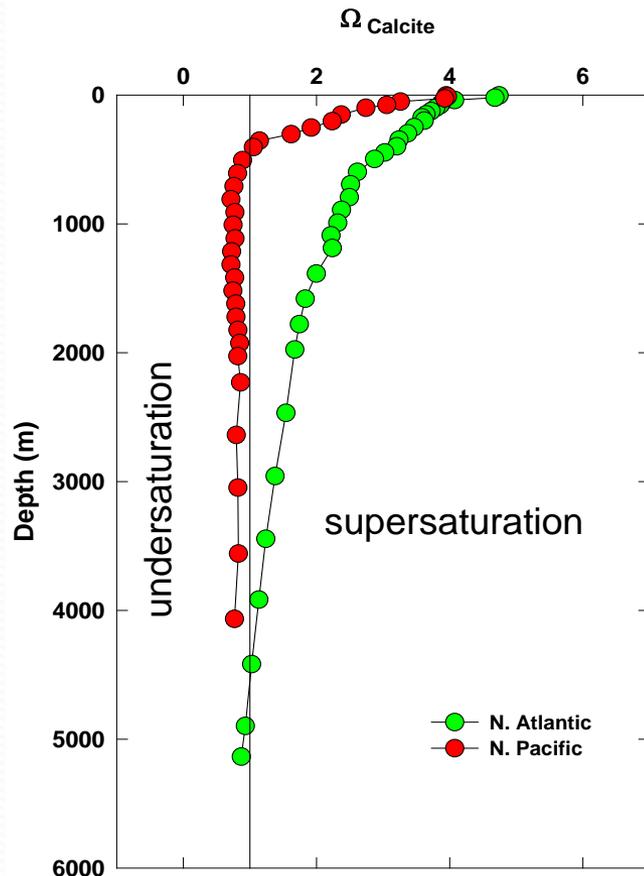
It is estimated that 75-95% of all the $CaCO_3$ produced in the oceans is dissolved in the water column or near the sediment-water interface.

Solubility and saturation state of $CaCO_3$

The reaction describing the solubility of calcium carbonate is:

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

the equilibrium constant for this reaction, or the solubility constant is given by:

$$K° = \frac{(Ca^{2+})(CO_3^{2-})}{(CaCO_3)} = \frac{(Ca^{2+})(CO_3^{2-})}{1}$$

$K°_C = 10^{-8.48}$ @ 25°C, 1 atm
$K°_A = 10^{-8.31}$ @ 25°C, 1 atm

$$K° = [Ca^{2+}][CO_3^{2-}]\, \gamma(Ca^{2+})\, \gamma(CO_3^{2-}) = K^* \, \gamma(Ca^{2+})\, \gamma(CO_3^{2-})$$

$K^*_C = 4.4 \times 10^{-7}$ mol^2 kg^{-2} @ 25°C, 1 atm and $S_p = 35$
$K^*_A = 6.6 \times 10^{-7}$ mol^2 kg^{-2} @ 25°C, 1 atm and $S_p = 35$

Saturation state of a solution with respect to calcite or aragonite is defined as:

$$\Omega_{C\ or\ A} = \frac{(Ca^{2+})(CO_3^{2-})}{K°_{C\ or\ A}} = \frac{[Ca^{2+}][CO_3^{2-}]}{K^*_{C\ or\ A}}$$

$\Omega > 1$, the solution is supersaturated
$\Omega = 1$, the solution is at equilibrium
$\Omega < 1$, the solution is undersaturated

Calcite and aragonite stoichiometric solubility

TABLE 3

The average of measured stoichiometric solubility constants of calcite in seawater at various salinities and temperatures, in mole^2 kg^{-2} SW $\times$ 10^7

S‰	5°C	25°C	40°C
44.00	—	5.55 ± 0.50(16)*	—
35.00	4.41 ± 0.20(32)	4.39 ± 0.20(32)	4.11 ± 0.29(16)
25.00	2.90 ± 0.14(16)	2.76 ± 0.13(16)	—
15.00	1.64 ± 0.10(16)	1.52 ± 0.02(16)	—
5.00	0.540 ± 0.017(16)	0.489 ± 0.013(16)	—

* Values in parentheses represent the number of independent measurements from which the average and standard deviation were calculated.

TABLE 4

The average of measured stoichiometric solubility constants of aragonite in seawater at various salinities and temperatures, in mole^2 kg^{-2} SW $\times$ 10^7

S‰	5°C	25°C	40°C
44.00	—	8.48 ± 0.22(16)*	—
35.00	6.82 ± 0.18(29)	6.65 ± 0.12(28)	5.90 ± 0.20(16)
25.00	4.74 ± 0.20(16)	4.41 ± 0.15(16)	—
15.00	2.94 ± 0.09(16)	2.43 ± 0.09(16)	—
5.00	0.987 ± 0.029(12)	0.861 ± 0.025(13)	—

* Values in parentheses represent the number of independent measurements from which the average and standard deviation were calculated.

Dissolved Ca²⁺ in the Pacific

NORMALIZED CALCIUM (mM)
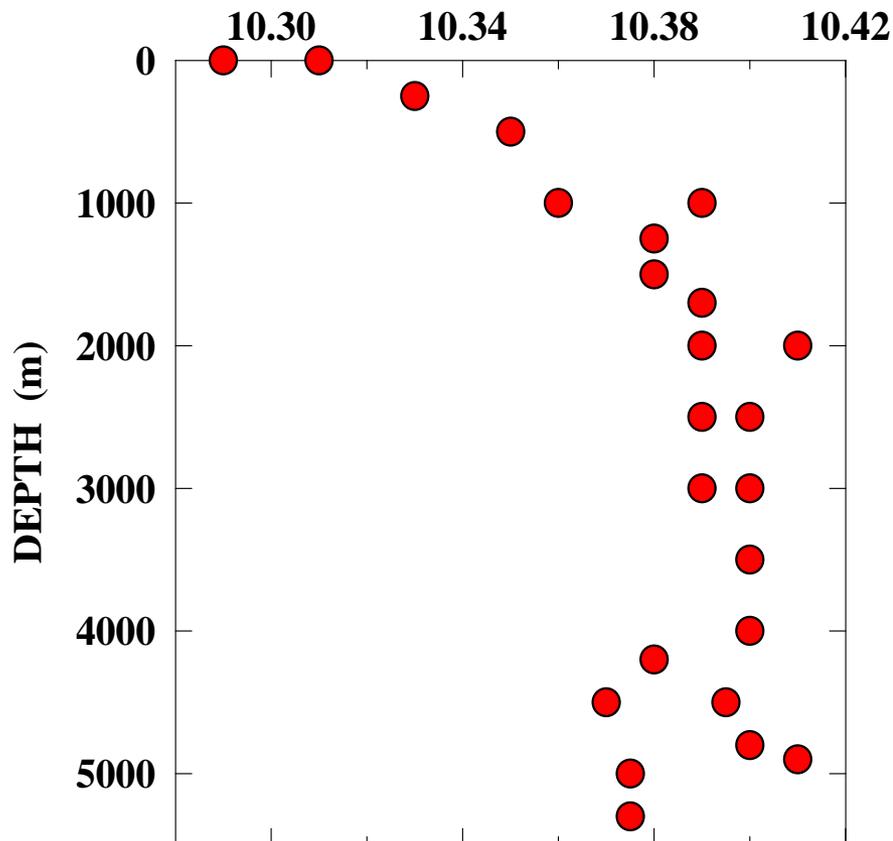
$$\Omega_{C\,or\,A} = \frac{[Ca^{2+}]\,[CO_3^{2-}]}{K^*_{C\,or\,A}}$$

Since $[Ca^{2+}]$ is more or less conservative in the ocean, its concentration at any depth in the water column is determined by the salinity and since salinity does not vary considerably below a few hundred meters, $[Ca^{2+}]$ varies only slightly. Hence, the saturation state depends mostly on variations of $[CO_3^{2-}]$ and K^*s_p.

Impact of pH

The pH in surface waters is mostly affected by CO_2 uptake by photosynthesizing organisms and may vary on the order of 0.5-0.7 pH units. At depth, in the vicinity of the O_2 minimum, pH is affected by the release of CO_2 through the degradation of organic matter sinking through the water column.

$$CO_2 + H_2O \underset{\text{respiration}}{\overset{\text{photosynthesis}}{\rightleftharpoons}} \text{``}CH_2O\text{''} + O_2$$
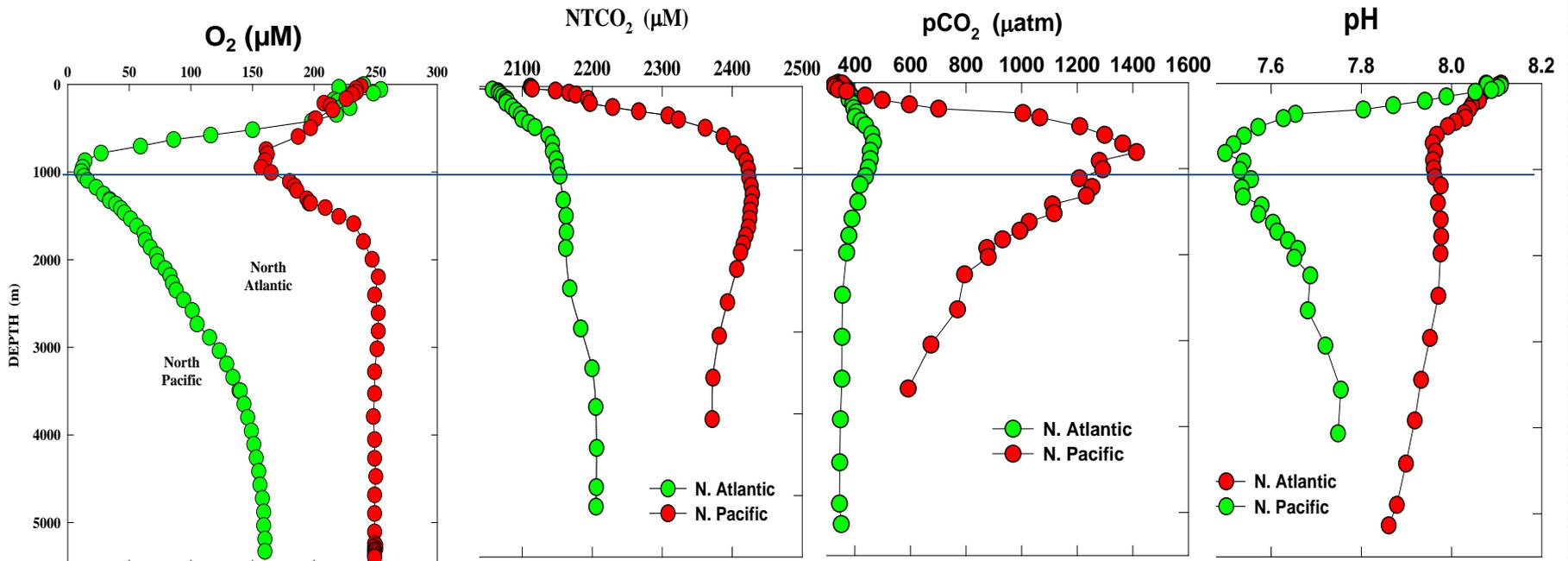
Accumulation of metabolic CO_2 along the conveyor belt

TCO$_2$ (μM/kg)
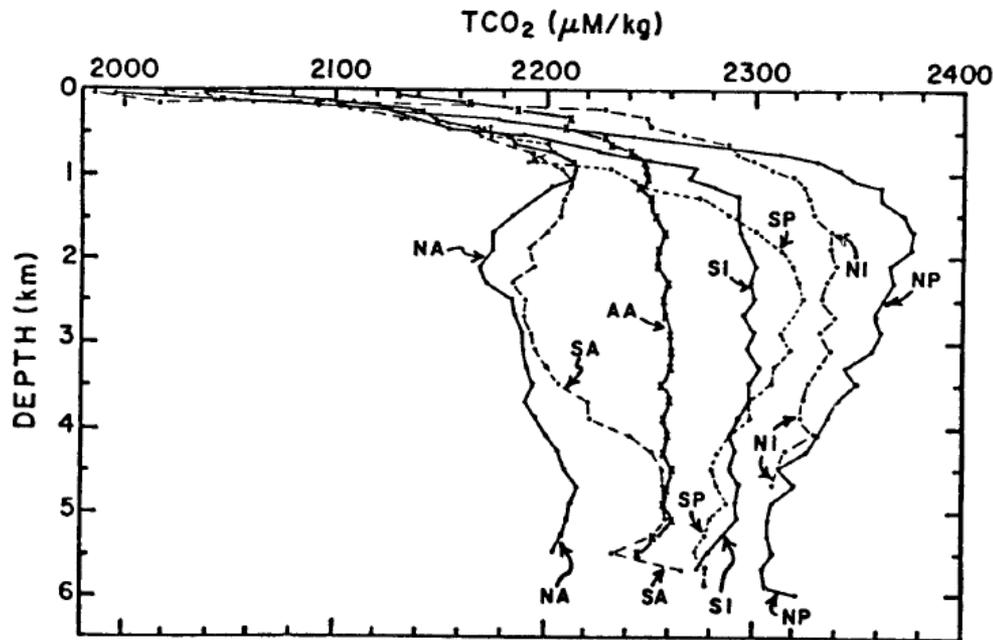
Fig. 2. Average oceanic concentrations of dissolved inorganic carbon, calculated from the GEOSECS data [from Takahashi et al., 1981]. Data are averages for the following ocean regions: NA, North Atlantic; SA, South Atlantic; AA, Antarctic region south of latitude 45°S; SI, South Indian; NI, North Indian; SP, South Pacific; and NP, North Pacific.

$$\text{``CH}_2\text{O''} + O_2 \rightarrow CO_2 + H_2O$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$
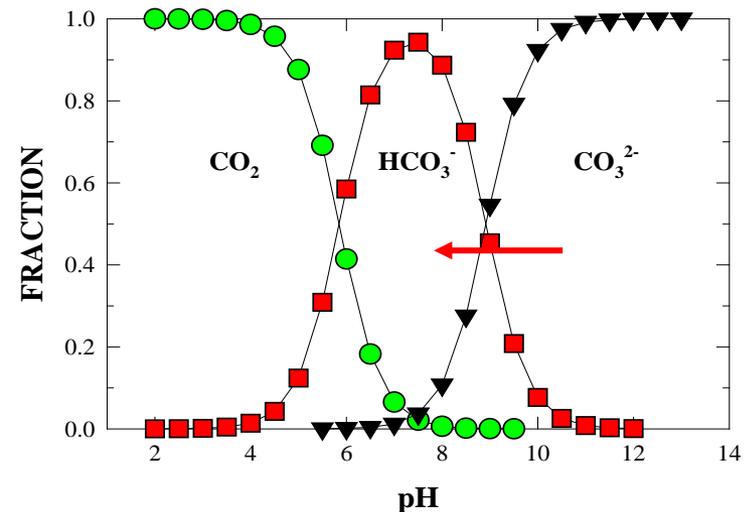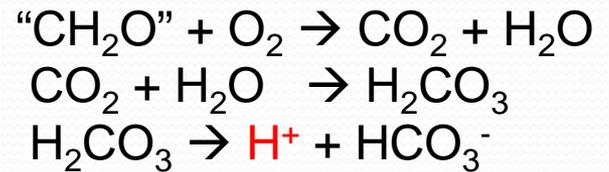
Effect of pressure on the solubility of $CaCO_3$

Variations of the solubility of calcite and aragonite as a function of pressure (depth) can be calculated according to:

$$\ln\left[\frac{K^P_{(C\ or\ A)}}{K^o_{(C\ or\ A)}}\right] = -\left[\frac{\Delta V_{(C\ or\ A)}}{RT}\right](P\text{-}1) + \left[\frac{0.5\ \Delta K_{(C\ or\ A)}}{RT}\right](P\text{-}1)^2$$

where
- P is the absolute pressure (in atmosphere or bar)
- ΔV and ΔK are, respectively, the change in volume and compressibility following the ionization of the solid
- R is the gas constant (83.15 cm^{-3} bar K^{-1} $mole^{-1}$ or 82.06 cm^{-3} atm K^{-1} mol^{-1})
- T is the absolute temperature (K)

$$\Delta V = \Sigma \overline{V}_i\ (products) - \Sigma \overline{V}_i\ (reactants) = \overline{V}Ca^{2+} + \overline{V}CO_3^{2-} - \overline{V}CaCO_3(s)$$

$$\Delta K = \Sigma \overline{K}_i\ (products) - \Sigma \overline{K}_i\ (reactants) = \overline{K}Ca^{2+} + \overline{K}CO_3^{2-} - \overline{K}CaCO_3(s)$$

ΔV_C = -16.00 + 13.18 -36.93 = -39.75 cm^3 $mole^{-1}$ at S_p =35, t = 25°C

ΔV_A = -37.02 cm^3 $mole^{-1}$

$\Delta K_C = \Delta K_A$ = -10.59 x 10^{-3} cm^3 bar^{-1} $mole^{-1}$

ex: at 5000 m, K_C^P/K_C^o = 2.55

CaCO$_3$ production and export

CaCO$_3$ export (mol m^{-2} y^{-1})
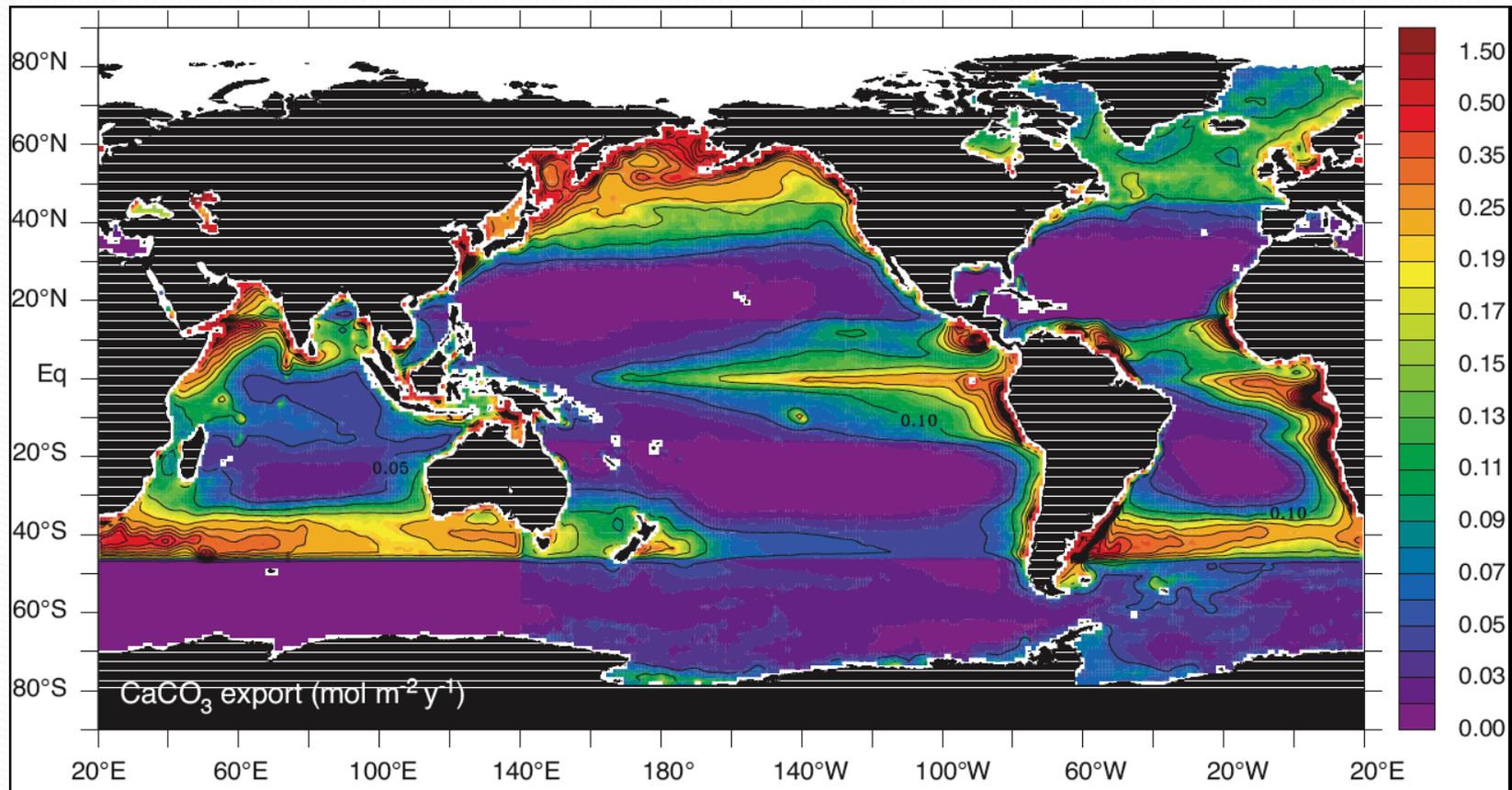
Dilution by terrigenous sedimentation

Sediment-laden water discharges into the northern Gulf of Mexico from the Mississippi and Atchafalaya Rivers. MODIS Aqua NASA satellite image (April 7, 2009)

Saturation state of the oceanic water column
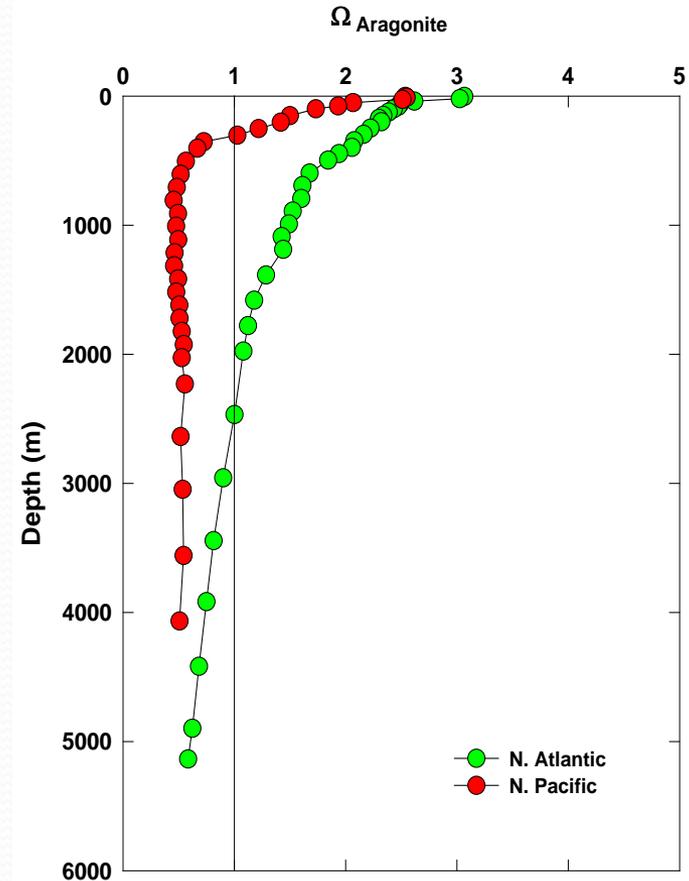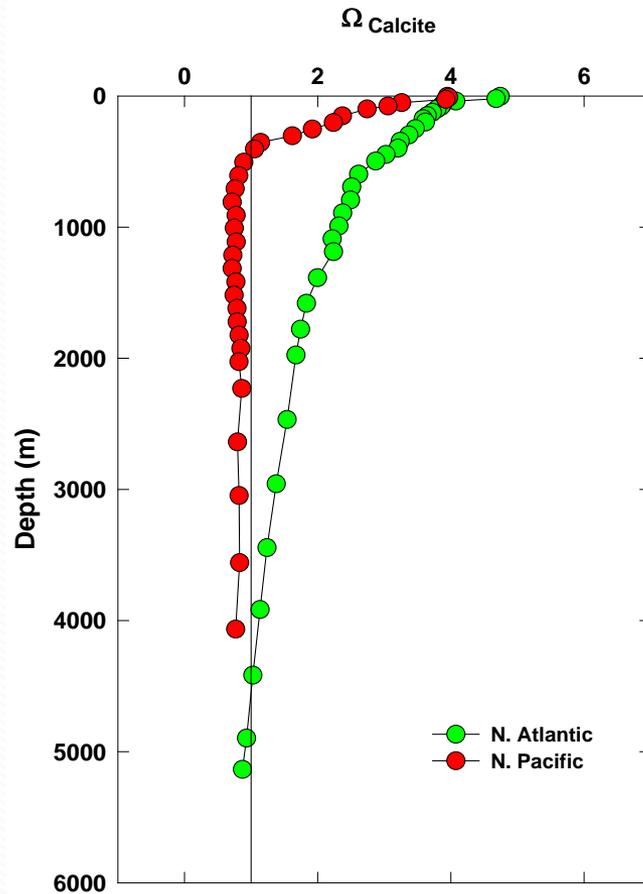
Accumulation of metabolic CO_2 along the thermohaline conveyor belt
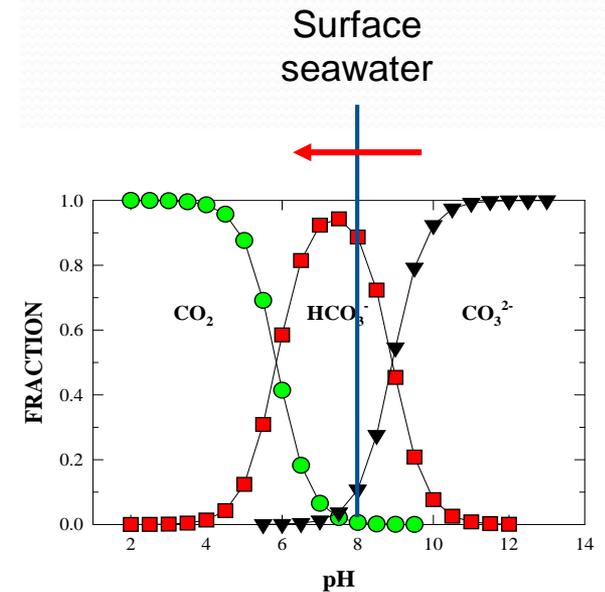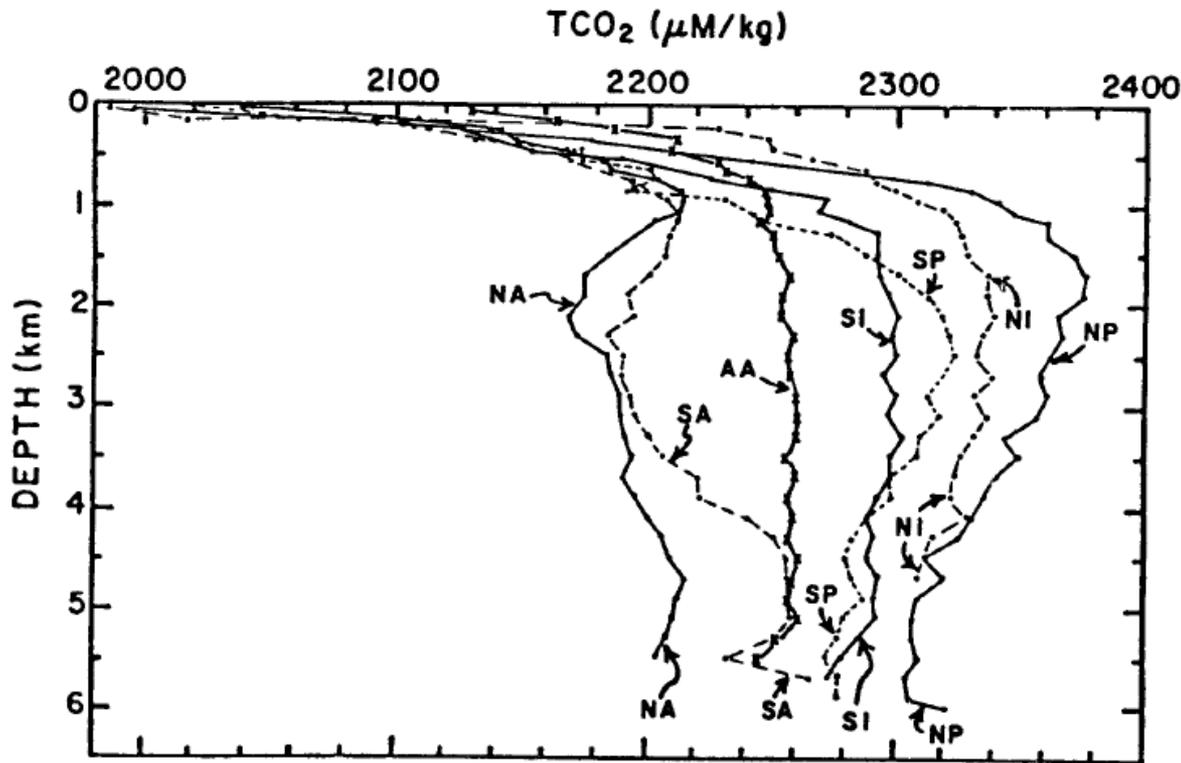
At the pH of seawater, $TCO_2 = DIC \approx [HCO_3^-] + [CO_3^{2-}]$
$A_c = [HCO_3^-] + 2[CO_3^{2-}]$
$[CO_3^{2-}] \approx A_c - TCO_2$

Distribution of CaCO$_3$-rich sediments

Since the tests of calcareous organisms falling from the surface ocean dissolve as they settle through the undersaturated portion of the water column, carbonate saturation and depth exert an important influence on the pattern of carbonate sedimentation in the oceans. If the ocean system behaved ideally, …

>30% CaCO$_3$
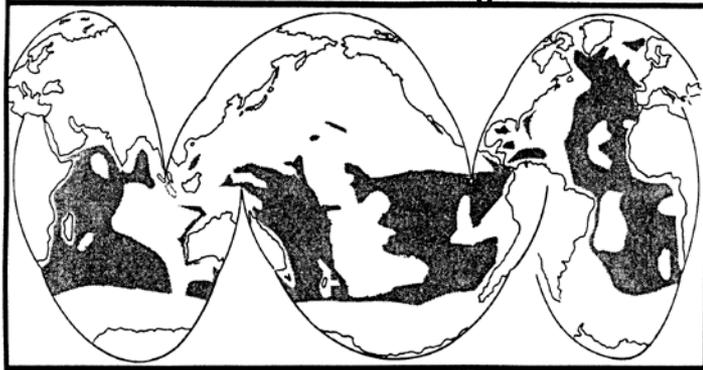
>70% CaCO$_3$

Sediment marker horizons
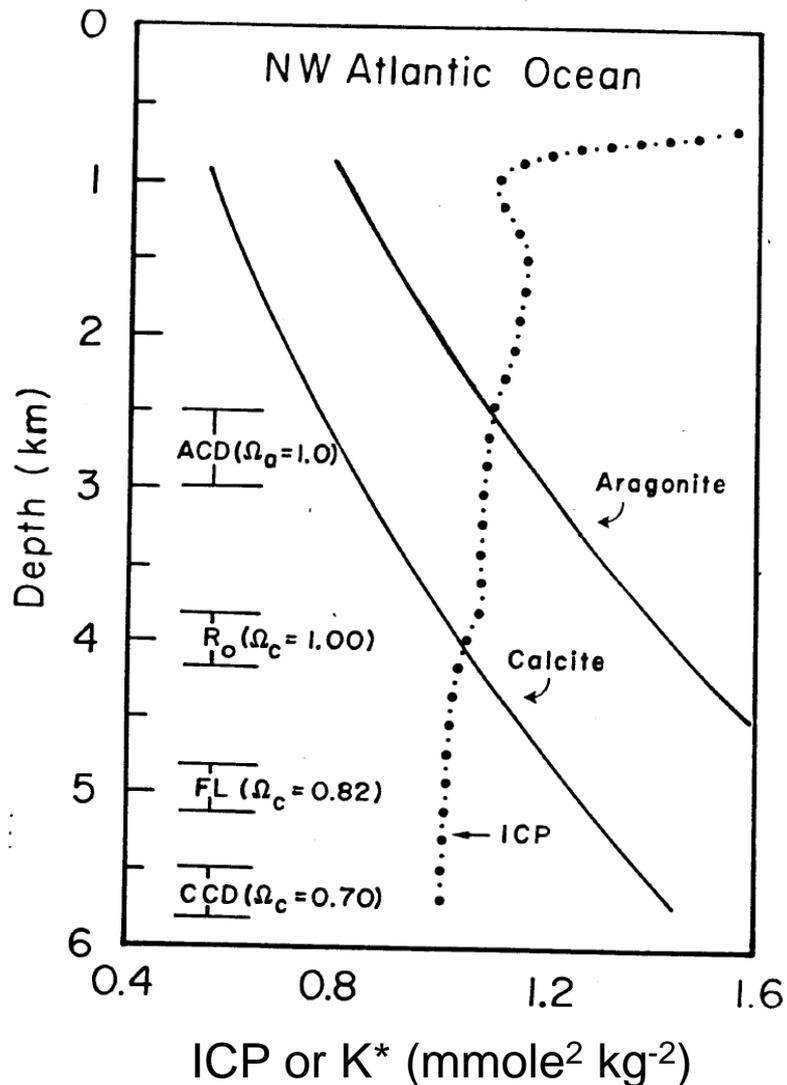
NW Atlantic Ocean

ACD – aragonite compensation depth
Depth below which little (<10%) or no aragonite accumulates in the sediment.

Ro – calcite saturation level
Depth at which the water column is in equilibrium (saturated) with respect to calcite.

FL – foraminiferal lysocline
Depth at which the calcite dissolution rate increases significantly.

CCD – calcite compensation depth
Depth below which little (<10%) or no calcite accumulates in the sediment.

The aragonite compensation depth
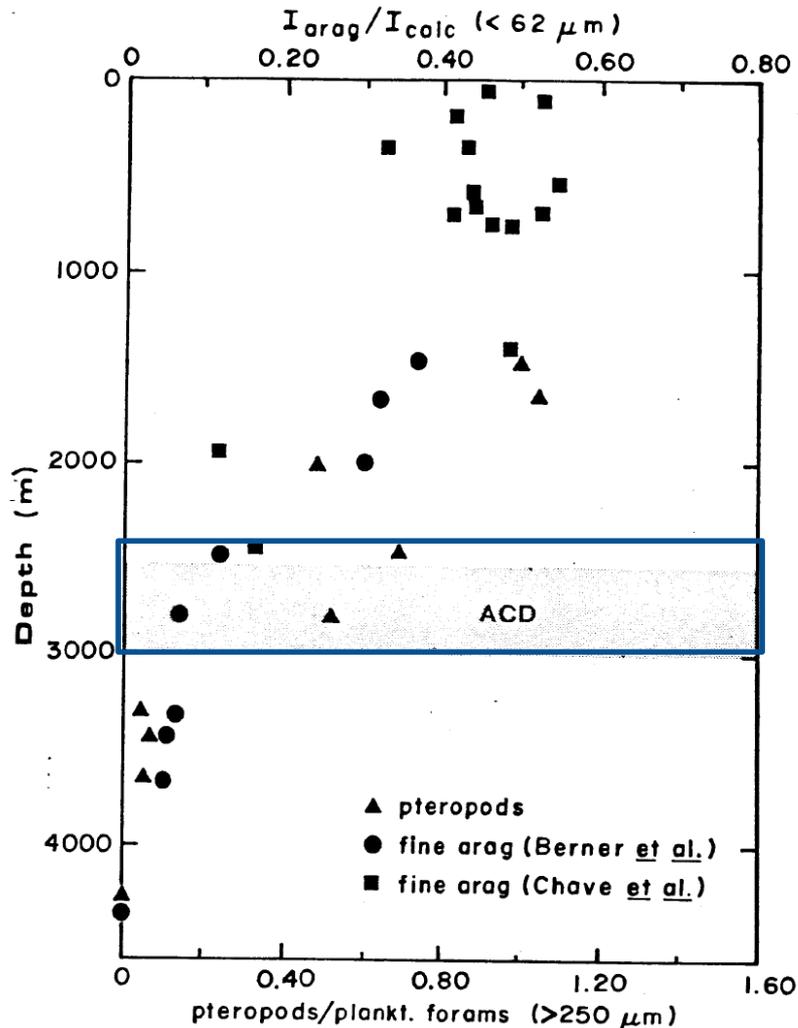
$$\Omega_{C \text{ or } A} = \frac{[Ca^{2+}] \, [CO_3^{2-}]}{K^*_A}$$

In the sediment:
"CH$_2$O" + O$_2$ $\rightarrow$ CO$_2$ + H$_2$O
CO$_2$ + H$_2$O $\rightarrow$ H$_2$CO$_3$
H$_2$CO$_3$ $\rightarrow$ H$^+$ + HCO$_3^-$
(or H$_2$CO$_3$ + CO$_3^{2-}$ $\rightarrow$ 2HCO$_3^-$)

H$^+$ + CaCO$_3$ $\rightarrow$ Ca^{2+} + HCO$_3^-$
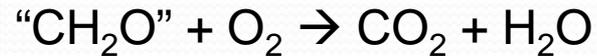
Aragonite Saturation Depth
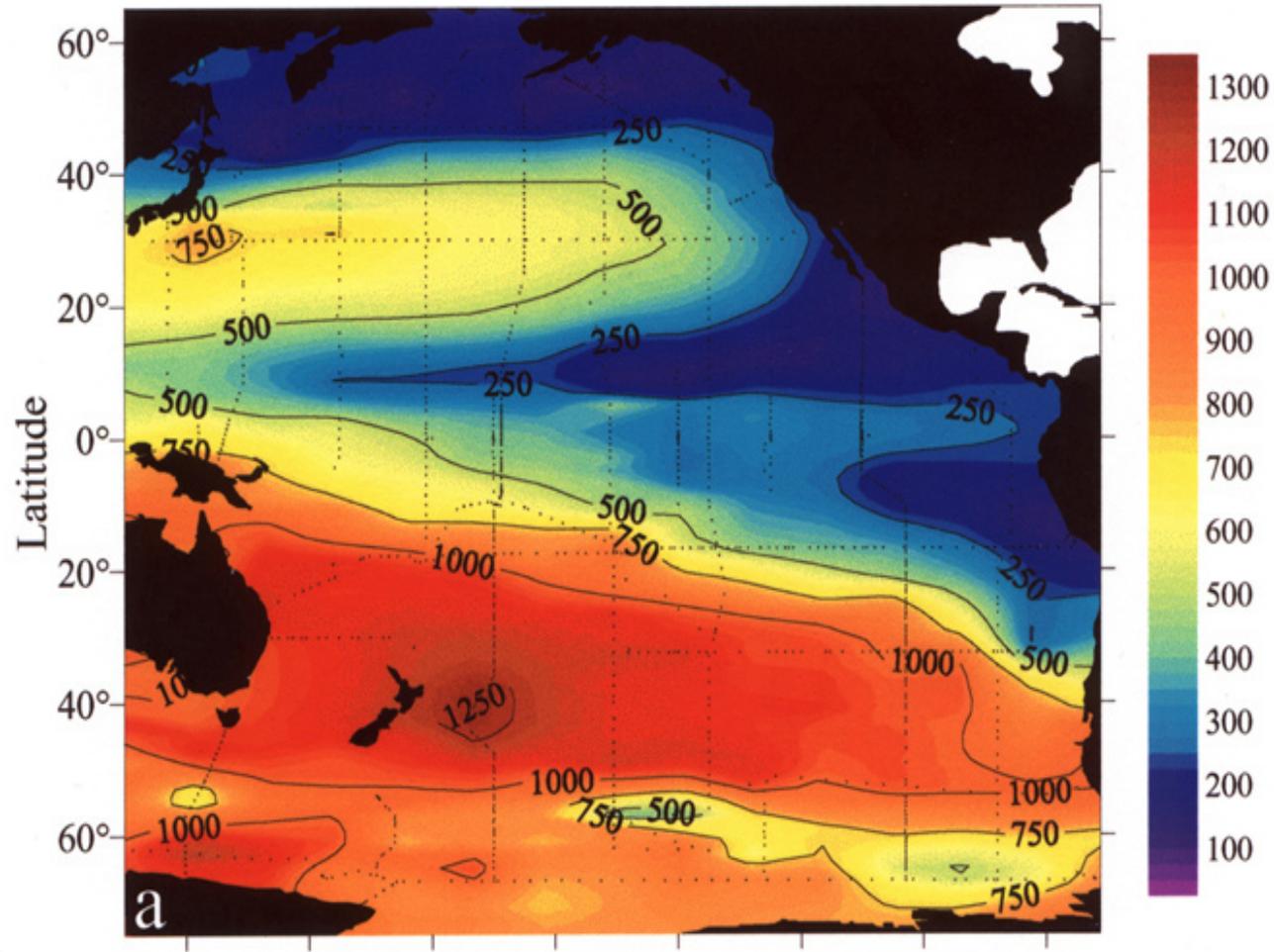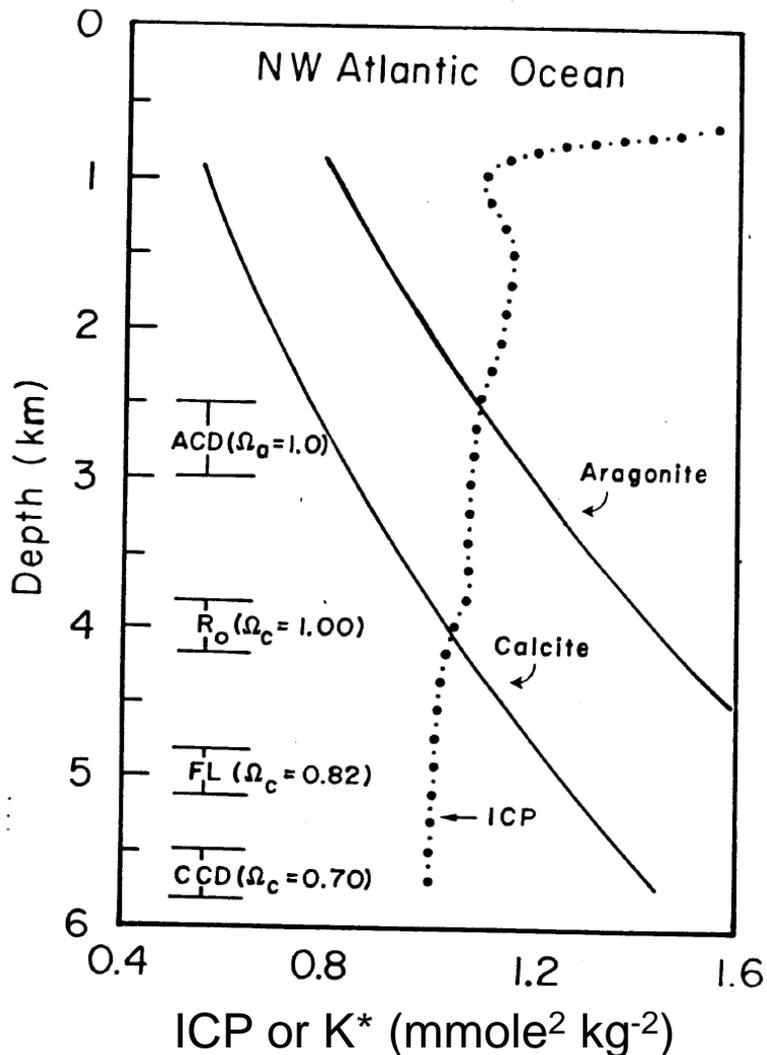
Sediment marker horizons

ACD – aragonite compensation depth
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Depth at which the water column is in equilibrium (saturated) with respect to calcite.

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Depth at which the calcite dissolution rate increases significantly.

CCD – calcite compensation depth
Depth below which little (<10%) or no calcite accumulates in the sediment.

Calcite Saturation Depth
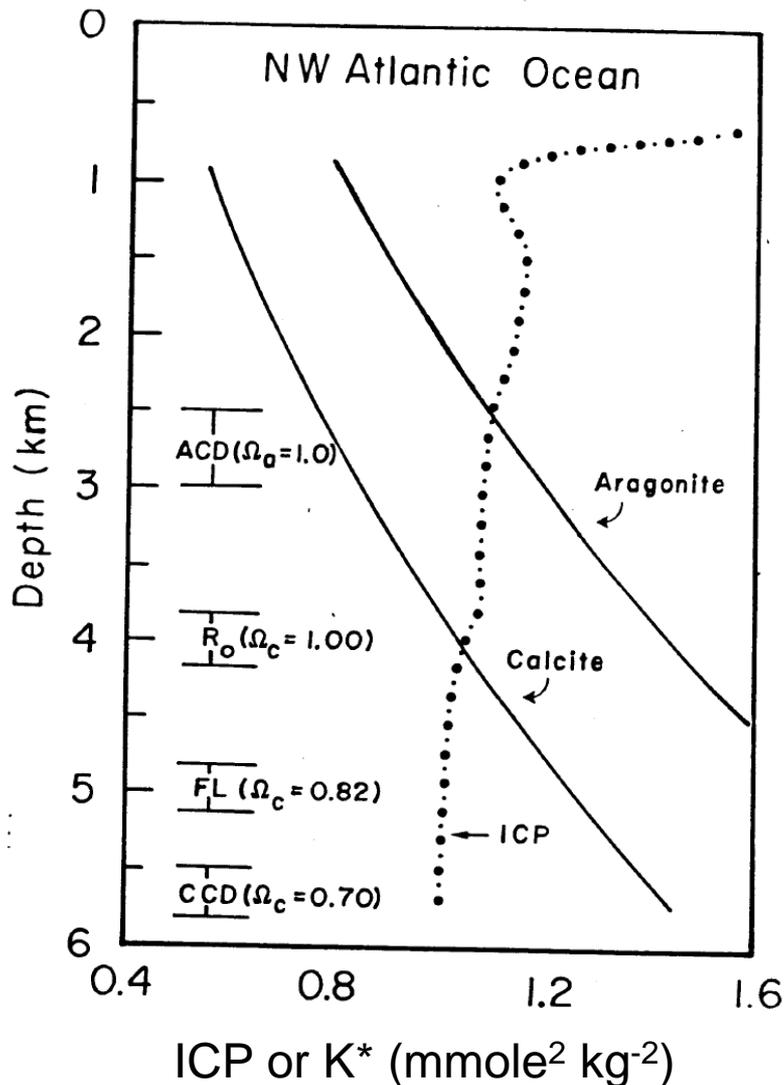
Sediment marker horizons

NW Atlantic Ocean

ACD – aragonite compensation depth
Depth below which little (<10%) or no aragonite accumulates in the sediment.

Ro – calcite saturation level
Depth at which the water column is in equilibrium (saturated) with respect to calcite.

FL – foraminiferal lysocline
Depth at which the calcite dissolution rate increases significantly.

CCD – calcite compensation depth
Depth below which little (<10%) or no calcite accumulates in the sediment.

Foraminiferal lysocline
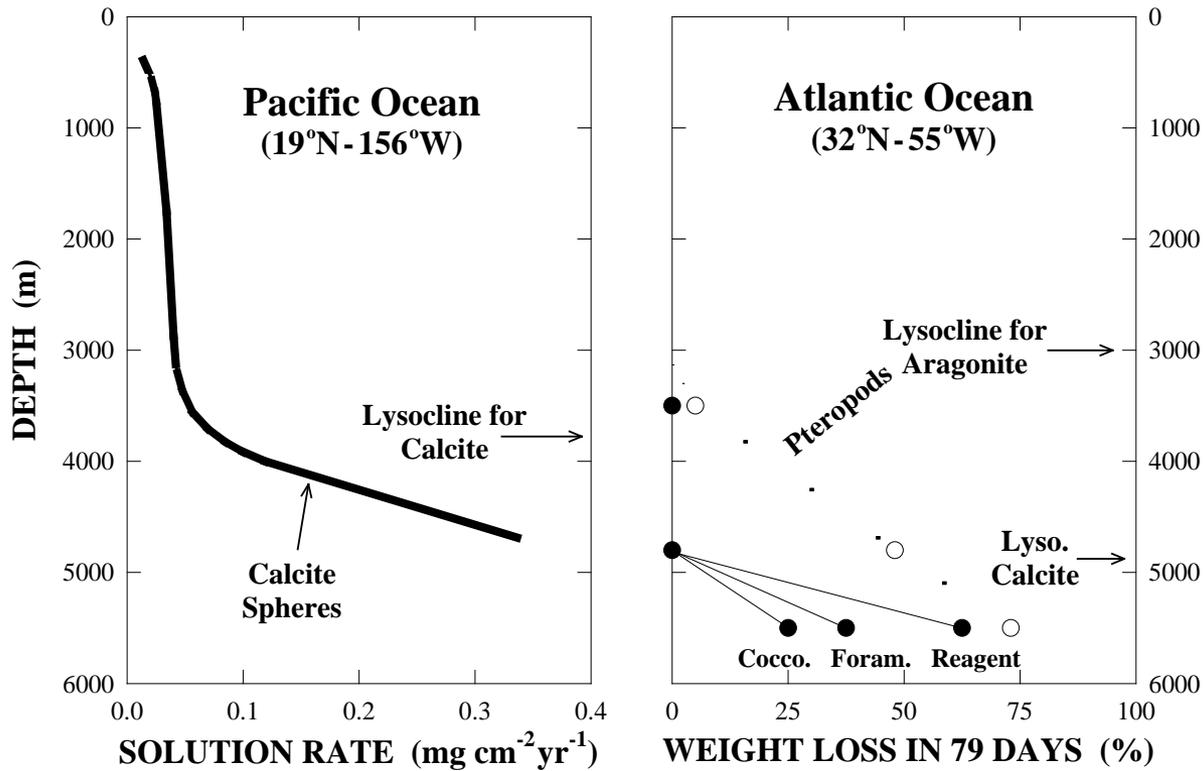
Depth of lysocline in the oceans

Sediment marker horizons
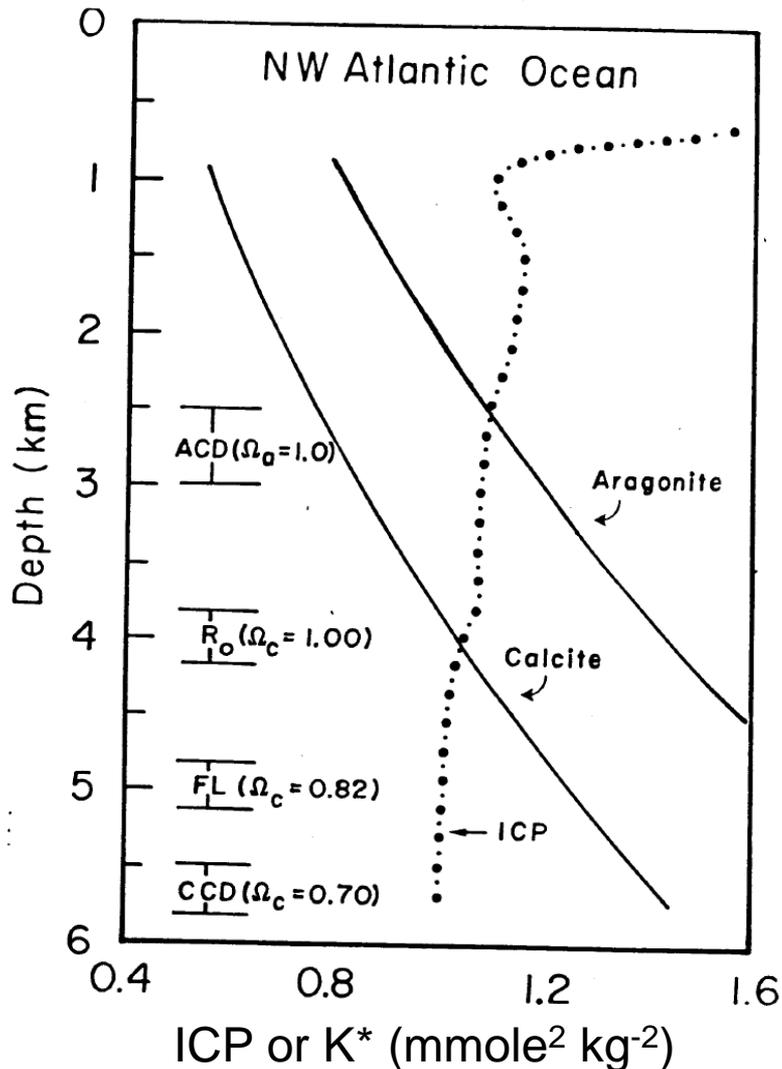
NW Atlantic Ocean

ACD – aragonite compensation depth
Depth below which little (<10%) or no aragonite accumulates in the sediment.

Ro – calcite saturation level
Depth at which the water column is in equilibrium (saturated) with respect to calcite.

FL – foraminiferal lysocline
Depth at which the calcite dissolution rate increases significantly.

CCD – calcite compensation depth
Depth below which little (<10%) or no calcite accumulates in the sediment.

Calcite loss in the Pacific
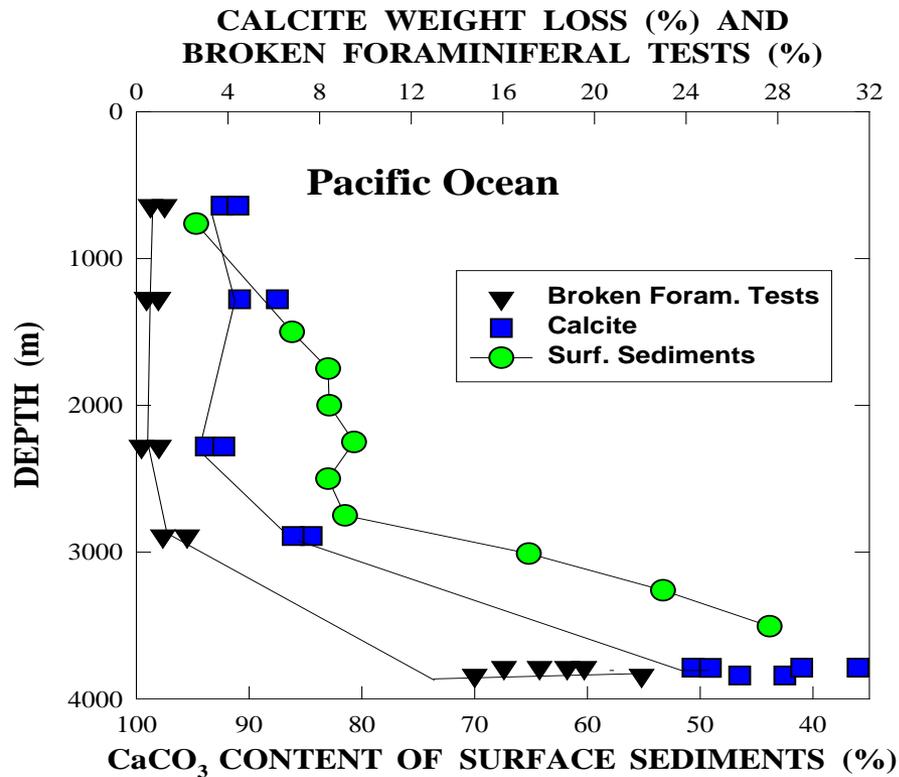
R$_o$, Lysocline and CCD in the Eastern Atlantic
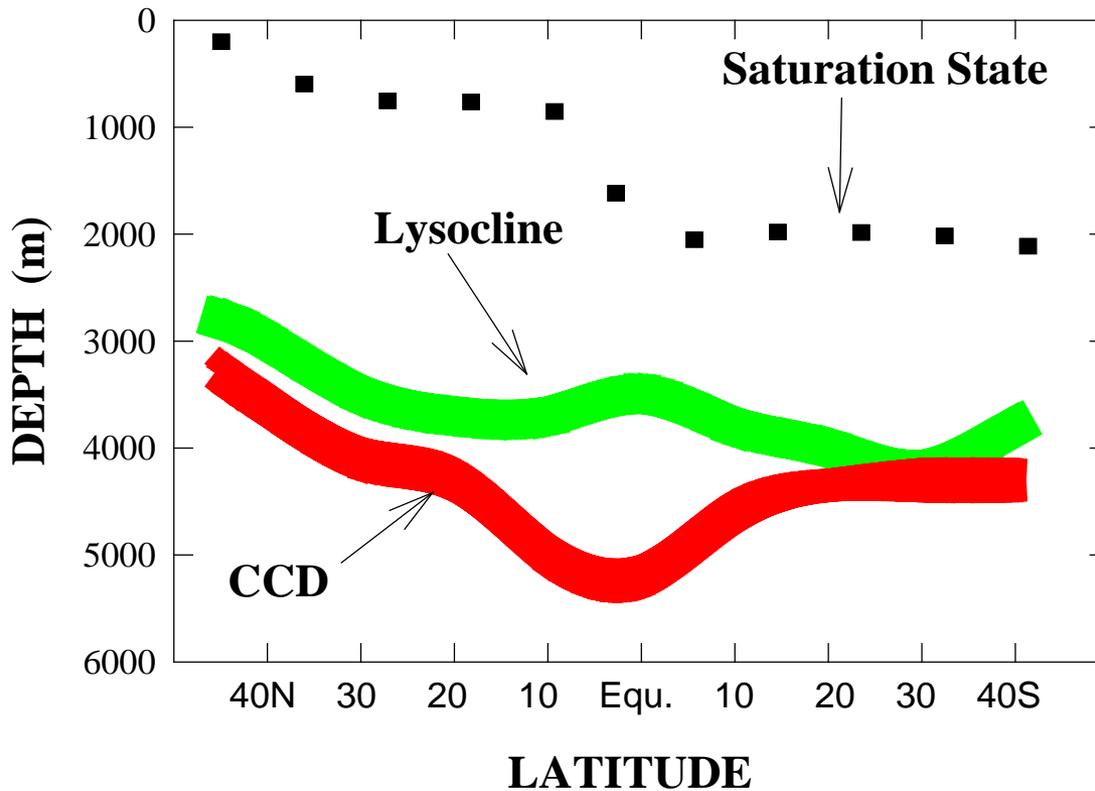
Carbonate precipitation and dissolution balance
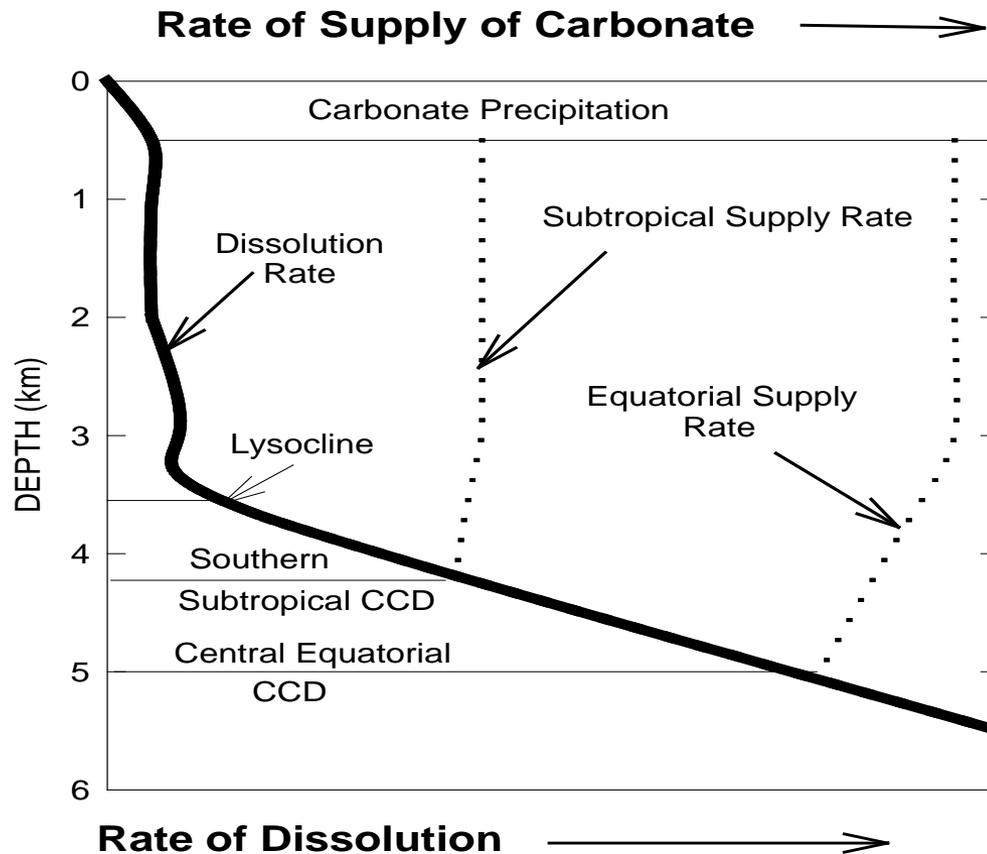
CaCO$_3$ production
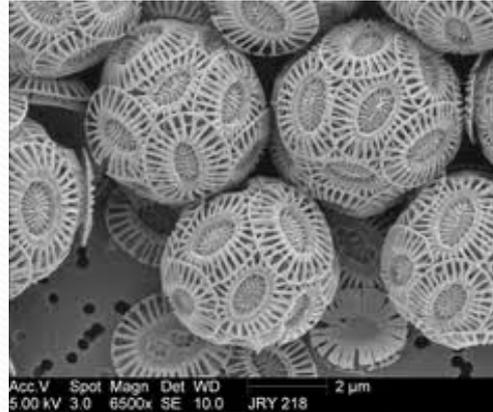
Pteropods
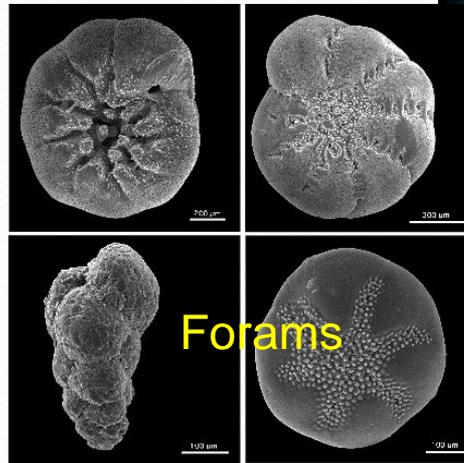
Forams

The overall calcite flux to the sediments is estimated to be 7 times greater than the aragonite flux.

Organic matter flux at depth
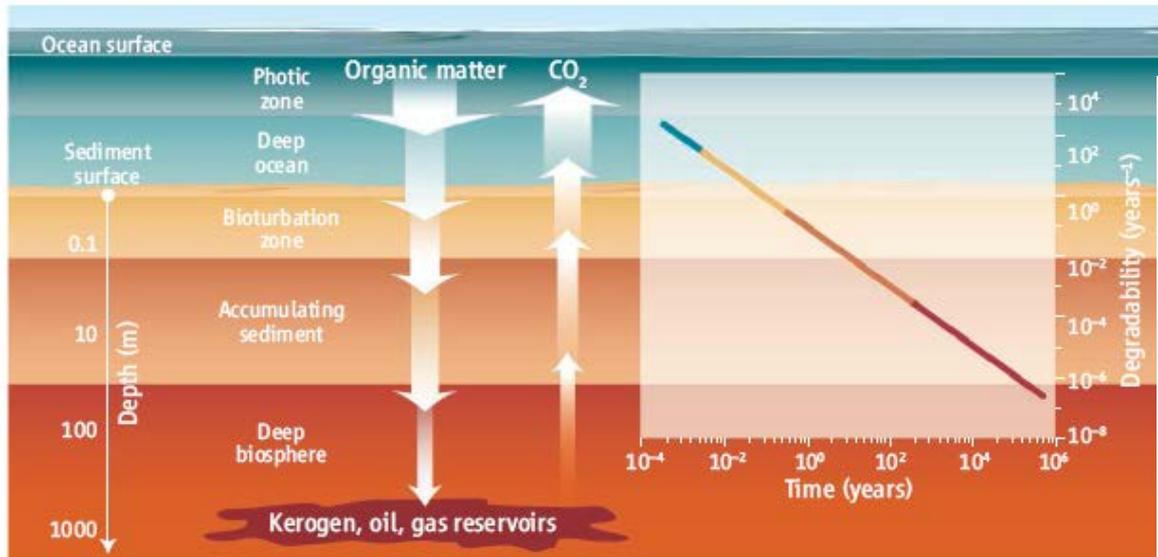
From: Middelburg and Meysman (2007) Science 316: 1294-1295

Sediments at 5000 m receive about 10 times less organic matter than at 3000 m.

In the sediment:
"CH_2O" + O_2 → CO_2 + H_2O
CO_2 + H_2O → H_2CO_3
(or H_2CO_3 + CO_3^{2-} → $2HCO_3^-$)
H^+ + $CaCO_3$ → Ca^{2+} + HCO_3^-
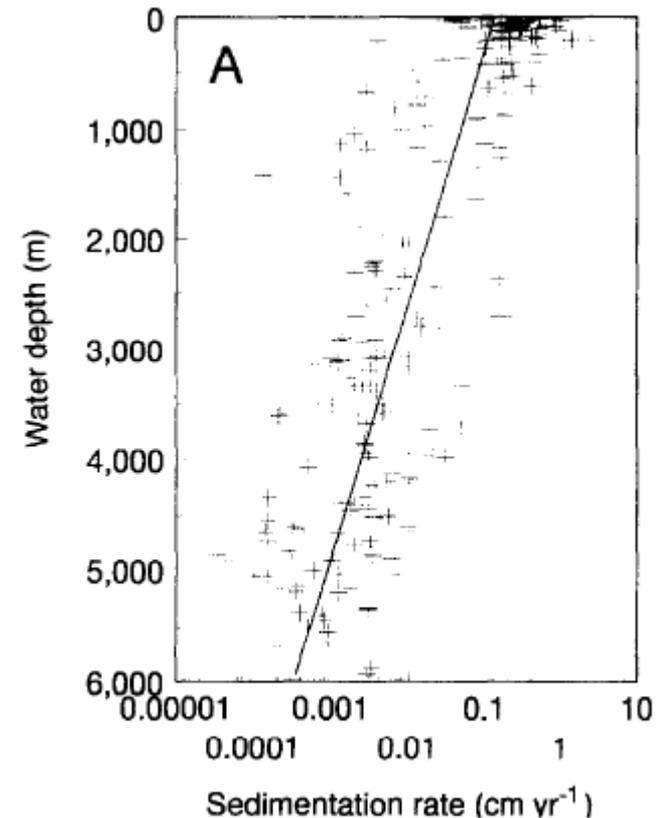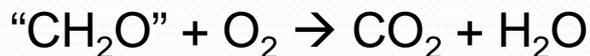
From: Middelburg et al. (1997)
Deep-Sea Res. I 44: 327-344

Phosphate dissolution inhibition
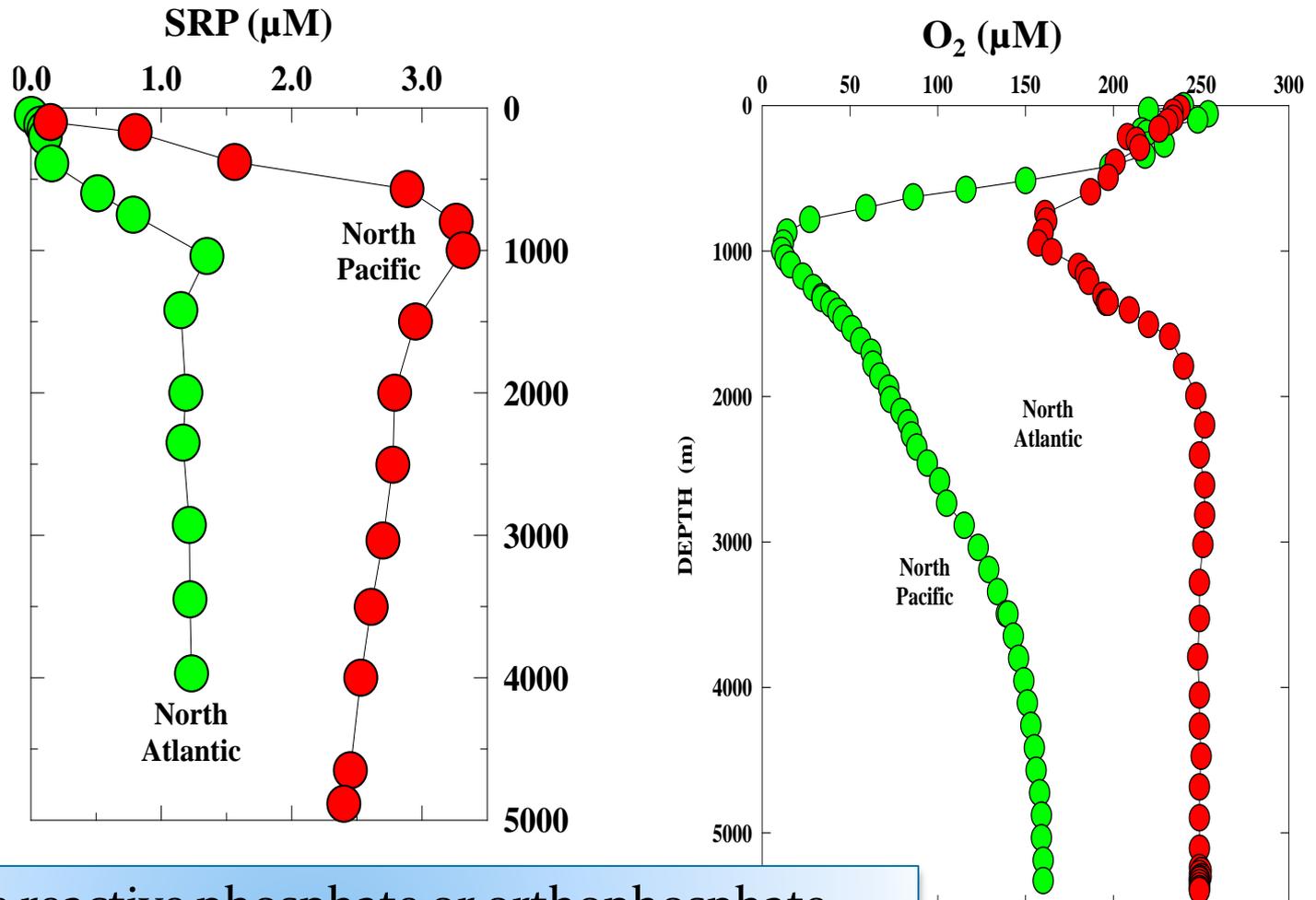
SRP = soluble reactive phosphate or orthophosphate

Encapsulation
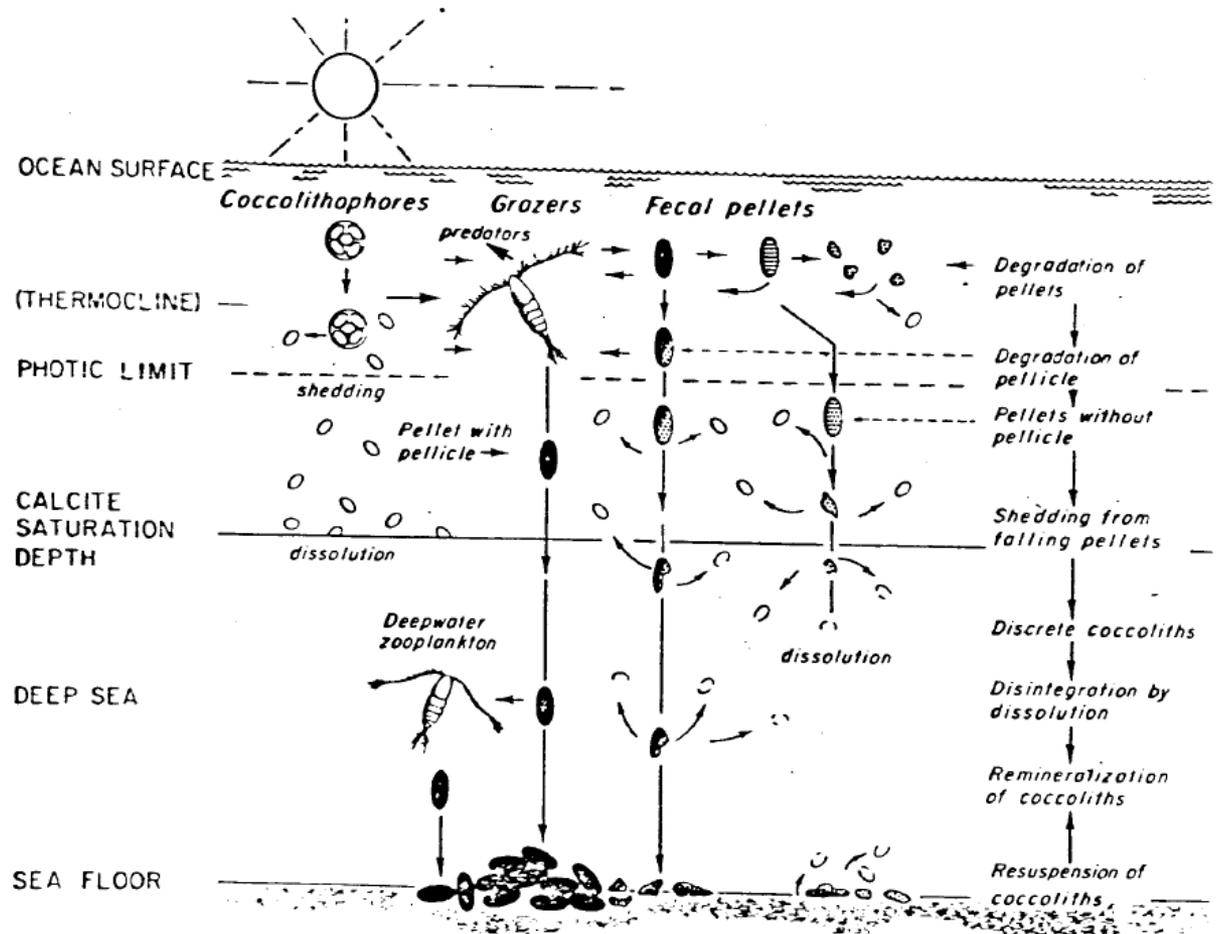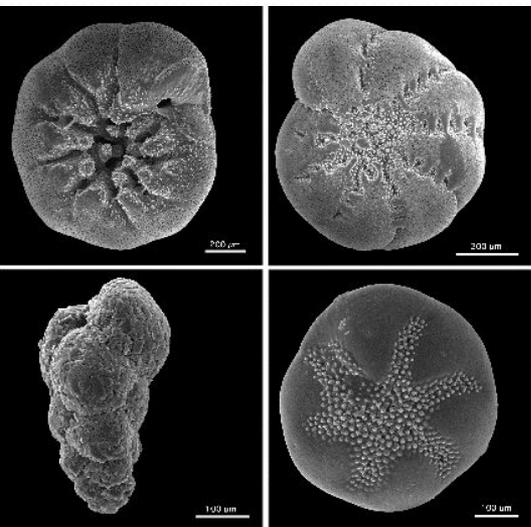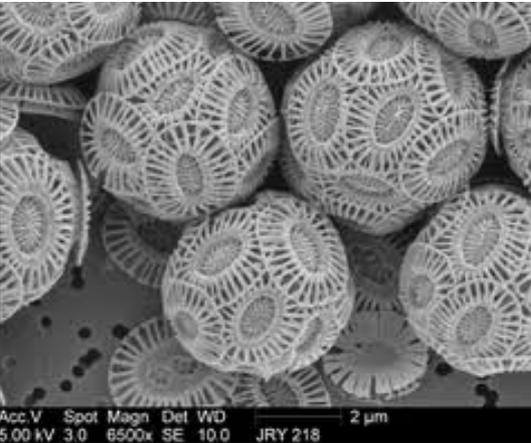
The coccolith population makes up 25-50% of the total $CaCO_3$ flux to the deep sea.

The Dangers of Ocean Acidification

Doney, Scientific American, March 2006

Uptake of CO_2 from the atmosphere causes acidification of the ocean (pH decreases).

$$CO_{2(gas)} \rightarrow CO_{2(aq)} + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+$$

$$H^+ + CO_3^{2-} \rightarrow HCO_3^-$$
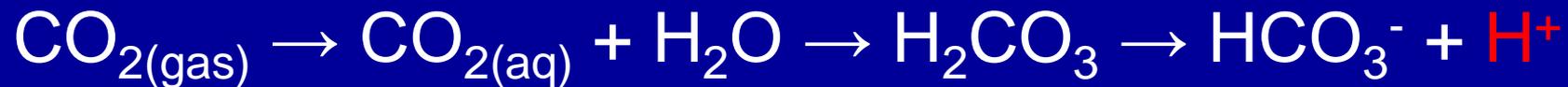
Record of ocean acidification
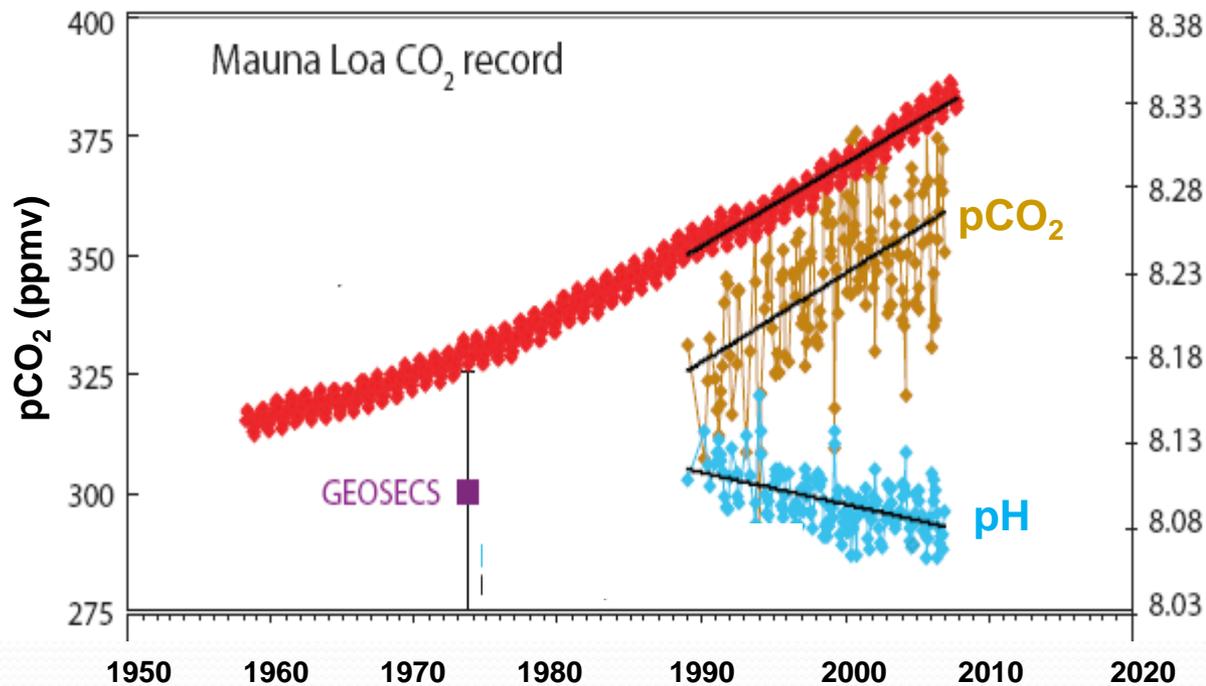
An estimated decrease of 0.1 pH unit over the last century.
The increase is 100 times faster than any change in acidity experienced by marine organisms for at least the last 20 million years.

Record of ocean acidification

Time-series of mean carbonic acid system measurements within selected depth layers at Station ALOHA, 1988-2007.
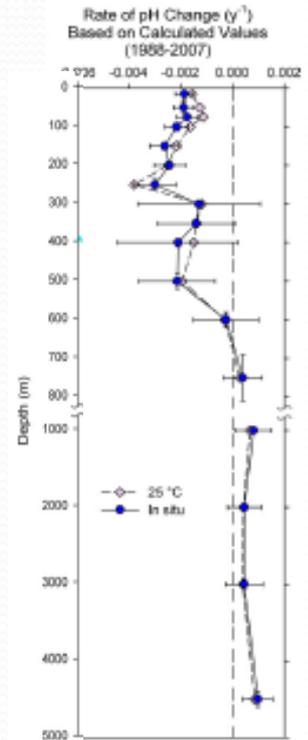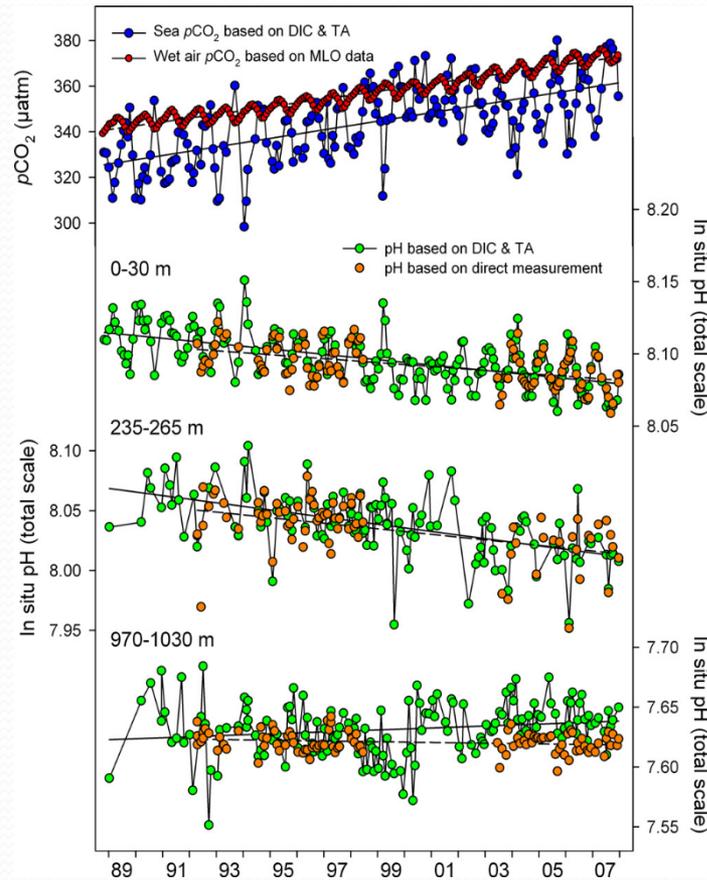
The kinetic processes of gas exchange and transport at the air-sea interface operate on a time scale of about one year, but the exchange time with the deep ocean is on the order of a thousand years. Hence, the ocean as a whole has not equilibrated in response to the increased atmospheric pCO_2.

From: Dore et al. (2009) PNAS, v. 106: 12235-12240

52a/76

Records of ocean acidification
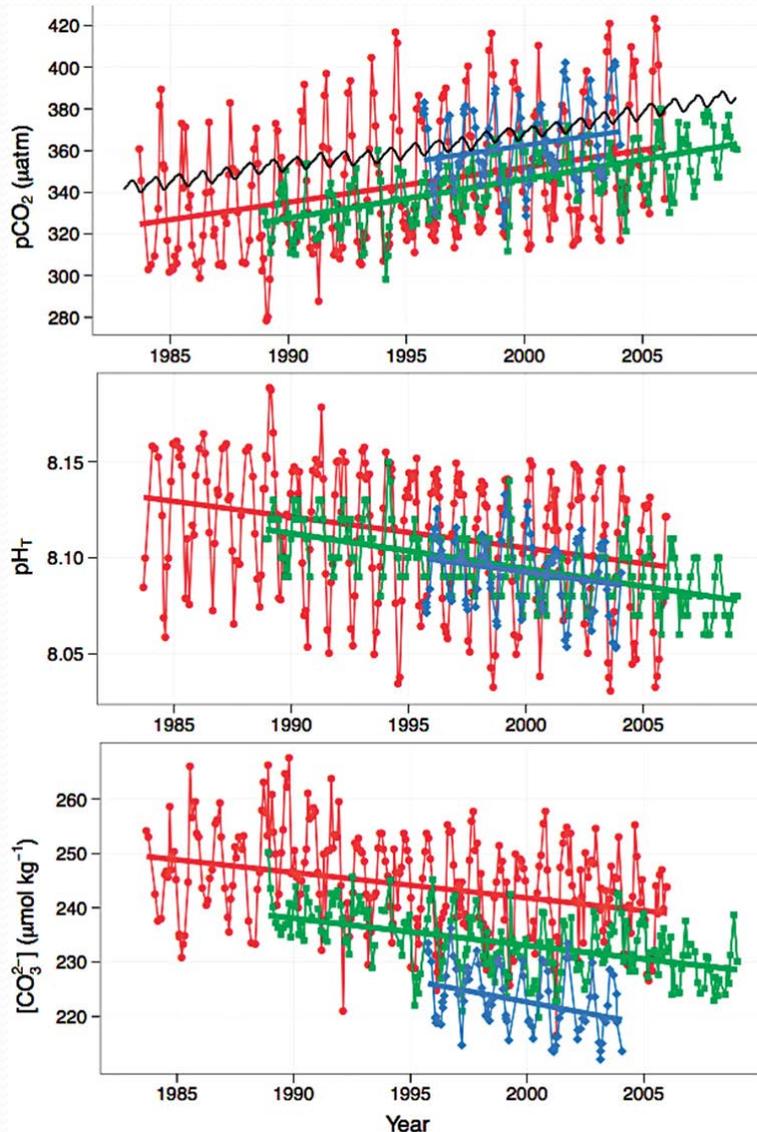
Surface ocean pCO_2, pH_T, and $[CO_3^{2-}]$ as recorded at:

-the Bermuda Atlantic Time-Series Station (BATS; red),

-the Hawaii Ocean Time-series (ALOHA; green),

-and the European Station (Canary Islands) for Time-series Observations in the Ocean (ESTOC; blue) over the past few decades.

Atmospheric pCO_2 is shown in lockstep with pCO_2 in the ocean by the black line

From: Mackenzie and Andersson Geochem. Perspectives (2013).

Saturation state of surface waters

$$\Omega = ([Ca^{2+}][CO_3^{2-}])/K^*_{C \text{ or } A}$$
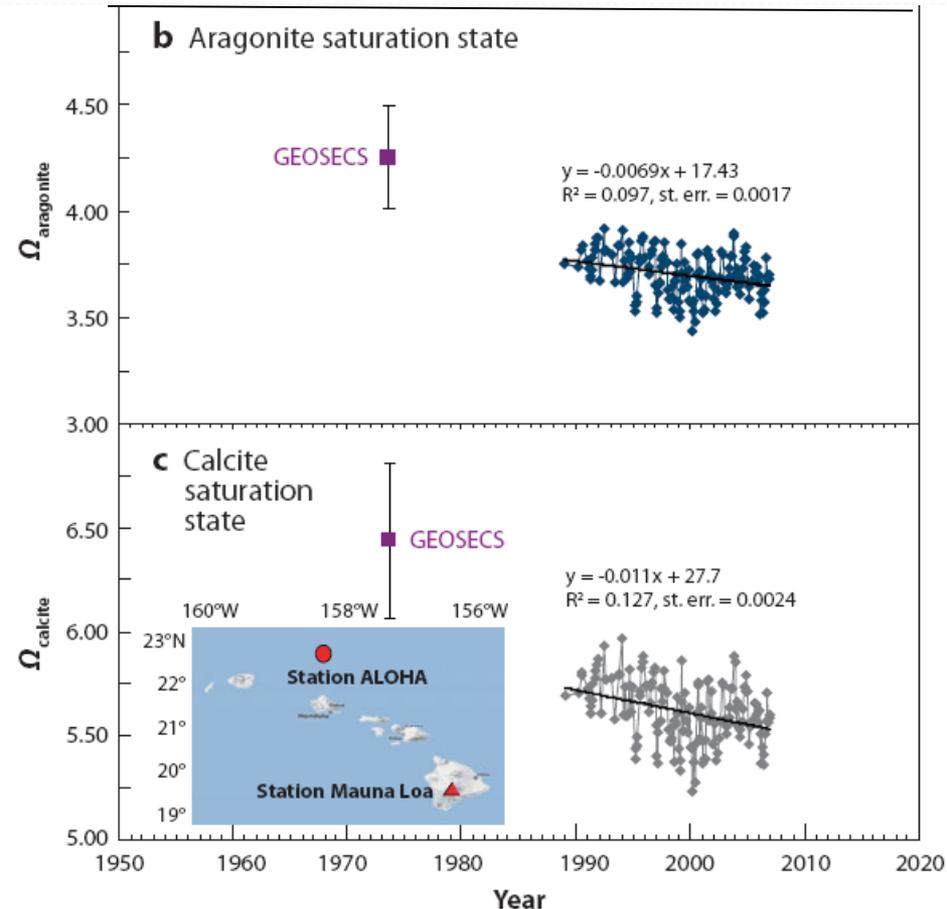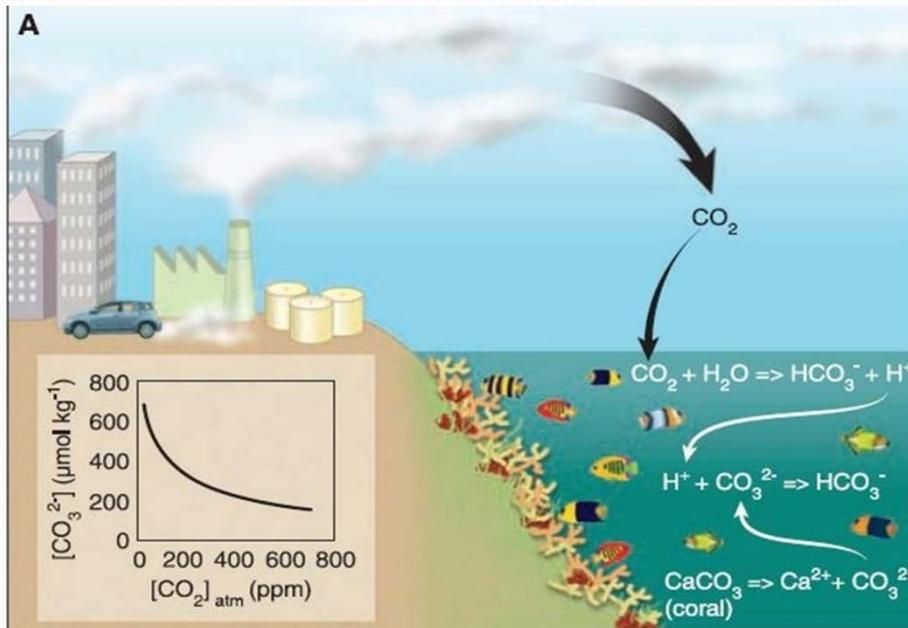
Sea-surface ΔpCO_2 in the oceans
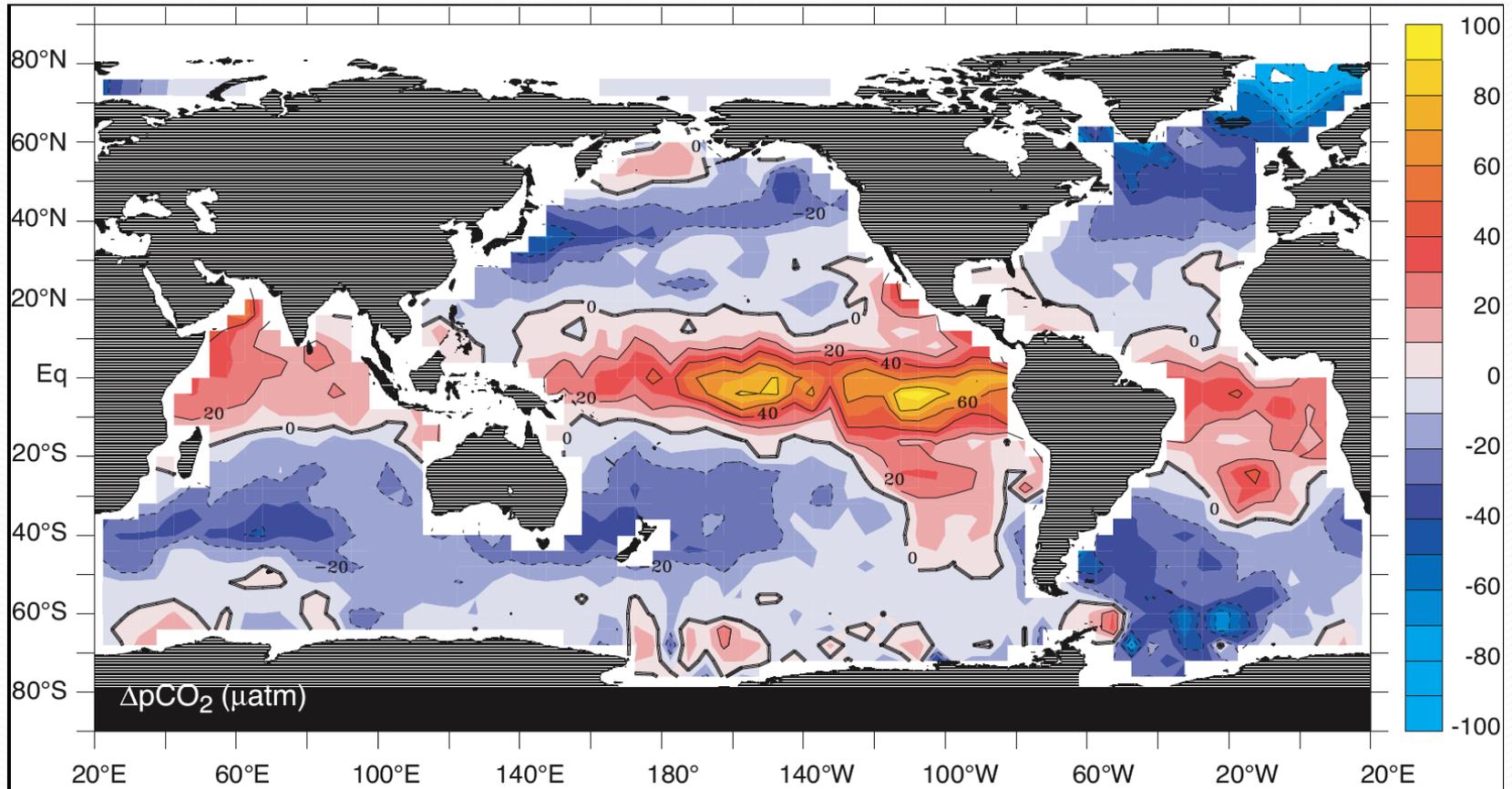
The meridional distribution of anthropogenic CO_2 in the Pacific, along σ_θ = 26.0 and 27.3.
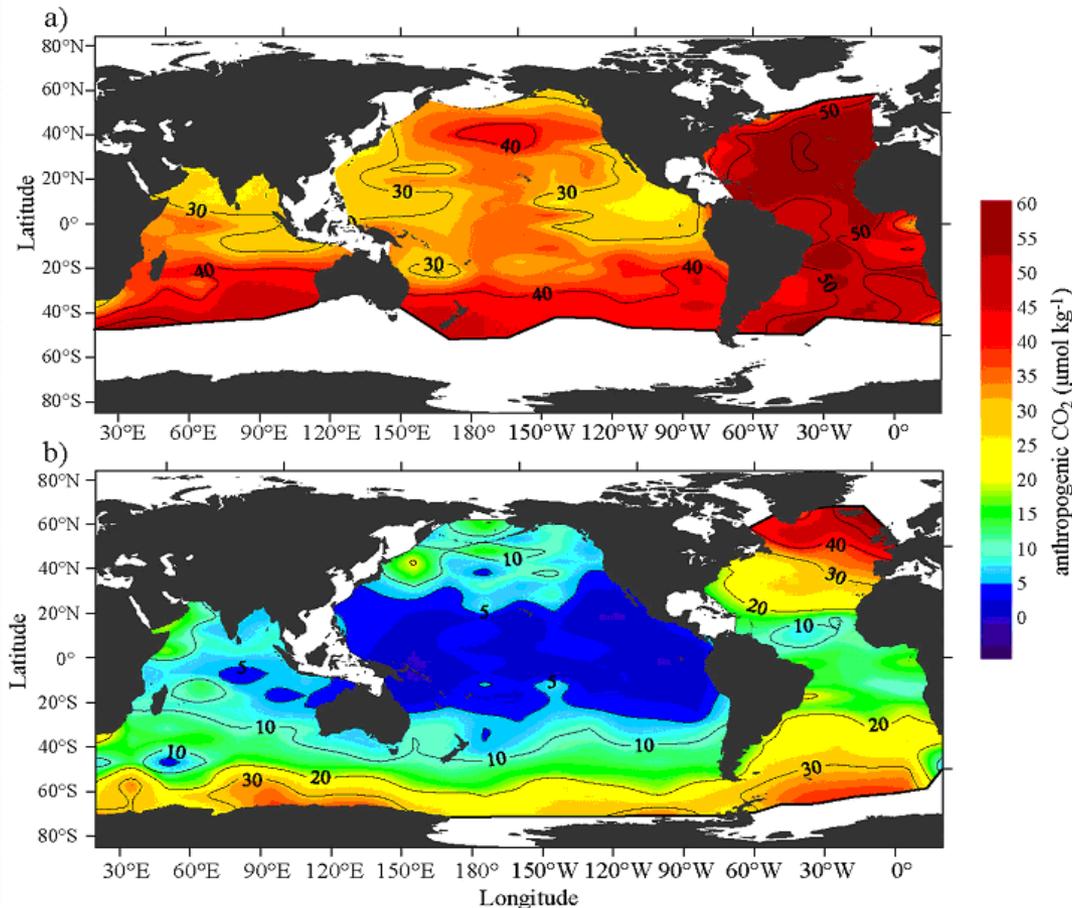
The largest inventories and deepest penetration of anthropogenic CO_2 are associated with the subtropical convergence. Penetration is very shallow in the tropics.

Penetration of anthropogenic CO_2 in the South Atlantic
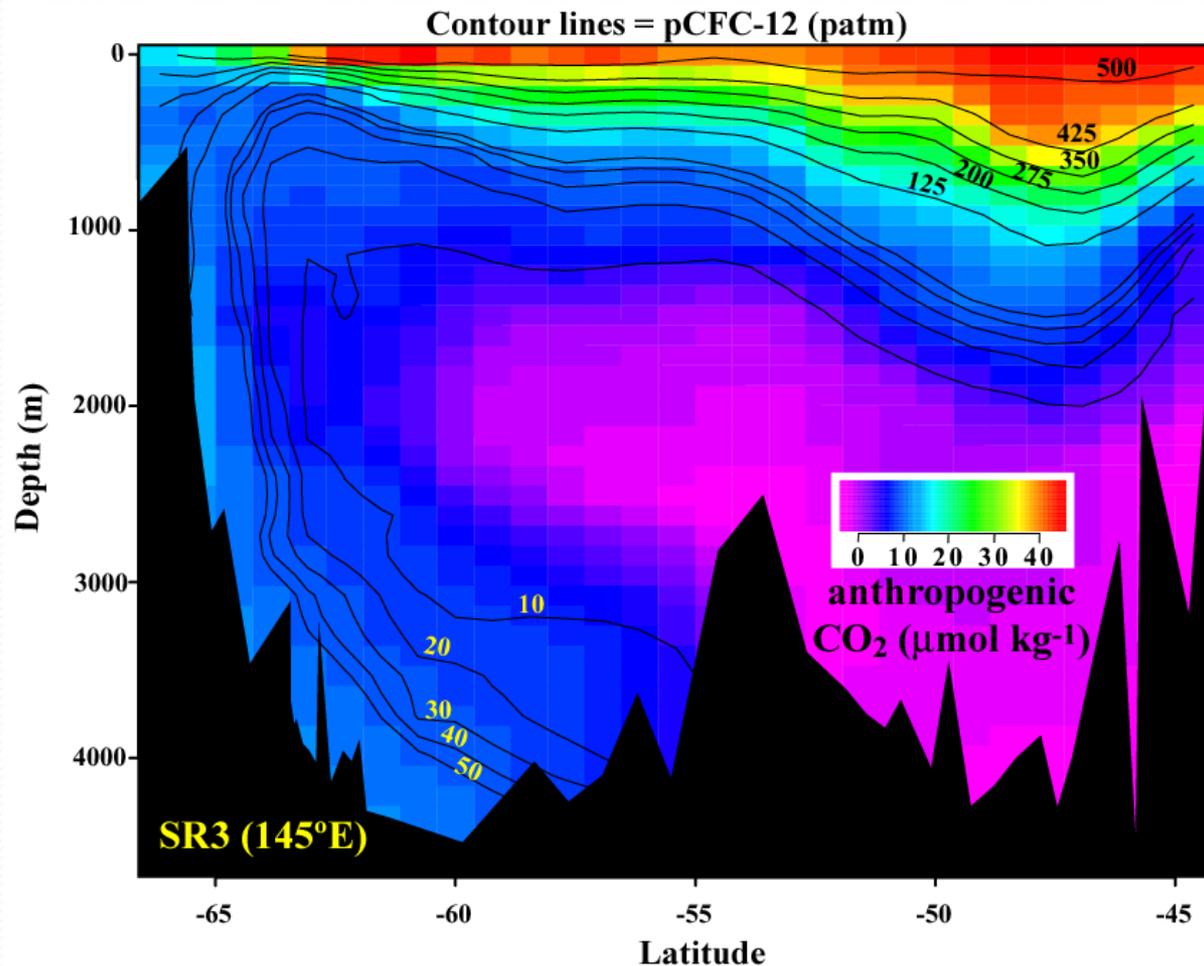
Anthropogenic CO_2 is Shoaling Carbonate Saturation Horizons

$$\Omega_{C\,or\,A} = \frac{[Ca^{2+}]\,[CO_3^{2-}]}{K^*_{C\,or\,A}}$$

when $\Omega_{C\,or\,A} < 1$, $CaCO_3$ dissolves.

Anthropogenic CO_2 has contributed to a shoaling of the saturation horizons by 30-200 m from pre-industrial to present.
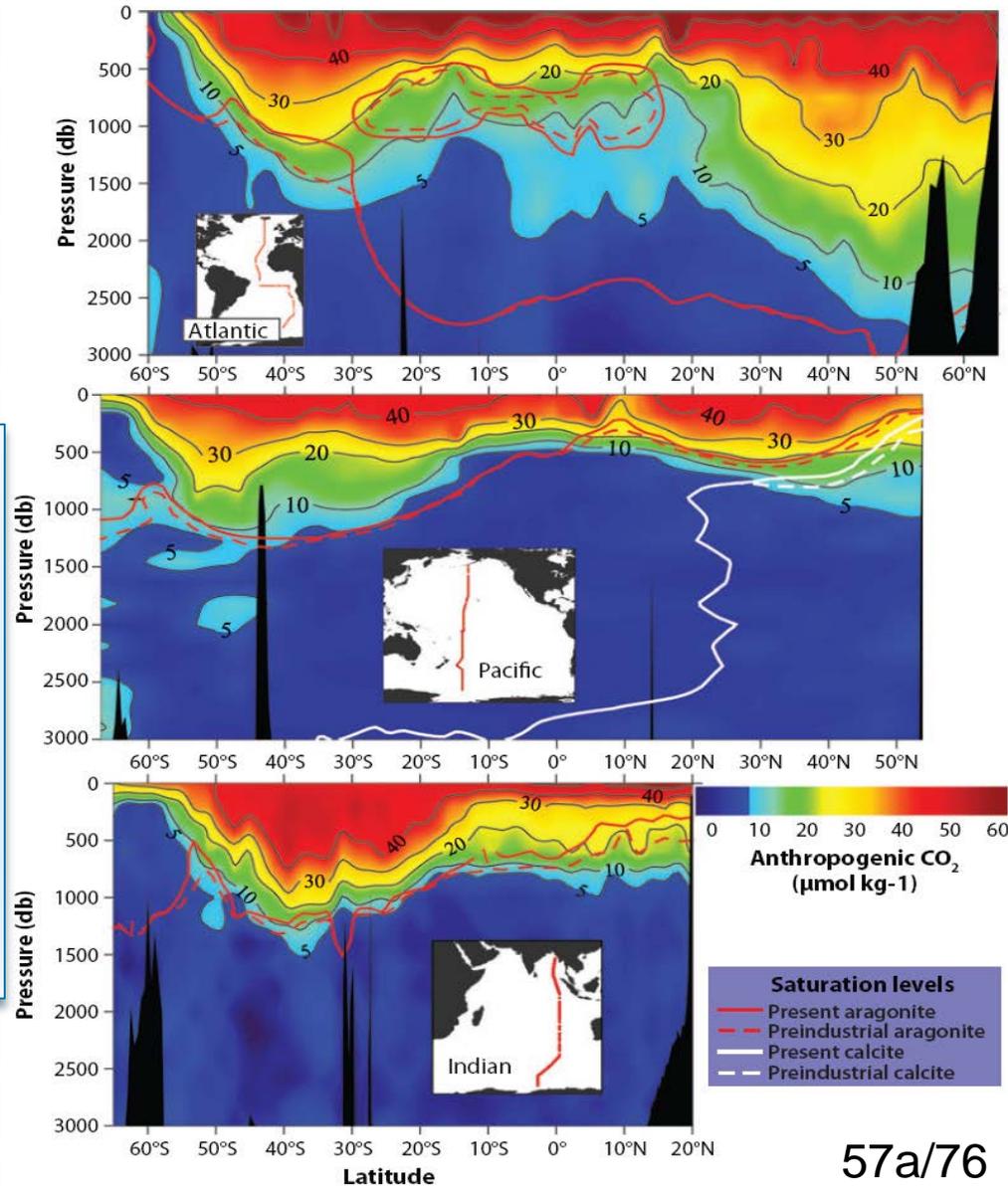
Fraction anthropogenic dissolution
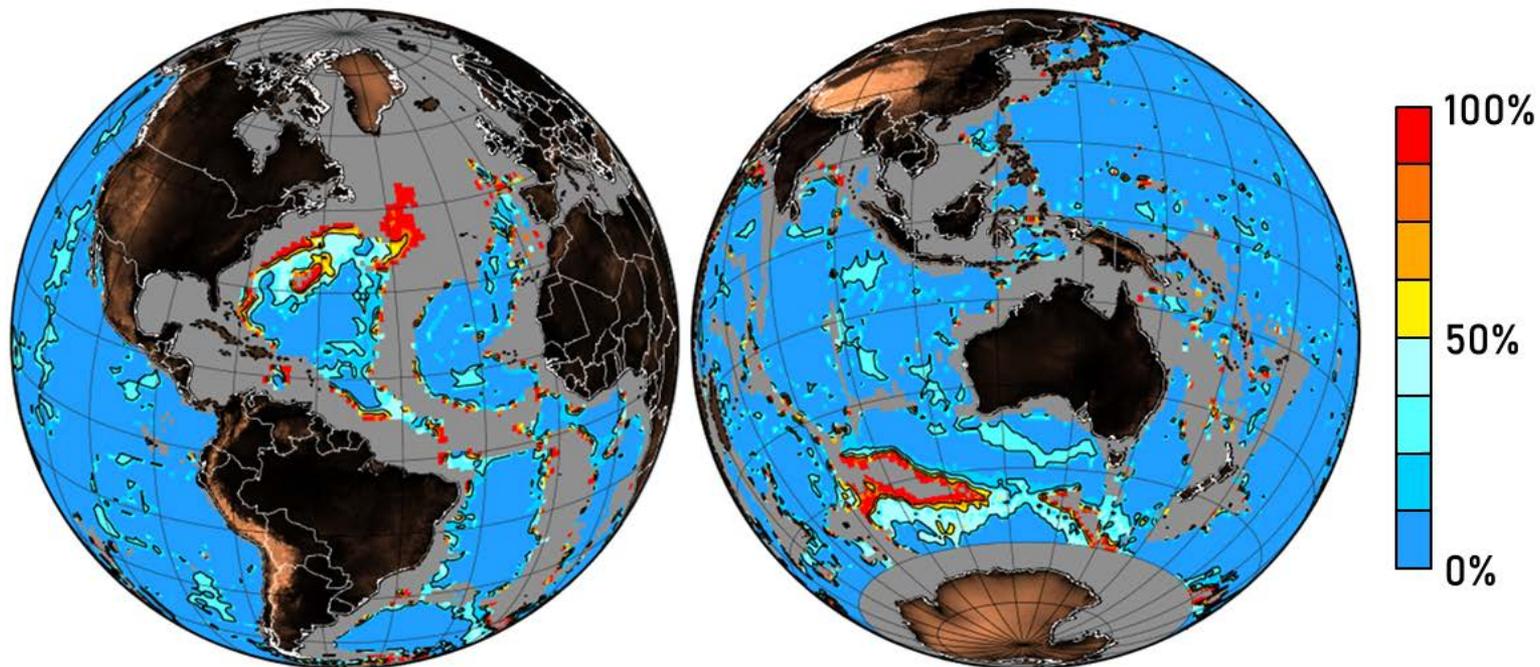
Significant anthropogenic dissolution occurs in the Northwestern Atlantic, where it accounts for 40 to 100% of the total dissolution and where the compensation depth (CCD) has shoaled by about 300 m. Other sites of dissolution are found in the Southern Atlantic, the Indian and Pacific Oceans.

From: Sulpis et al. (PNAS, 115: 11700-11750, 2018)

Futur CO_2 emission scenarios
(Intergouvernmental Panel on Climate Change)
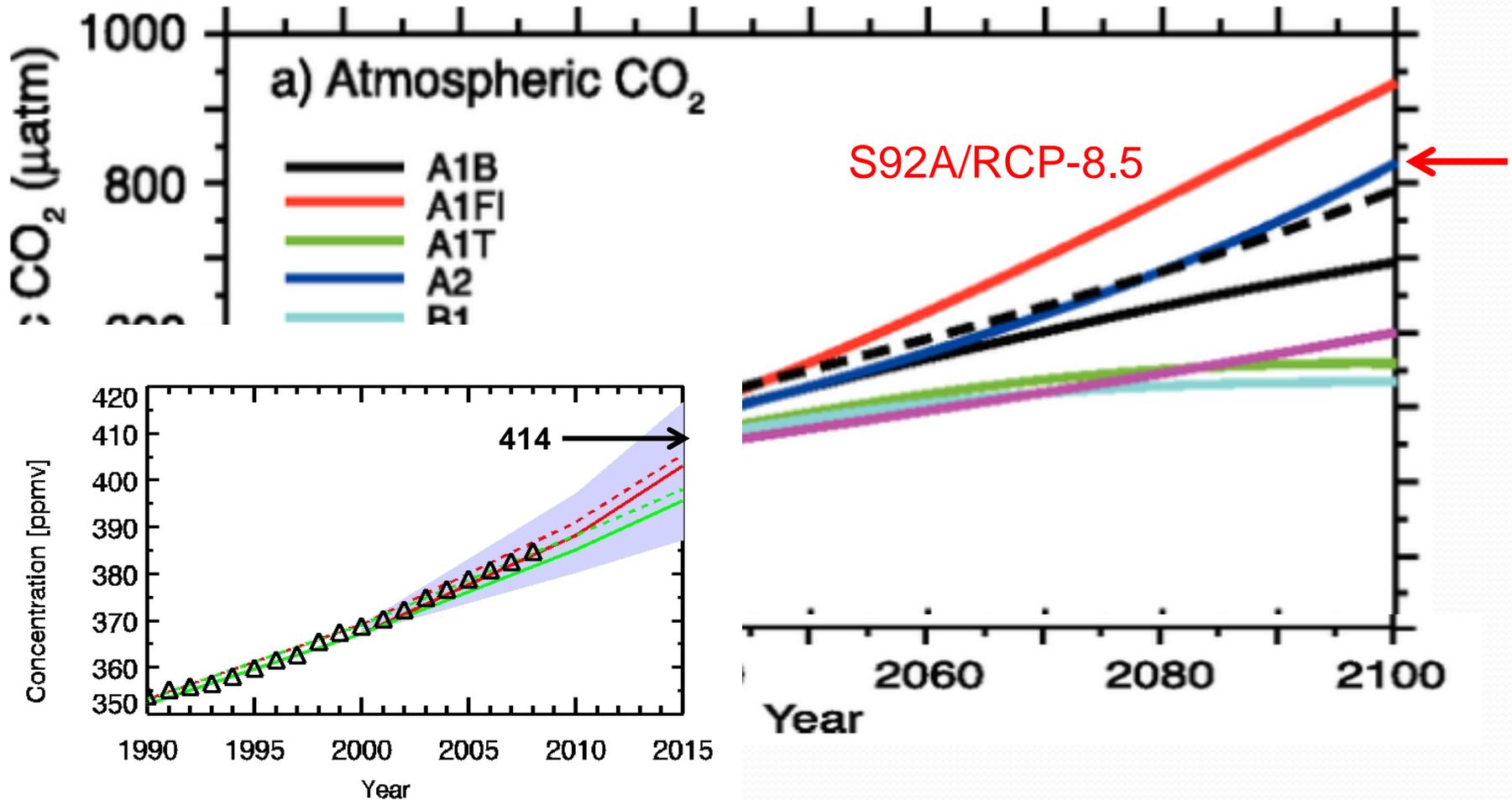
Futur global ocean pH scenarios
(Intergouvernmental Panel on Climate Change)

From: http://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch10s10-4-2.html
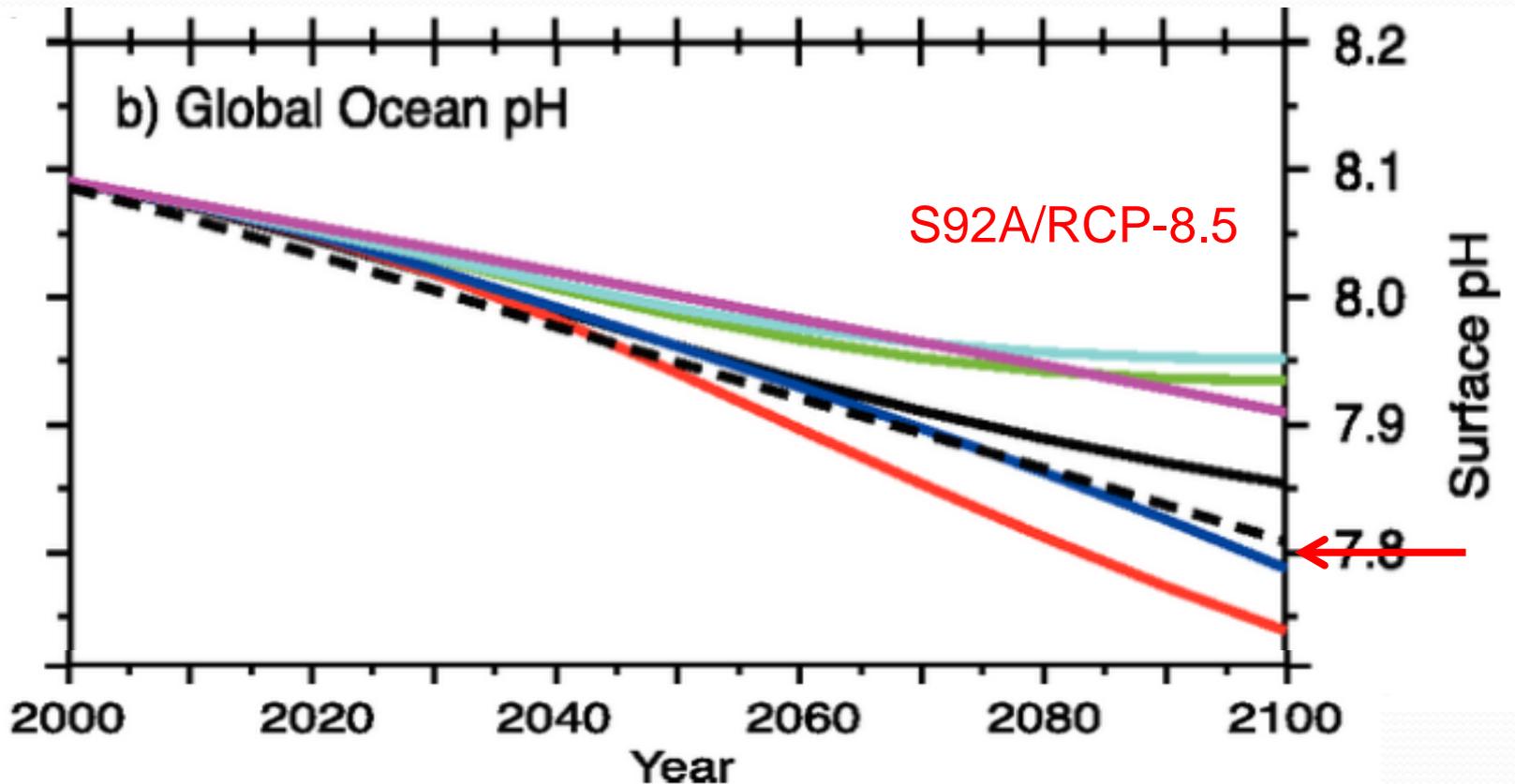
Biological responses: (bio)mineralization
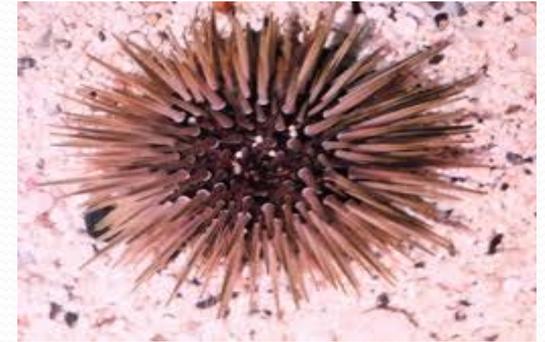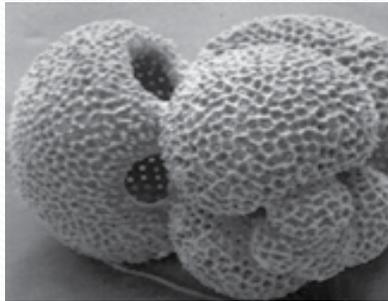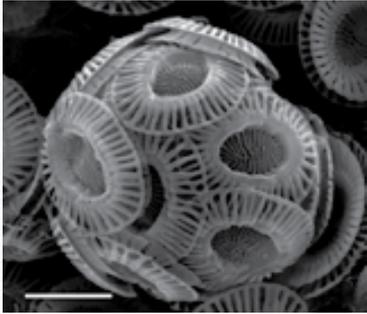
Biological responses

Response	Species		Nbr	⟋	⟍	—	⌒	
Calcification		Coccolithophores	29	4	**18**	4	3	
		Calcifying Algae	4	0	1	1	**2**	
		Crustaceans	6	**3**	1	2	0	
		Corals	3	0	**3**	0	0	
		Echinoderms	3	1	1	0	1	
		Molluscs	10	0	**9**	0	1	
Photosynthesis		Coccolithophores	26	**9**	5	7	5	
		Algae	5	1	2	2	0	
Reproduction		Echinoderms	7	0	3	3	1	
		Molluscs	3	0	1	**2**	0	
Survival		Crustaceans	5	0	**3**	2	0	
		Molluscs	4	0	**4**	0	0	
Growth		Crustaceans	6	0	3	3	0	
		Corals	2	0	**2**	0	0	

Driving force to $CaCO_3$ precipitation

The reaction describing the precipitation of calcium carbonate is:

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

In many cases, the chemical reaction rates are expressed relative to the equilibrium state ($\Omega = 1$ or $\Delta G_{Rx} = 0$), at which the rate of the forward reaction is equal and opposite to that of the reverse reaction.

$$Rate = k\,(\Omega - 1)^n$$

where k is the rate constant and n is typically equal to 1 -3.
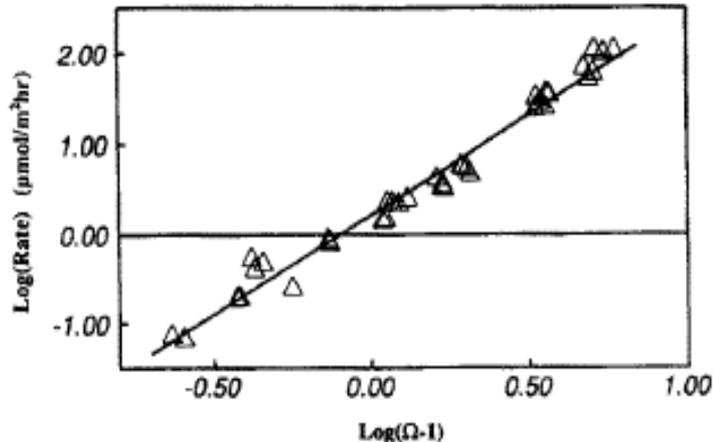
From: Zhong and Mucci (1993) GCA 57: 1409-1417.

FIG. 3. Log (rate) vs. log ($\Omega - 1$) for calcite obtained by the constant addition system in phosphate-free seawater at 25°C and $P_{CO_2} = 0.0031$ atm.

Shallow tropical corals and coral reefs

Photos of scleractinian coral *Oculina patagonica* after being maintained for 12 months in
(a) normal seawater (pH = 8.2; $\Omega_A \approx 3.6$) and
(b) acidified seawater (pH = 7.4; $\Omega_A \approx 0.1$).
From: Fine & Tchernov (2007) Science 315:1811 .

Analyses of cores from massive coral colonies of the Great Barrier Reef show that calcification rates declined 21% between 1988 and 2003.
From: Cooper et al. (2008) Glob. Change Biol. 14: 263-265.

Green and red algae

Halemida

Penicillus

10 cm

Coralline red algae
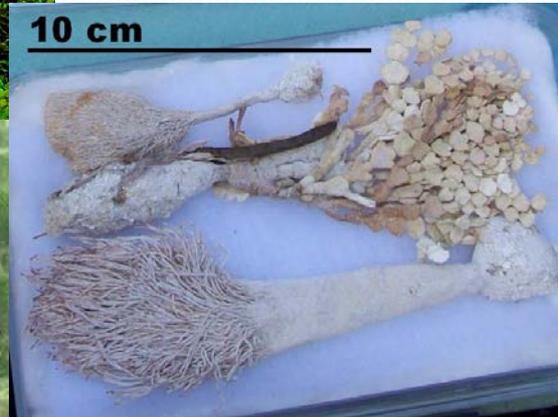
The global production of $CaCO_3$ by green algae may rival that of coral reefs but relatively few studies have been conducted on either green or red algae. A study of crustose coralline alga in Hawaii showed that both calcification rates and recruitment rates decline at lower carbonate saturation state ($\Omega_{Mg-C(13.6\%)} \approx 1.55$ vs 2.74)

From: Kuffner et al. (2007) Nature Geoscience 1: 77-140.

Other benthic invertebrates

Gazeau et al. (2007)

Mytilus edulis

Crassostreae gigas
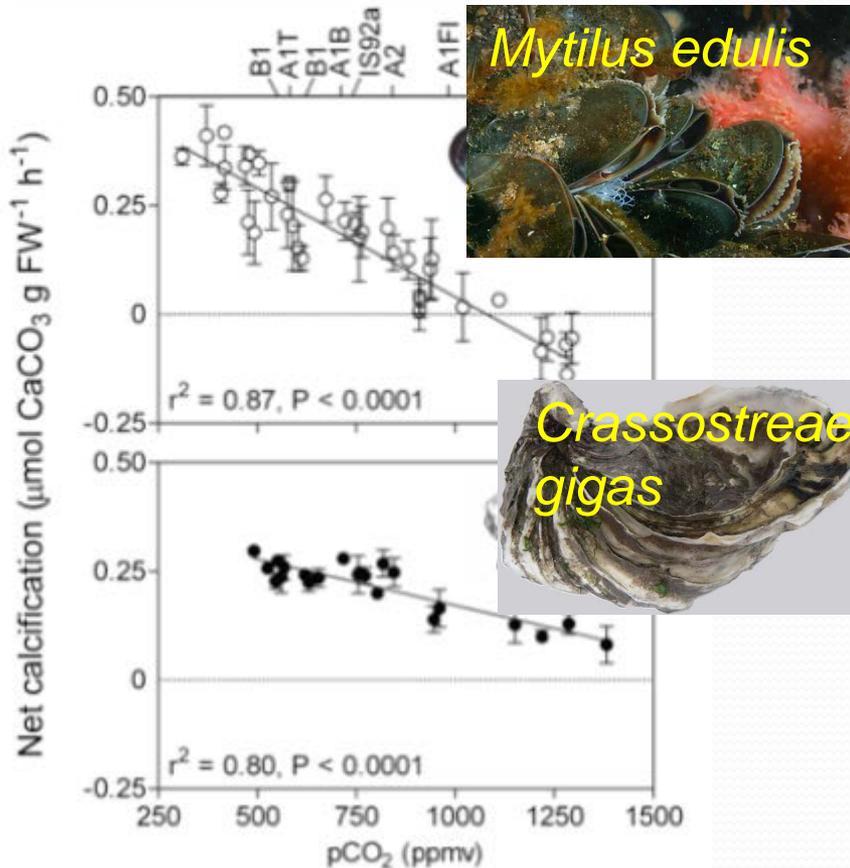
Mytilus edulis, 25% decrease in calcification rate at pCO_2 = 740 ppmv ($\Omega_A \approx 2.4$) and dissolved at pCO_2 > 1800 ppmv ($\Omega_A \approx 1.0$) upon a two-day exposure.

Crassostreae gigas, 10% decrease in calcification rate at pCO_2 = 740 ppmv ($\Omega_A \approx 2.8$, $\Omega_C \approx 5.3$) and 50% at pCO_2 > 1800 ppmv ($\Omega_A \approx 1.1$, $\Omega_C \approx 2$-2.5) upon a 2-day exposure.

From: Gazeau et al. (2007) Geophys. Res. Letts. 34: L07603
Also see: Parker et al. (2010) Mar. Biol. 157: 2435-2452.

Hemicentrotus pulcherrimum

Echinodetra mathei

Necora puber

Reduced shell growth was observed in the gastropod *Strombus lubuanus* and two sea urchins species when grown at 560 ppmv CO_2 over a 6-month period.
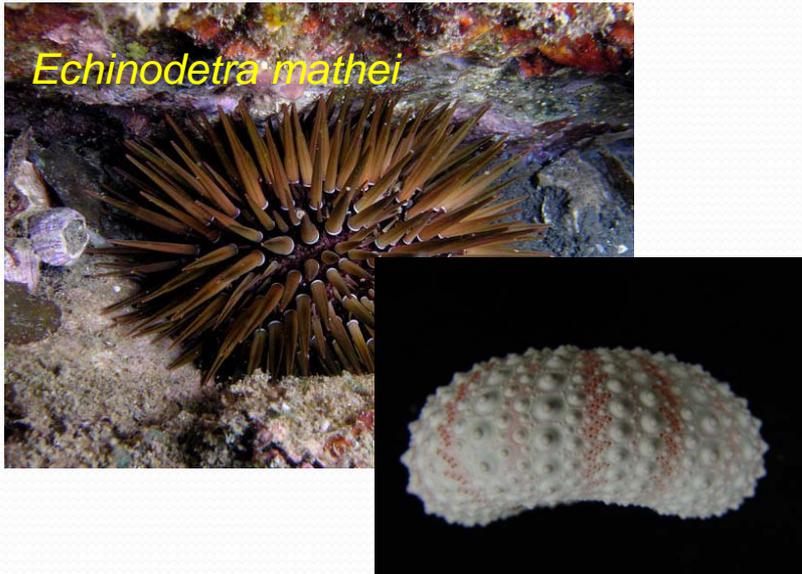
The response of early development stages of benthic invertebrates (bivalves, sea urchins, crustaceans) to CO_2-induced acidification include reduced fertilization success, developmental rates, larval size, and spicule skeletogenesis.

Planktonic Calcification

One third of the total marine $CaCO_3$ production.

Emiliania huxleyi

Gephyrocapsa oceanica
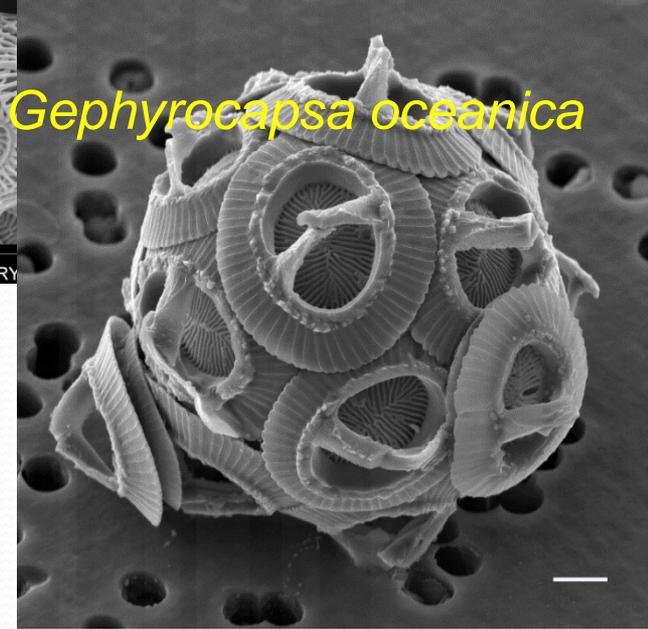
SeaWiFS satellite image of *Emiliani huxleyi* bloom, near Newfoundland, Canada

Several pelagic calcifying organisms have shown reduced calcification under elevated CO_2 conditions

pCO_2 280-380 ppmv
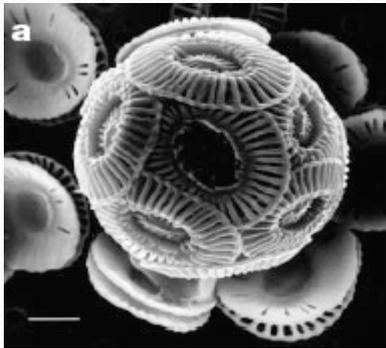
pCO_2 780-850 ppmv
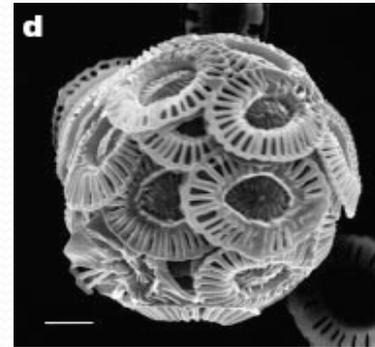
Calcification decreased

- 9 to 18%
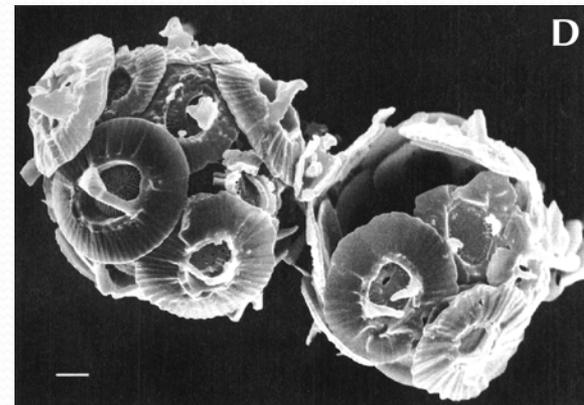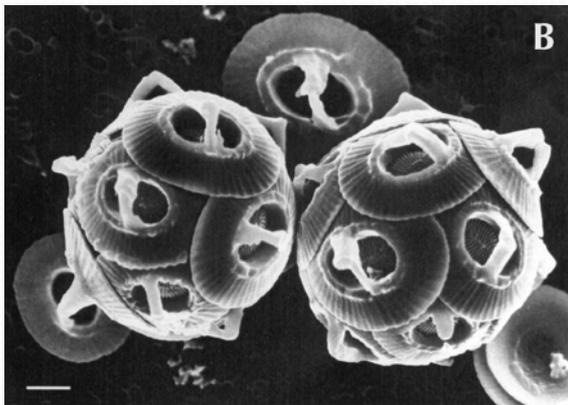
- 45%

Chemical Reactions of Carbonate Species in Seawater

CO_2

$CO_2 aq$ $(CO_2 + H_2O)$ $\overset{K_1}{\longleftrightarrow}$ $HCO_3^- + H^+$ $\overset{K_2}{\longleftrightarrow}$ $CO_3^{2-} + H^+$

$CaCO_3$ $\longleftrightarrow$ Ca^{2+}

calcification

$CaCO_3 + CO_2 + H_2O$

dissolution

$Ca^{2+} + 2HCO_3^-$
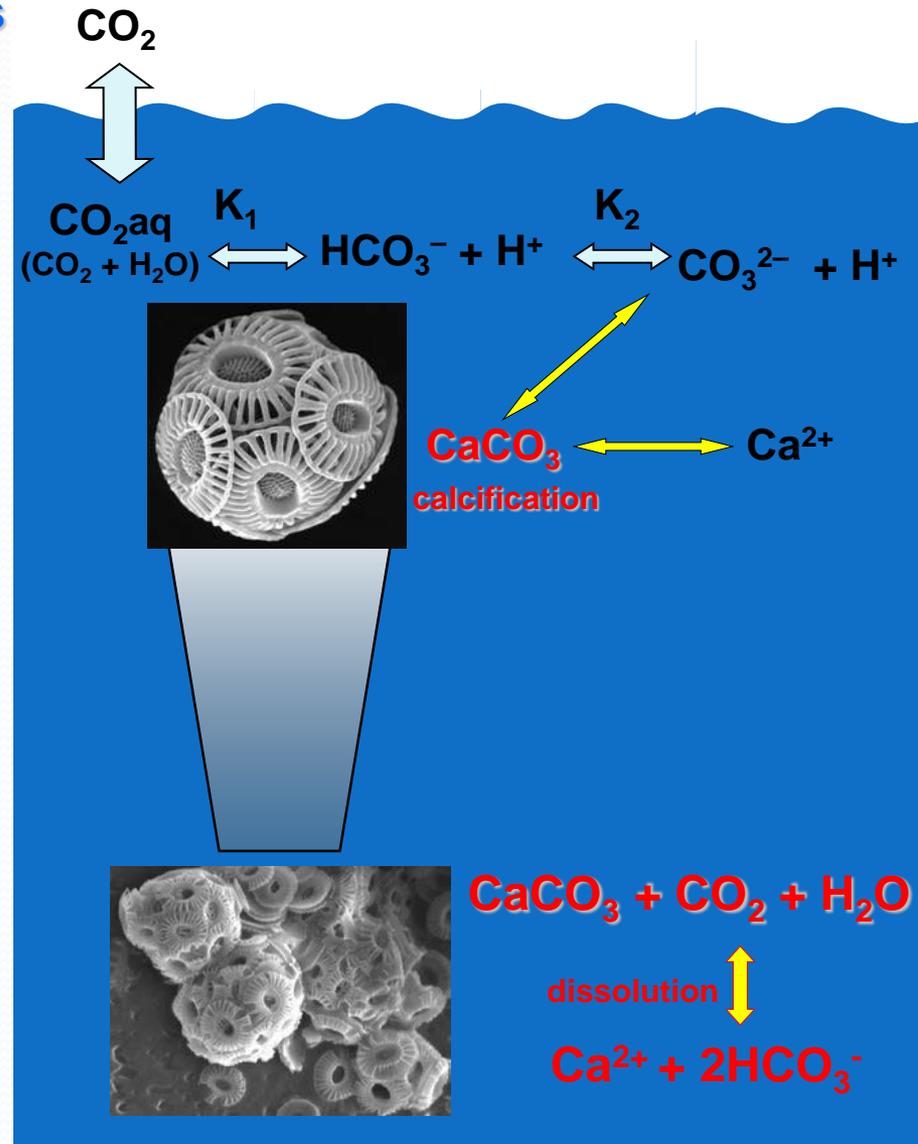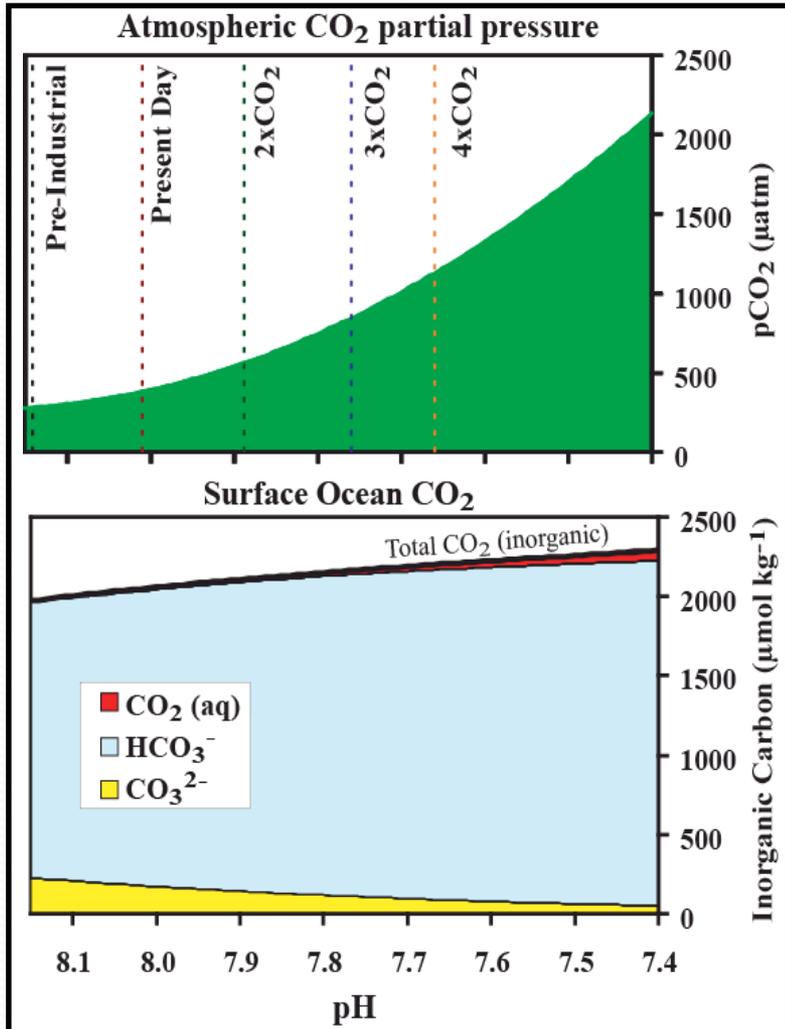
Pteropod response to acidification

Clio pyramidata

© 2003 - G. & Ph. Poppe

Data from a species of pteropod (*Clio pyramidata*) indicate net shell dissolution occurs in live pteropods when the saturation state of seawater with respect to aragonite is forced below 1. Even though the animals were actively swimming, shell dissolution occurs within 48 hours when live pteropods, collected in the subarctic Pacific, are exposed to aragonite undersaturation levels similar to those projected for Southern Ocean surface waters by year 2100.

Pteropod shell dissolution under 2100 scenario
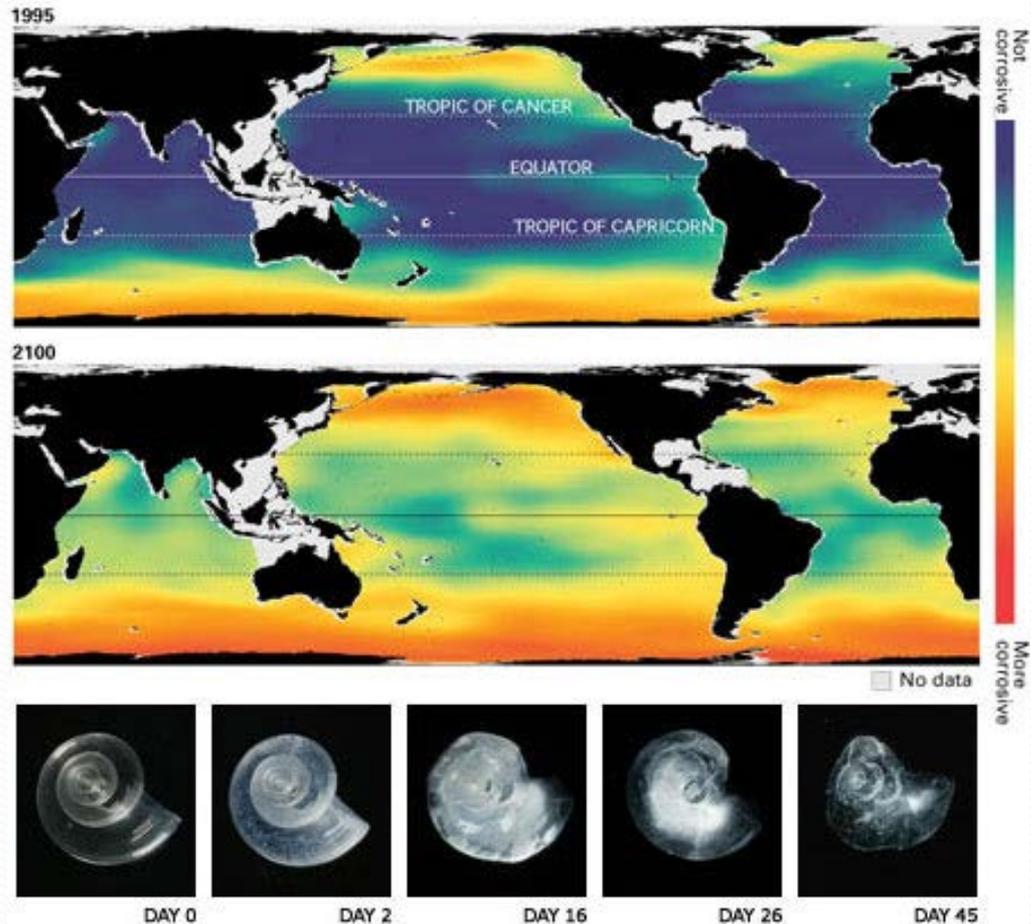
"If carbon dioxide continues to rise unchecked, computer models show that acidification will deplete carbonate ions in much of the ocean by 2100, turning the waters corrosive for many shell-building animals."

www.nationalgeographic.com

Projections of future surface seawater saturation state
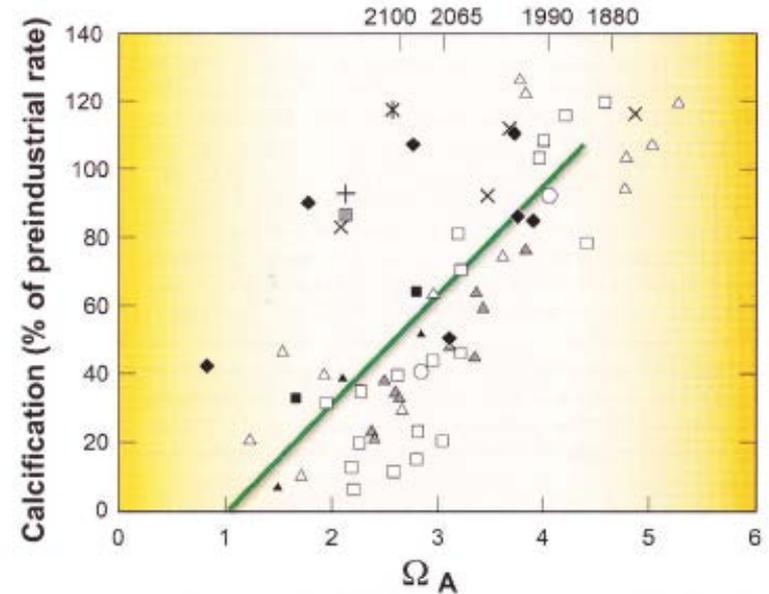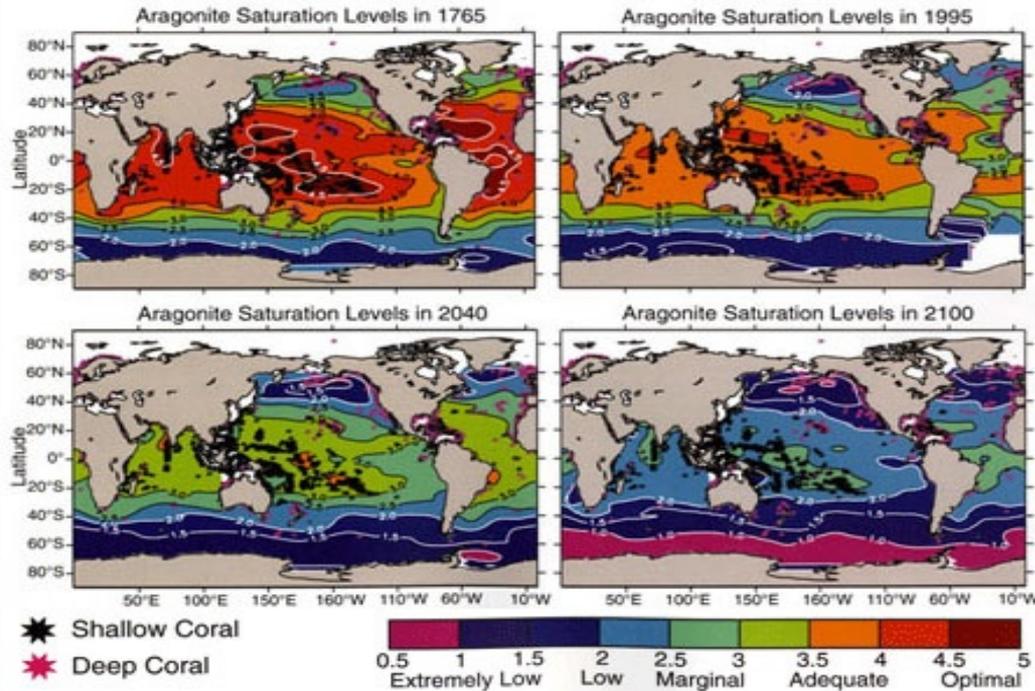
FIGURE 7 Percentage of the preindustrial rate of coral calcification (secretion of aragonite) as a function of the saturation state of aragonite (Ω_A) in seawater. Overlaid is a timescale showing the saturation state as a function of time. DATA FIT AND SUMMARIZED BY LANGDON AND ATKINSON (2005)

Primary production and nitrogen fixation

Most marine phytoplankton show little or no change in photosynthetic rates when grown under high pCO_2 conditions equivalent to ~760 ppmv, but … (Martin and Tortell, 2006, *Limnol. Oceanogr.* 51: 2111-2121).

… in all species of seagrasses tested to date, light-saturated photosynthetic rates (and reproductive output) increase dramatically with increase dissolved $CO_2(aq)$ concentration (see Palacios and Zimmerman, 2007, *Mar. Ecol. Prog. Ser.* 344: 1-13; Jiang et al., 2010, JIPB 52(10): 904-913).

Ecological and biogeochemical impacts

Clio pyramidata
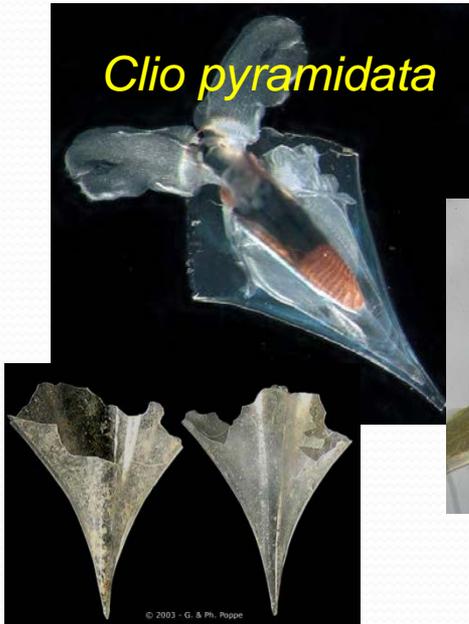
In the North Pacific, pteropods can be important prey of juvenile pink salmon, accounting in some years for >60% by weight of their diet (Armstrong et al., 2005, *DSR II*, 52: 247).

Obelia medusa

Aglantha digitale

In the North Sea, one study has provided an interesting link between decreasing ocean pH and increasing jellyfish frequency since 1970 (Attrill et al., 2007, Limnol. Oceanogr. 52: 480).

Projection of ocean acidification

$CaCO_3 + CO_2 + H_2O$
$\rightarrow Ca^{2+} + 2HCO_3^-$
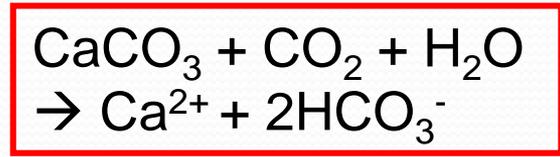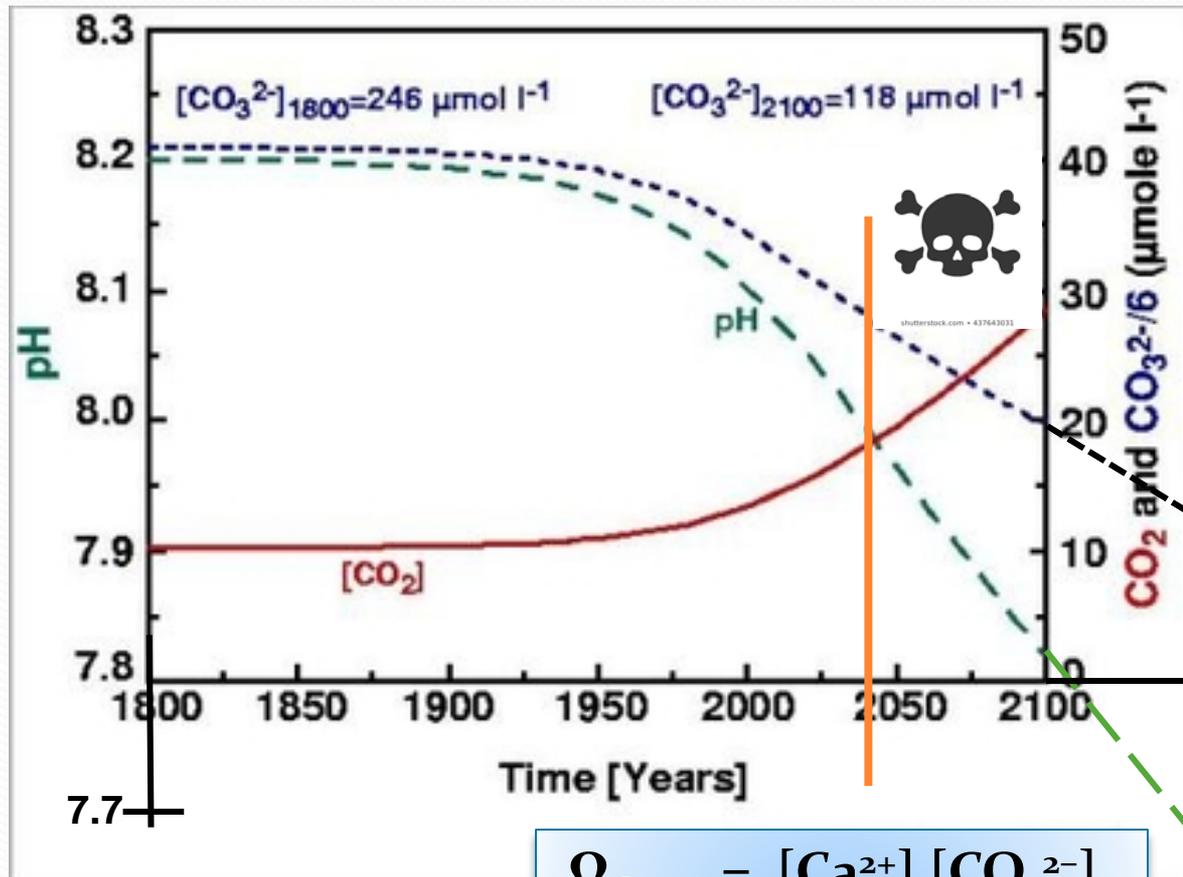
Dissolution of corals

$$\Omega_{C\,or\,A} = \frac{[Ca^{2+}]\,[CO_3^{2-}]}{K^*_{C\,or\,A}}$$

Variation in CaCO$_3$ dissolution rates between 2006-2035 and 2071-2100

Δr (mol m^{-2} yr^{-1})

From: Sulpis et al. (GBC, 33: 1654-1674, 2019)
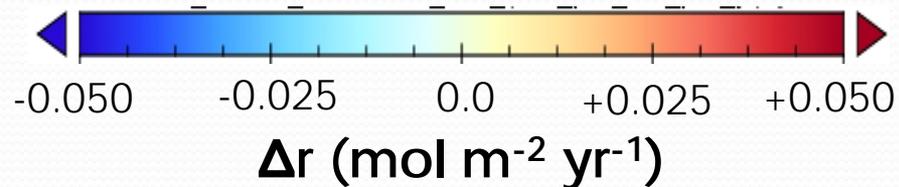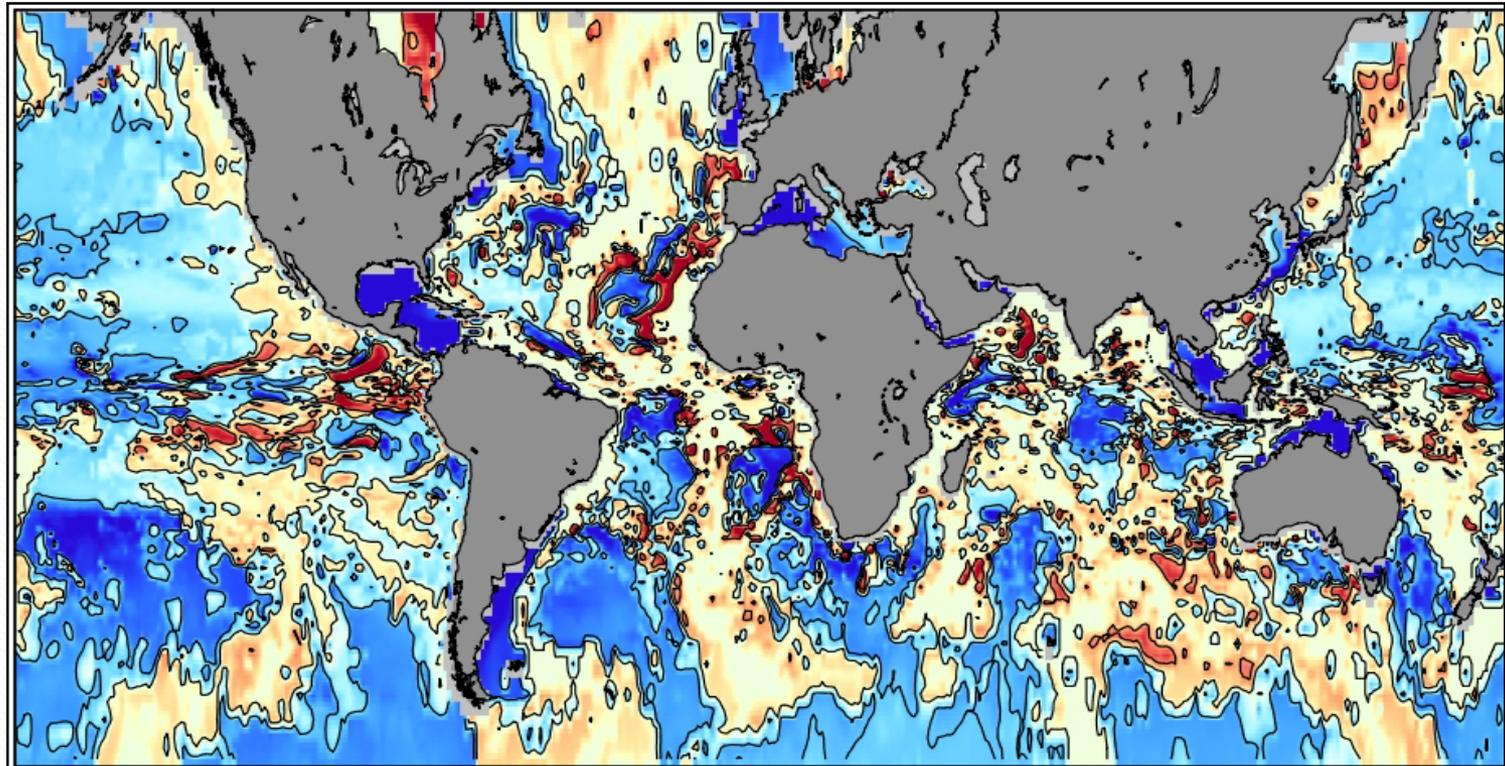
Volcanic carbon dioxide vents show ecosystem effects of ocean acidification.
Jason M. Hall-Spencer et al. Nature 454: 96-99, 2008