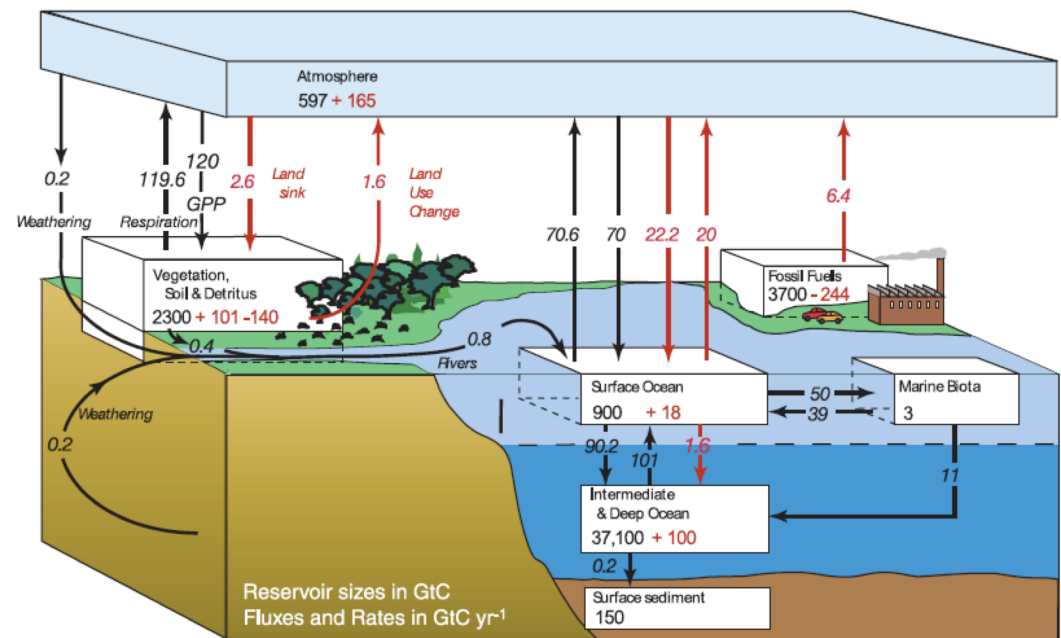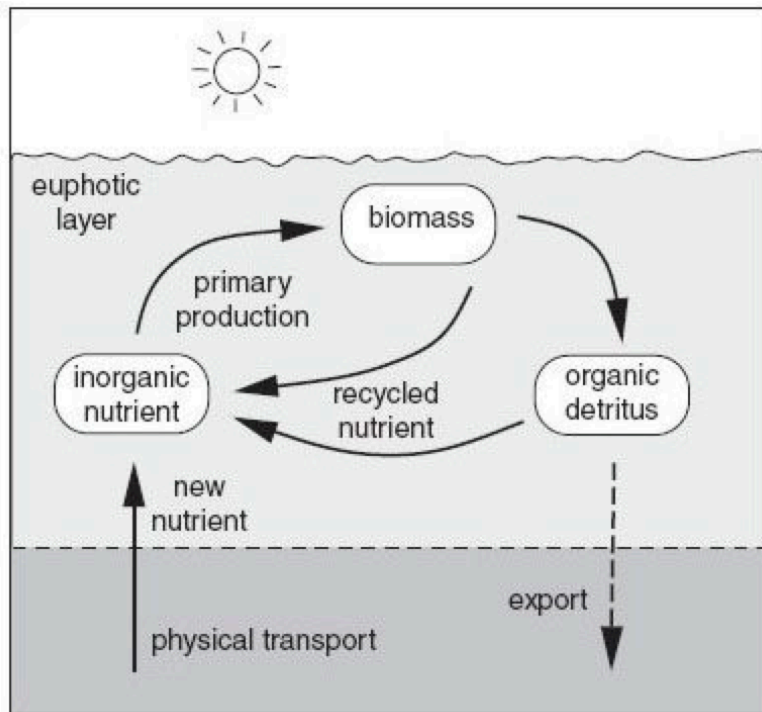# Week 12: Nutrient and carbon cycling
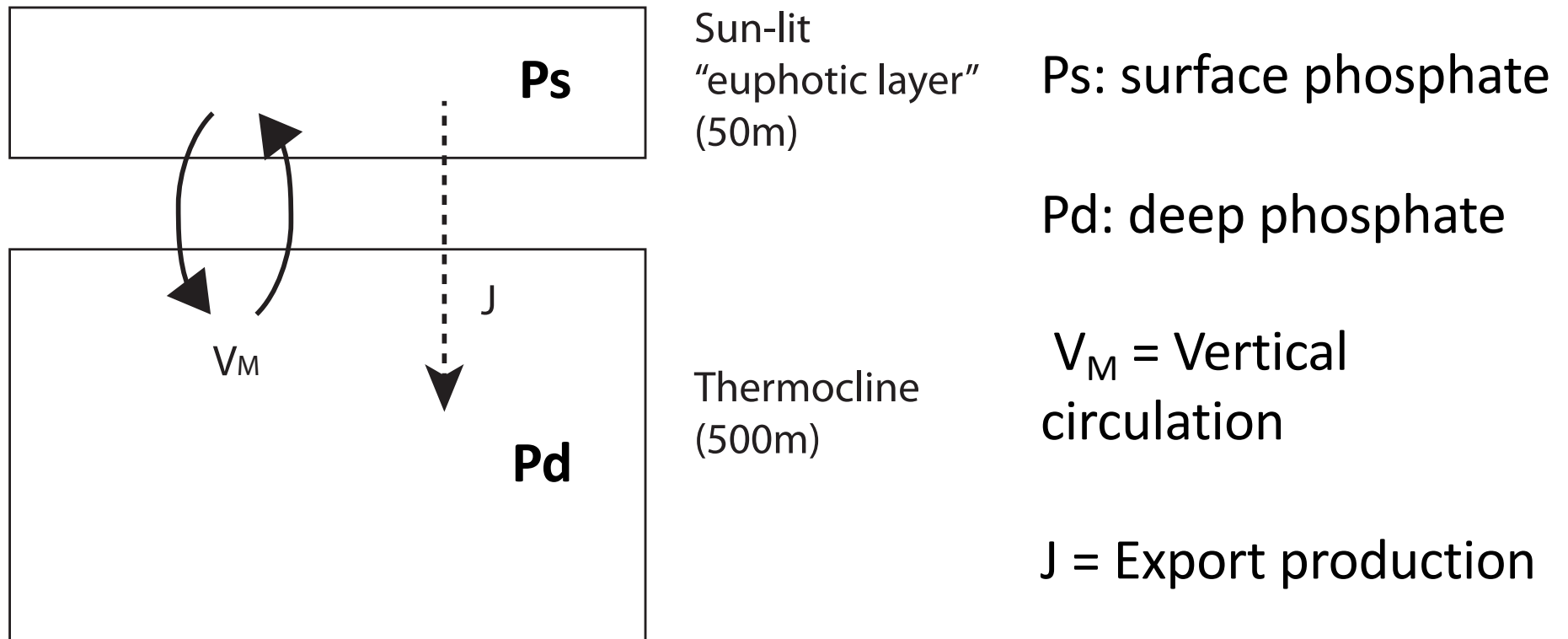
1 GtC (giga-tons C) = 1 PgC (peta-grams C) = 10^{15} gC
Figure credit: IPCC, N. Gruber

10-15PgC/yr: NCP ~ export of organic carbon from surface euphotic layer to the thermocline and deep waters

A simple nutrient cycle model

Ps

Sun-lit "euphotic layer" (50m)

V_M

J

Pd

Thermocline (500m)

Ps: surface phosphate

Pd: deep phosphate

V_M = Vertical circulation

J = Export production

Downward organic flux (J) is balanced by the vertical transport at steady state: the balance regulates the vertical gradient

2-box nutrient cycle model

$$V_s \frac{dP_s}{dt} = V_M(P_d - P_s) - \lambda_{bio} V_s P_s$$

$$V_d \frac{dP_d}{dt} = V_M(P_s - P_d) + \lambda_{bio} V_s P_s$$

V_s : volume of the surface box (m³)

V_d : volume of the deep box (m³)

V_M: vertical circulation rate (m³/s)

P_S: surface P concentration (molP/m³)

P_D: deep P concentration (molP/m³)

λ_{bio}: biological P export rate (1/s)

Steady state solutions

Conservation of nutrient

$$V_s P_s + V_d P_d = const$$

Solution for surface nutrient

$$P_s = \frac{P_d}{1 + \frac{\lambda_{bio} V_s}{V_M}}$$

Dimensionless number (γ) measuring relative strengths of biological P export and circulation supply.

Solution for export production

$$J = \left(\frac{\gamma}{1 + \gamma}\right) V_M P_d$$

Some numbers…

- Each year, human activity emits about 10PgC
  - About half of it remains in the atmosphere
  - Remaining half goes into the land and the ocean
- Each year, marine photosynthesis fixes 50PgC of carbon dioxide into organic matter
  - About 30% of it sinks to the thermocline/deep ocean
- The oceans contain 90+% of carbon molecule in the atmos/land/ocean system
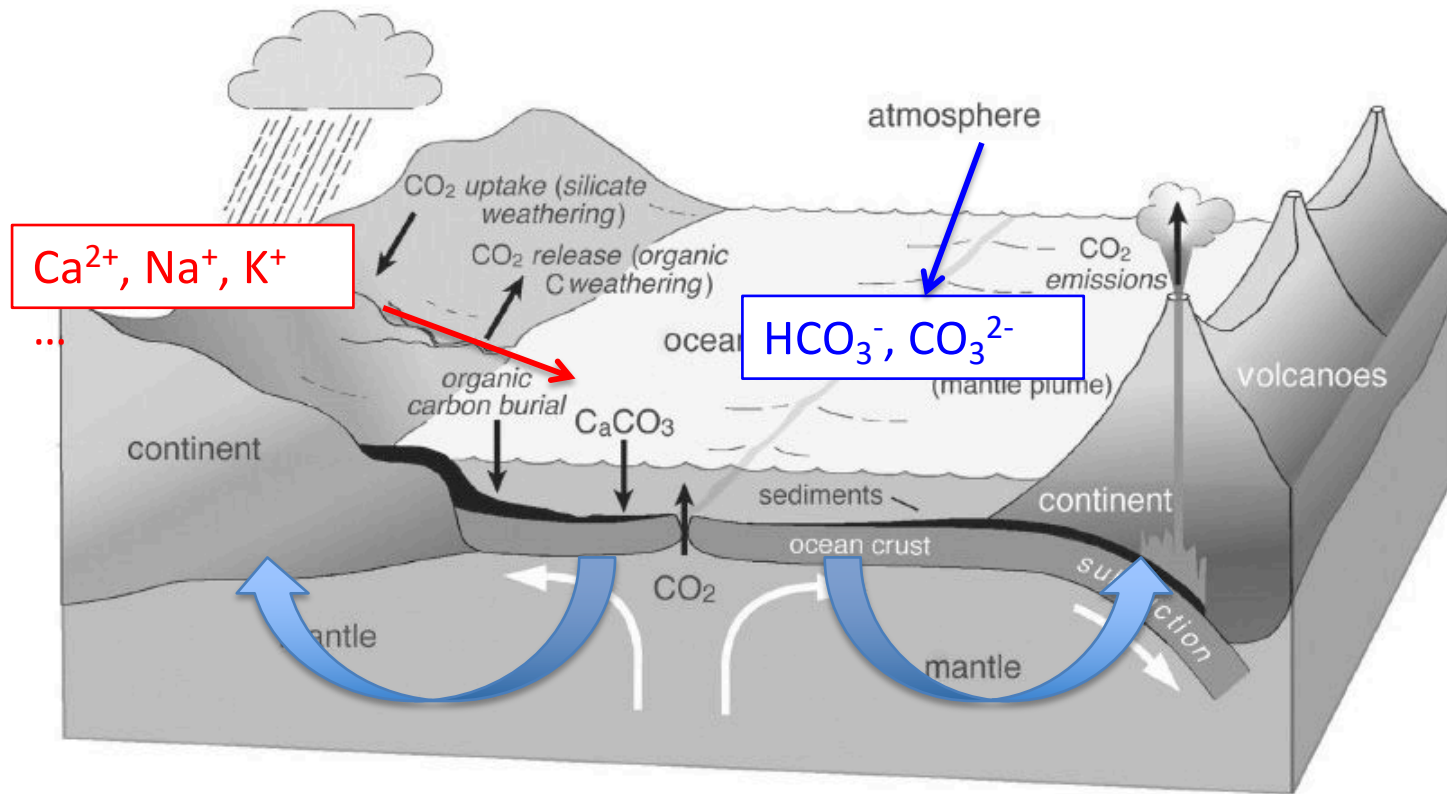 - 38,000 PgC as dissolved inorganic carbon

Why the oceans contain such a large amount of carbon?

- CO_2 is soluble and reacts with water
  - DIC (dissolved inorganic carbon) or Total Carbon

$$DIC = \underbrace{[CO_2*]}_{<1\%} + \underbrace{[HCO_3^-]}_{\sim 90\%} + \underbrace{[CO_3^{2-}]}_{\sim 10\%}$$
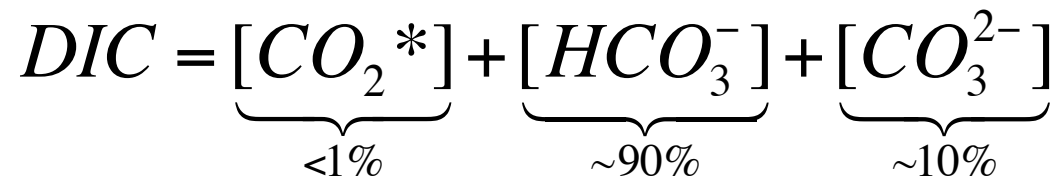
 - Why most of carbon molecules are in bicarbonate and carbonate ions?

Geological carbon cycle

- Cycling of carbon between rocks, air and seawater
- "Carbonate Buffer System": positive and negative ions must balance each other → electron balance
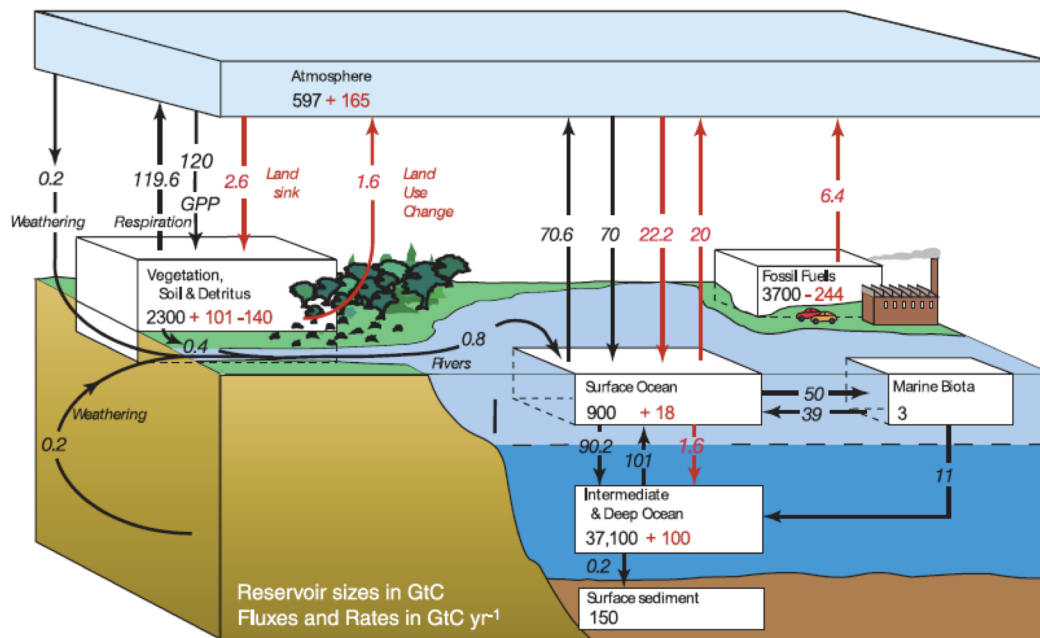
Residence time of nutrients and carbon

- MRT = (mean residence time)
  = (inventory) / (flux)

Inventory:
X PgC

Flux in

Flux out

Fluxes: Y PgC/yr
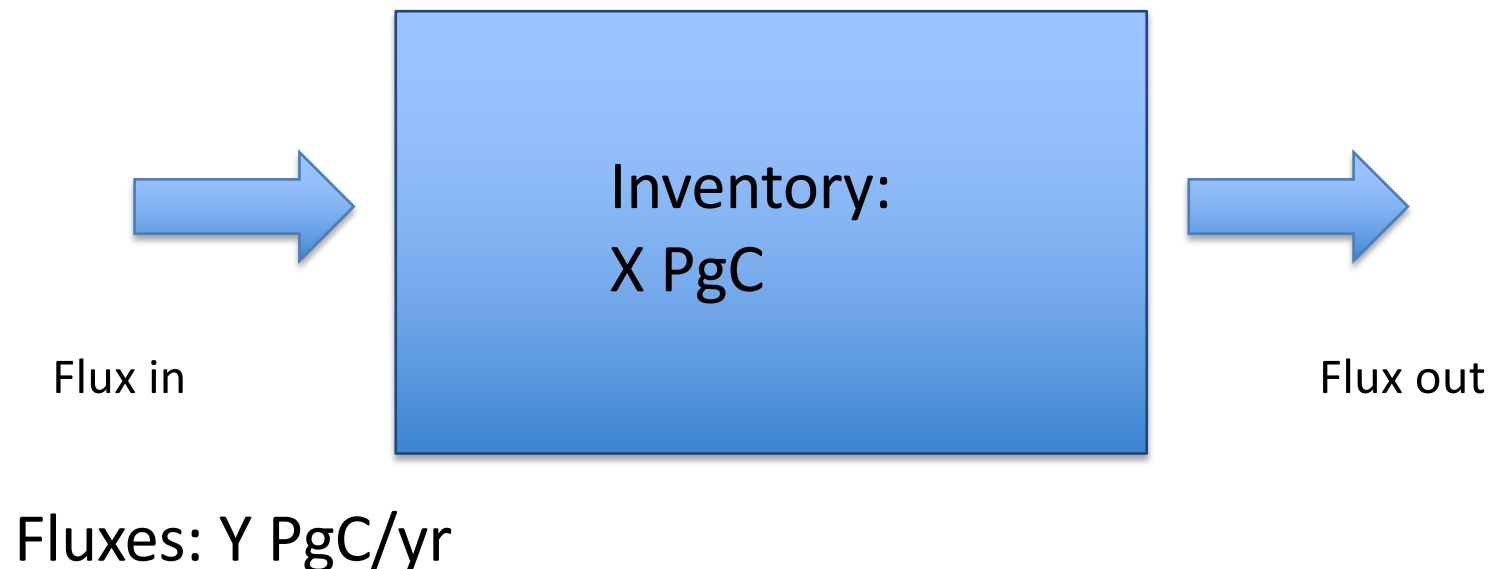
MRT = (X, PgC)/(Y, PgC/yr) = X/Y, yr

Example: what is the MRT of carbon biomass in the marine/land biota?

Carbon inventory in marine biota = 3PgC

NPP ~ 50 PgC/yr

MRT = 3 / 50 = 0.06 yr

c.f. Carbon inventory in land biota = 2300 PgC
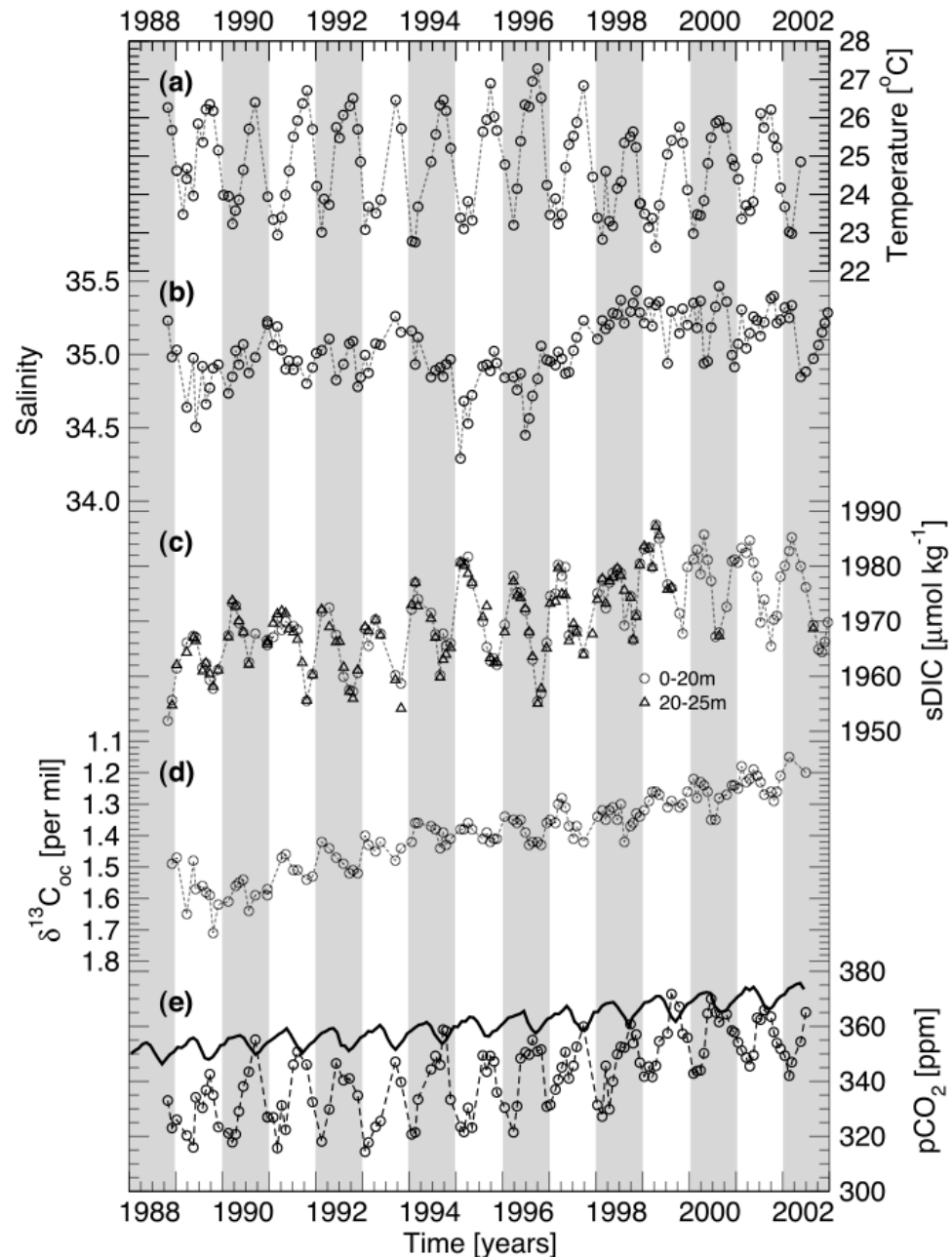NPP ~ 50 PgC/yr
MRT = 2300 / 50 = 46 yr

Observed seasonal cycle in Hawaii

- **Brix et al. (2004)**

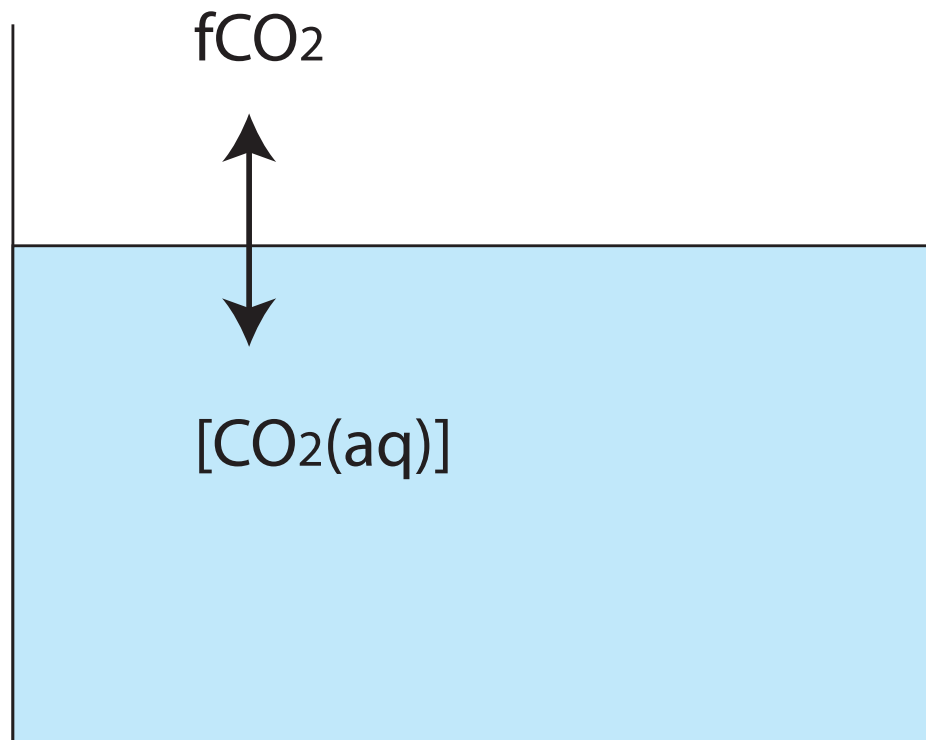During the summer, low DIC coincides with high SST → Biological C uptake and export.

pCO2 is high during the summer (low solubility)

Long term increase in C and decrease in C-13 (Suess effect)

Solubility of gases in the seawater

- CO_2 is a soluble gas
- Solubility of CO2 = how many CO2 molecule can be dissolved in a unit mass of seawater at equilibrium

fCO2

[CO2(aq)]

Note: Surface ocean is not always at equilibrium… sometimes under-saturated and super-saturated, depending on many factors including biological C uptake, heating/cooling, transport, etc.

Solubility: Henry's law

- CO_2 solubility (here, K_0) is a function of temperature and salinity (units: molC m^{-3} atm^{-1})

- Square bracket [] indicates concentration

- Fugacity (fCO2) and partial pressure (pCO2) are almost equivalent (~1%) difference → activity vs concentration
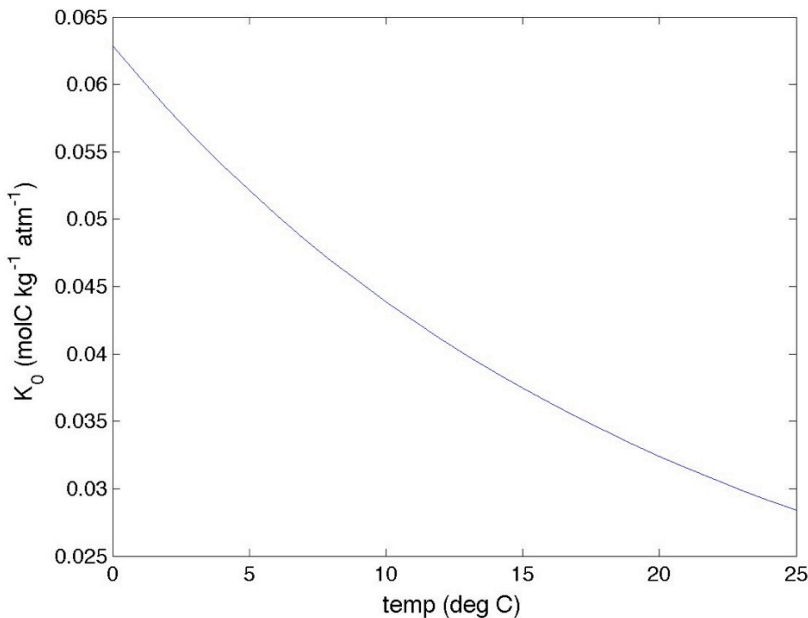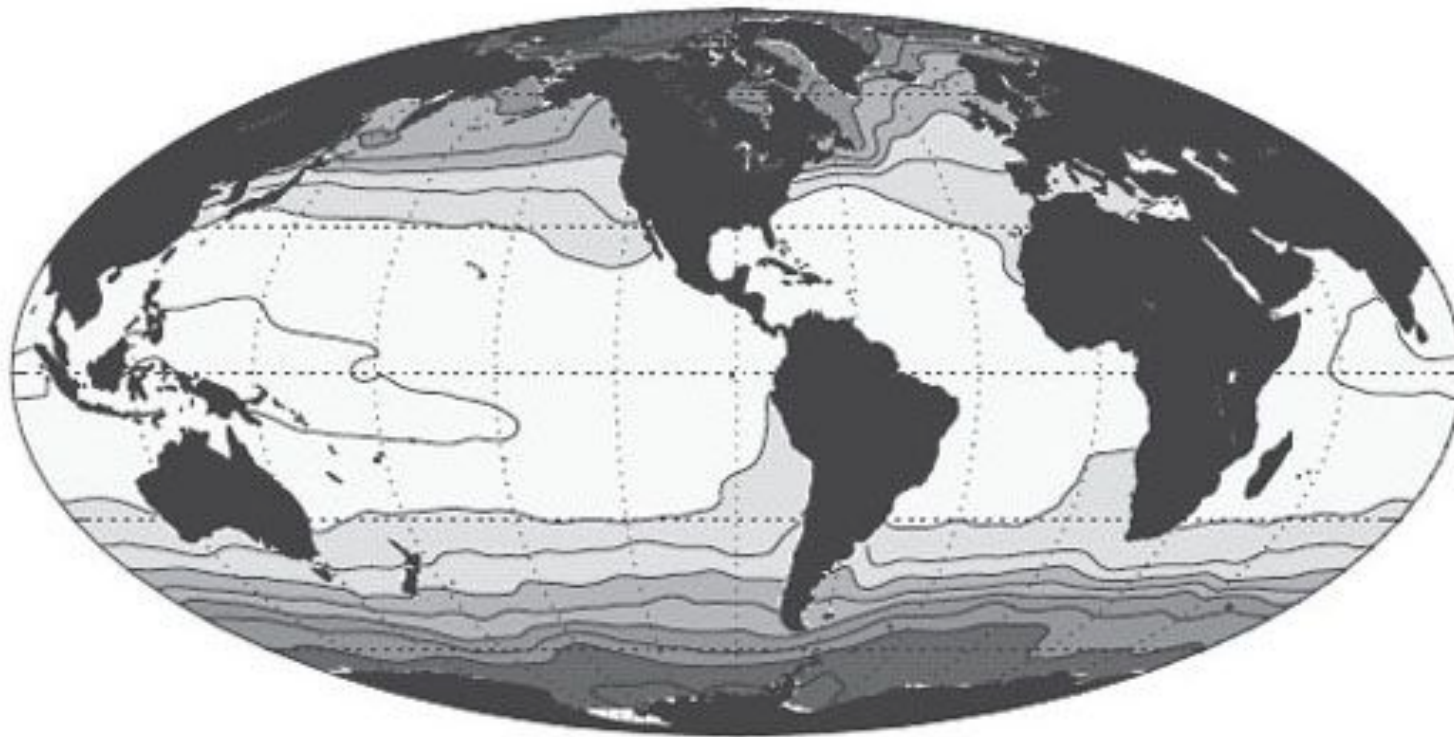

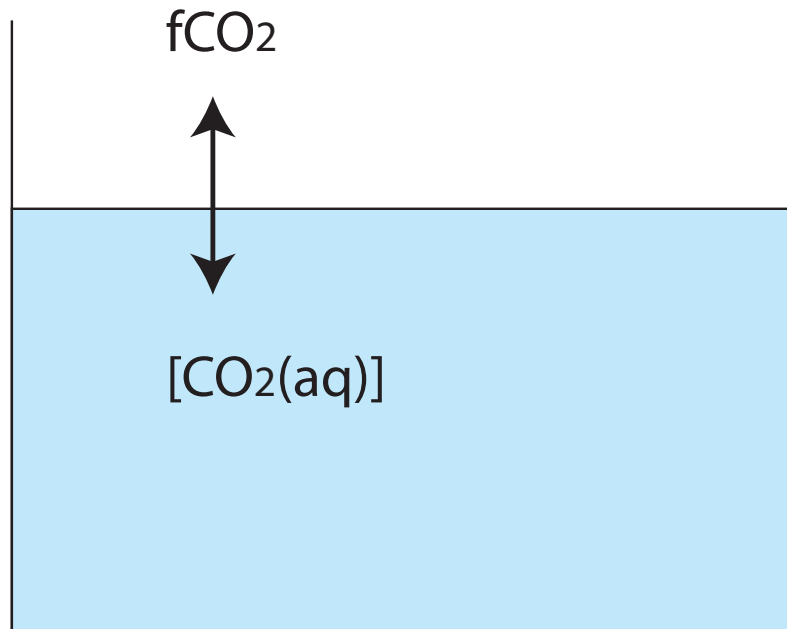$$[CO_2] = K_0 \, fCO_2$$
$$K_0 = K_0(T, S)$$
$$fCO_2 \sim pCO_2$$

Mapping the solubility of CO$_2$

(a) solubility (mol kg^{-1} atm^{-1})

0.02   0.03   0.04   0.05   0.06   0.07

Air-sea exchange

- Surface ocean exchanges gases with the overlying atmosphere: how does it happen?
- Two types of gas exchange kinetics
  - Diffusive gas exchange
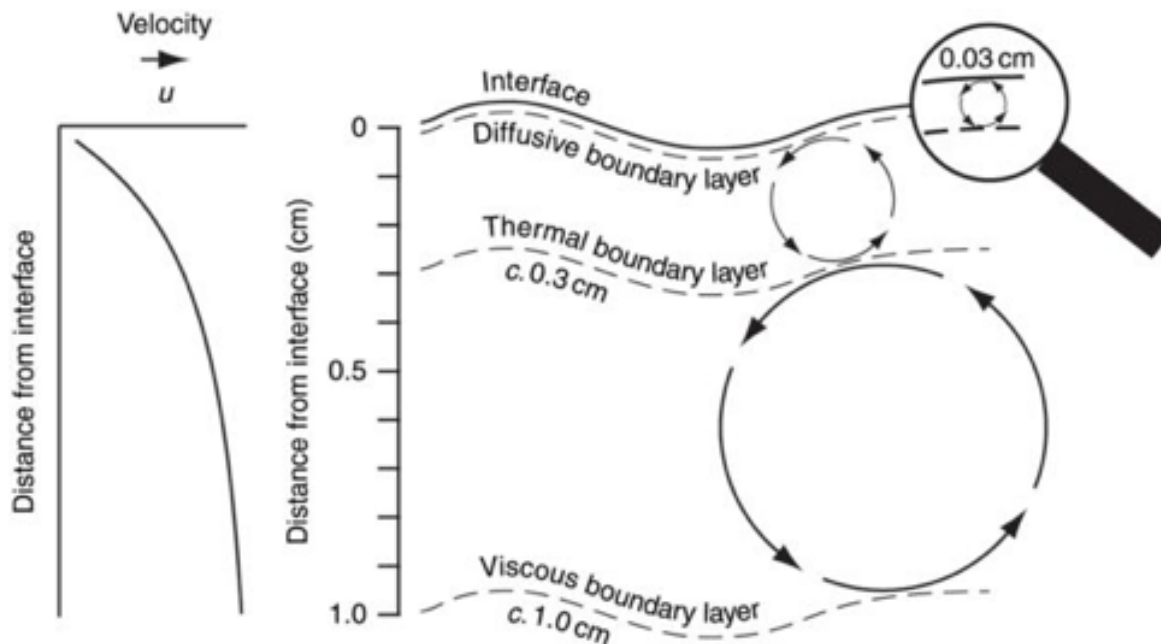 - Bubble mediated gas exchange

fCO_2

$[CO_2(aq)]$

The rate at which the gas molecule is exchanged at the air-sea interface depends on the types of physical processes responsible.

Diffusive gas exchange

- Molecular diffusion at the diffusive boundary layer
  - Enhanced by the turbulent mixing
- G: gas transfer coefficient (m s^{-1})

$$(outflux) = G\left([CO_2] - [CO_{2,sat}]\right)$$
$$= GK_0\left(pCO_{2,ocn} - pCO_{2,atm}\right)$$

Note: diffusive flux is down-gradient between ocean and atmosphere.

The rate coefficient (G) depends on the near-surface turbulence

Velocity

u

Distance from interface

Distance from interface (cm)

0

0.5

1.0

Interface

0.03 cm

Diffusive boundary layer

Thermal boundary layer
c. 0.3 cm

Viscous boundary layer
c. 1.0 cm

Controls on air-sea gas transfer rates

- G: gas transfer coefficient (ms^{-1})
  - Turbulence in the surface ocean
  - Depends on:
    - Surface wind speed
    - Schmidt number (Sc)
      - Viscosity of the water
      - Molecular diffusivity of gas in the water

$$S_C = \frac{\text{Viscosity}}{\text{Diffusivity}}$$
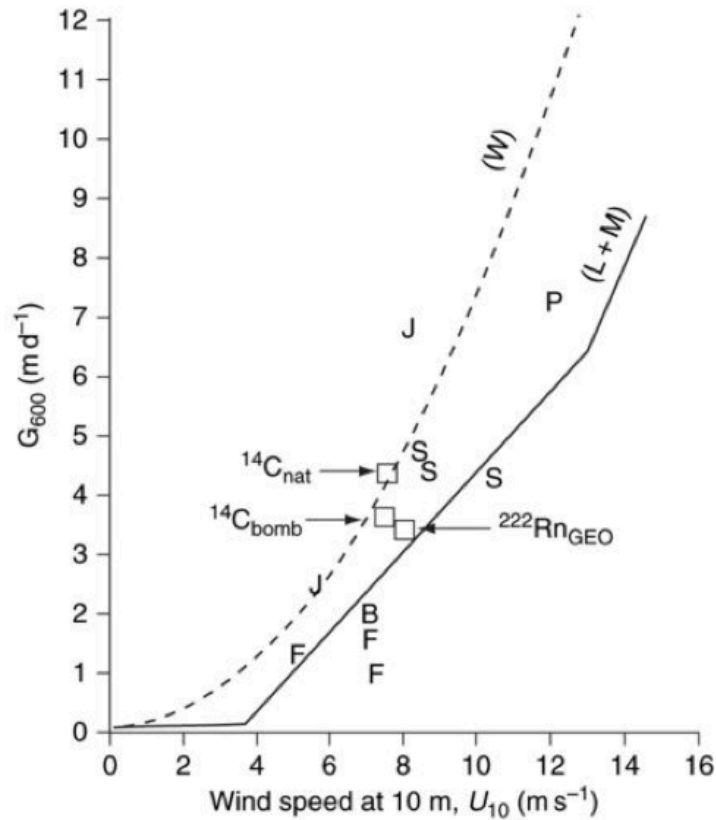
$$G = G_0(U_{spd})S_C^{-n}$$

Wind dependence of G

Figure 10.6. Gas transfer rates normalized to a Schmidt number of 600, G_{600}, from global ^{14}C and localized ^{222}Rn measurements in the ocean as a function of wind speed measured at 10 m above the air–water interface, U_{10}. ^{14}C$_{nat}$ and ^{14}C$_{bomb}$ are the gas exchange rates determined from natural and bomb-produced ^{14}C discussed in the text. The box labeled Rn$_{GEO}$ represents the average result from over 100 ^{222}Rn measurements in the oceans during the GEOSECS
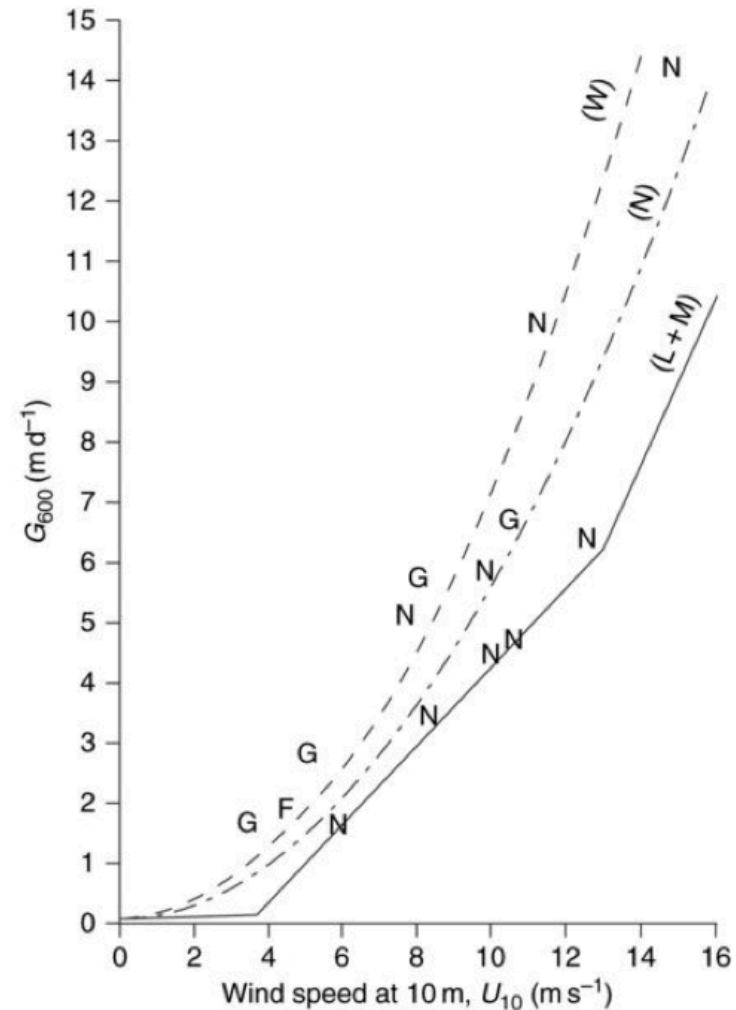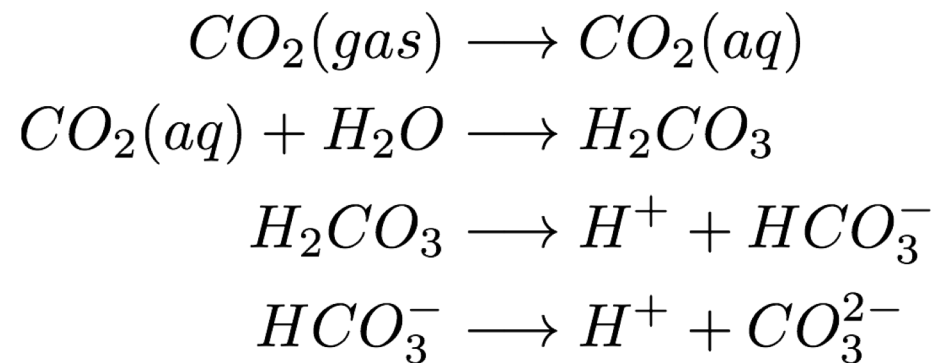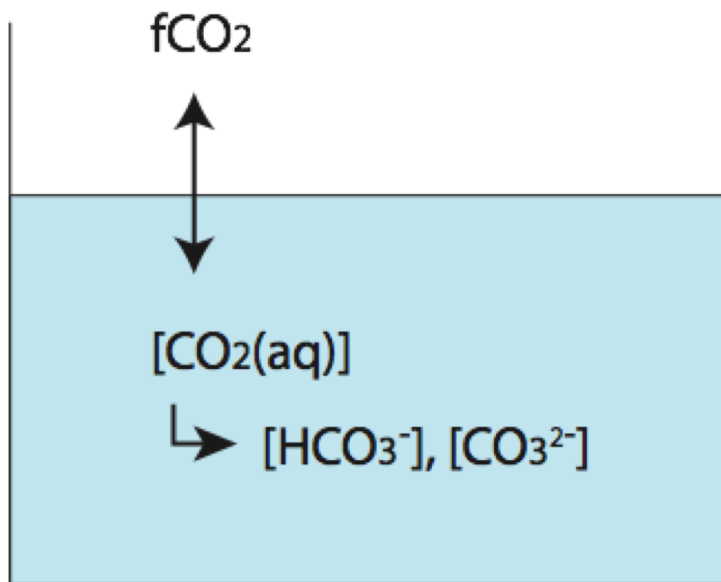
Figure 10.7. Gas transfer velocity, G_{600}, as a function of wind speed, U_{10}, for all dual tracer experiments. N is from the North Sea,

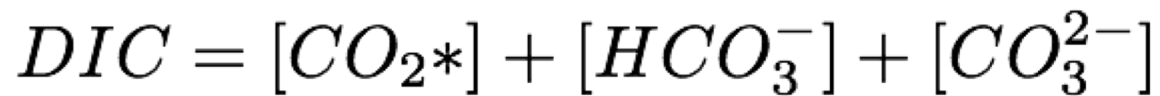# Carbonate chemistry

- Formation of HCO3 and CO3 ions

$$CO_2(gas) \longrightarrow CO_2(aq)$$
$$CO_2(aq) + H_2O \longrightarrow H_2CO_3$$
$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$
$$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$$

Dissolved inorganic carbon

- CO₂ reacts with water to form bicarbonate and carbonate ions
- In aquatic system, carbon inventory is expressed as the sum of inorganic C species

$$[CO_2*] = [CO_2(aq)] + [H_2CO_3]$$
$$DIC = [CO_2*] + [HCO_3^-] + [CO_3^{2-}]$$
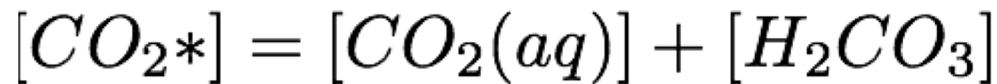
~1% ~90% ~10%

Local Chemical Equilibrium

- These reactions reaches chemical equilibrium within a few minutes

$$CO_2 + H_2O \longleftrightarrow H^+ + HCO_3^-$$
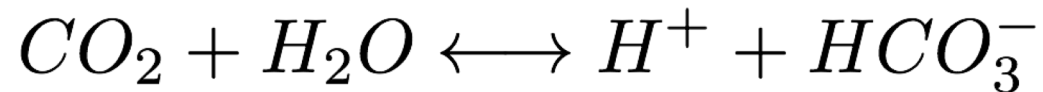
$$K_1(T, S, p) = \frac{[H^+][HCO_3^-]}{[CO_2*]}$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$$
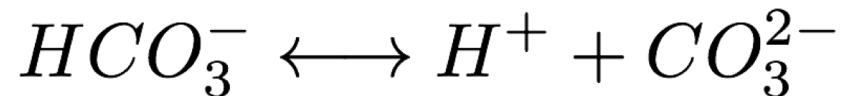
$$K_2(T, S, p) = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

Partitioning of carbon molecule
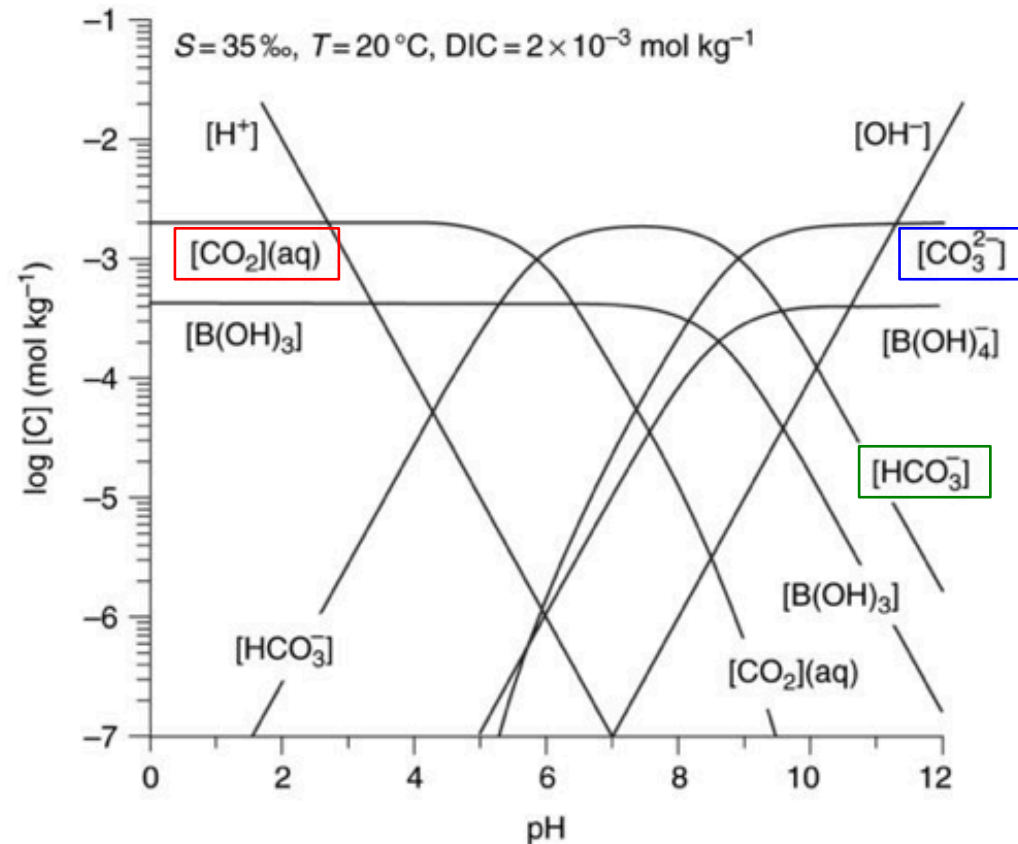
Figure 4.2. Concentrations of the species of the acid–base pairs of carbonate, borate and water in seawater as a function of pH. (Salinity, $S = 35$, temperature, $T = 20$ °C and DIC = 2.0×10^{-3} mol kg^{-1}.)

Partitioning of carbon molecule

$$DIC = [CO_2*] \left(1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right)$$

$$pH = -log_{10}[H^+]$$
$$pK_1 = -log_{10} K_1$$

$$pK_1 \sim 6, \ pK_2 \sim 9$$

At present climate,
pH = 8,

$$\frac{K_1}{[H^+]} \sim 10^2, \ \frac{K_1 K_2}{[H^+]^2} \sim 10$$

Carbonate buffer

- Acid-neutralizing ability of the seawater
  - Initially adding CO_2 molecule increases $[H^+]$
  - Additional $[H^+]$ reacts with carbonate ion
    - Bicarbonate increases twice the rate of initial CO2 addition
    - The change in $[H^+]$ is suppressed as a net effect

$$CO_2 + H_2O \longleftrightarrow H^+ + HCO_3^-$$
$$H^+ + CO_3^{2-} \longleftrightarrow HCO_3^-$$
$$\rule{10cm}{0.4pt}$$
$$CO_2 + CO_3^{2-} + H_2O \longleftrightarrow 2HCO_3^-$$
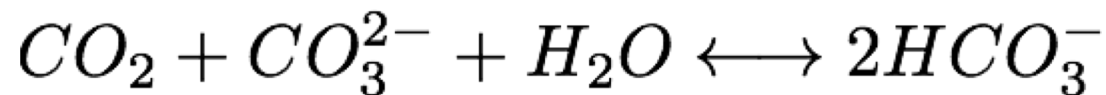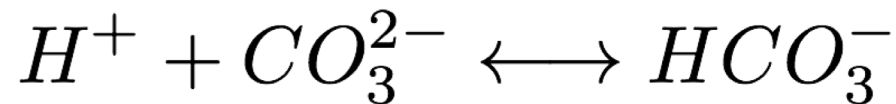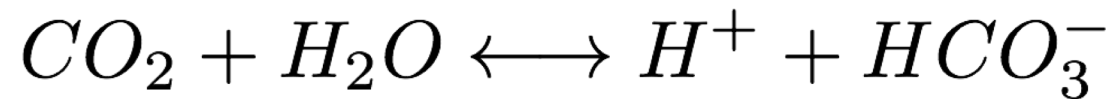
Alkalinity and pH of the seawater

- ## Consider electric neutrality
  - Cations (Na^+, Mg^{2+}, K^+, Ca^{2+}, …)
  - Anions (Cl^-, HCO_3^-, CO_3^{2-}, …)

  - Group cations and anions into strong and weak ions

$$[Na^+] + 2[Mg^{2+}] + [K^+] + 2[Ca^{2+}]... = [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}]...$$

$$A_T = [Na^+] + 2[Mg^{2+}] + [K^+] + 2[Ca^{2+}] - [Cl^-]...$$
$$= [HCO_3^-] + 2[CO_3^{2-}]...$$
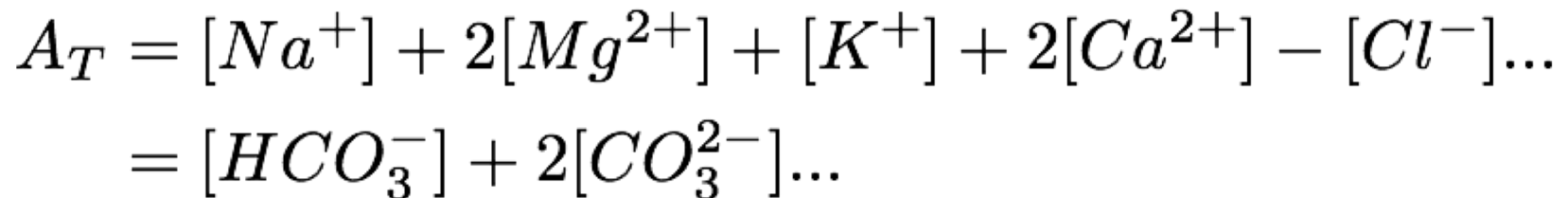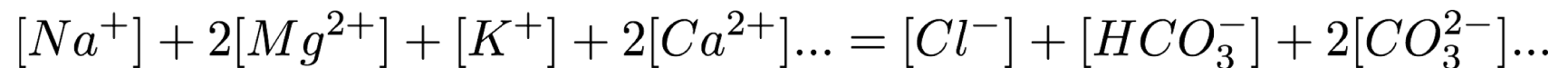
Carbonate alkalinity

- Alkalinity (A_T), carbonate alkalinity (A_C) and DIC
  - Carbonate alkalinity (A_C: about 90% of A_T) contains only bicarbonate and carbonate ions.

$$0.9A_T \sim A_C = [HCO_3^-] + 2[CO_3^{2-}]$$

$$DIC \sim [HCO_3^-] + [CO_3^{2-}]$$

$$A_C \sim [HCO_3^-] + 2[CO_3^{2-}]$$

Useful approximations

$$DIC \sim [HCO_3^-] + [CO_3^{2-}]$$

$$A_C \sim [HCO_3^-] + 2[CO_3^{2-}]$$

Thus

$$[CO_3^{2-}] \sim A_C - DIC$$

$$[HCO_3^-] \sim 2DIC - A_C$$
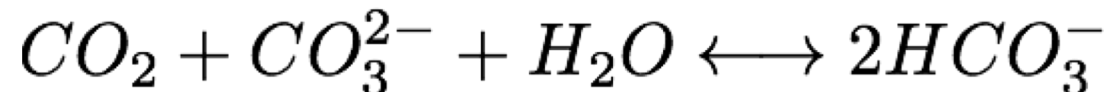
Note: CO_2 addition will increase DIC but not alkalinity. HCO_3^- increases twice the rate of DIC at the expense of CO_3^{2-}

And,

$$[H^+] \sim K_2 \left(\frac{2DIC - A_C}{A_C - DIC} \right) \qquad [CO_2*] \sim \frac{K_2}{K_1} \left(\frac{\{2DIC - A_C\}^2}{A_C - DIC} \right)$$

Control of pH
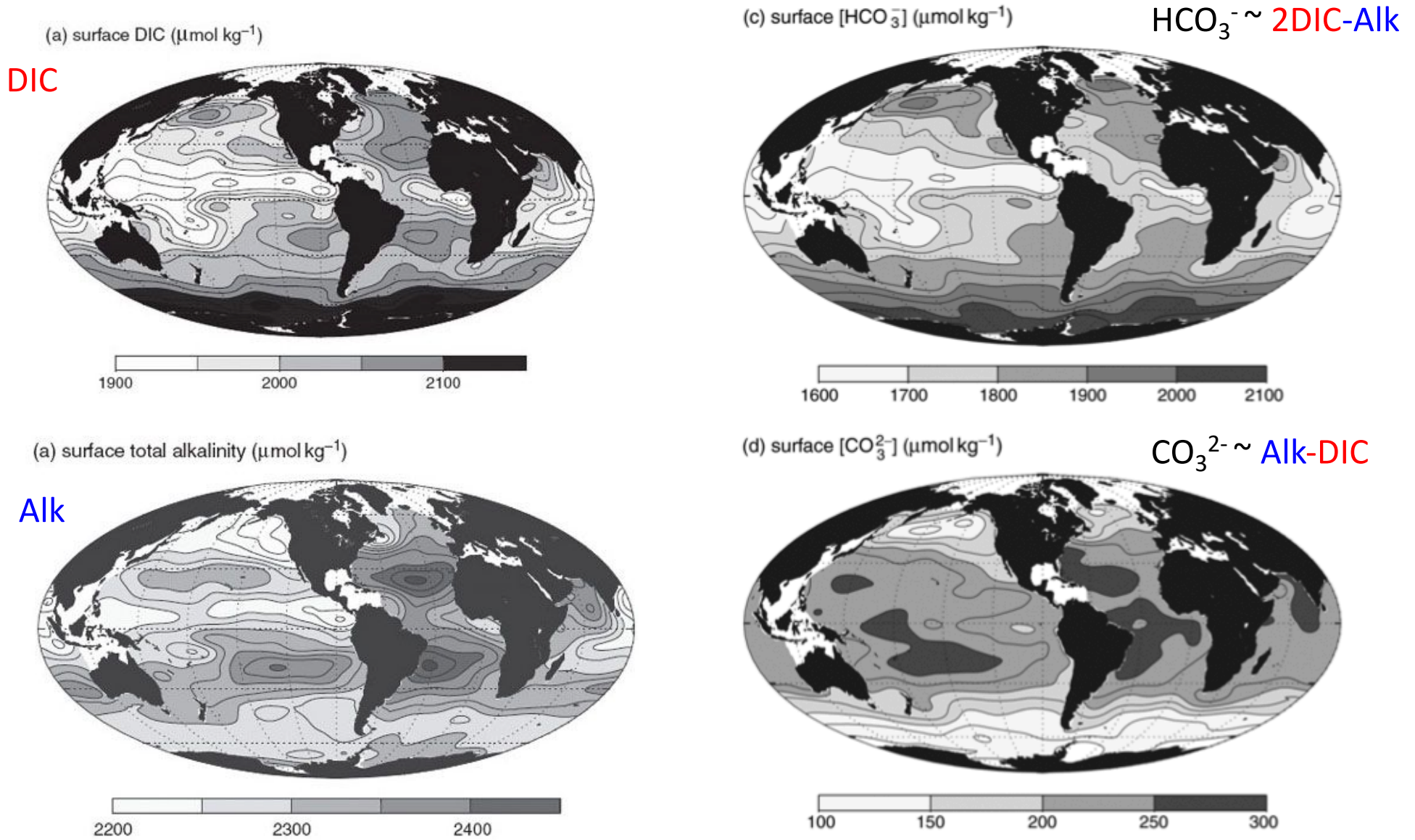
- On average the pH of seawater is about 8.
  - The pH is maintained by the balance between CO_2 and alkalinity level of the seawater.

$$CO_2 + CO_3^{2-} + H_2O \longleftrightarrow 2HCO_3^-$$

  - In a CO_2-rich ocean, the balance shifts to the right, i.e. ocean acidification.

$$[H^+] = K_2 \frac{[HCO_3^-]}{[CO_3^{2-}]} = K_2 \frac{2DIC - A_C}{A_C - DIC}$$

Spatial distributions

(a) surface DIC (μmol kg^{-1})

DIC


```
1900          2000          2100
```

(a) surface total alkalinity (μmol kg^{-1})

Alk


```
2200          2300          2400
```

(c) surface [HCO$_3^-$] (μmol kg^{-1})

$HCO_3^- \sim 2DIC-Alk$


```
1600   1700   1800   1900   2000   2100
```

(d) surface [CO$_3^{2-}$] (μmol kg^{-1})

$CO_3^{2-} \sim Alk-DIC$


```
100    150    200    250    300
```

Williams_Fig. 6.4c,d

DIC in the oceans
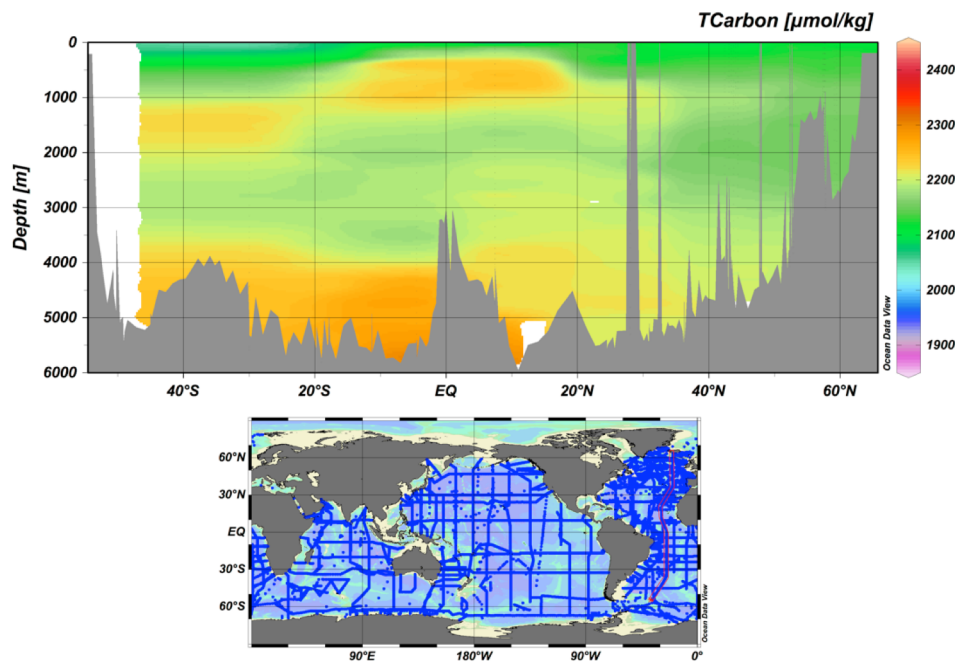
Atlantic

Pacific

WOCE (1990s)

Alk in the oceans

Atlantic

Pacific

WOCE (1990s)

Anthropogenic CO$_2$

So far, the oceans absorbed about 1/3 of CO$_2$ emission
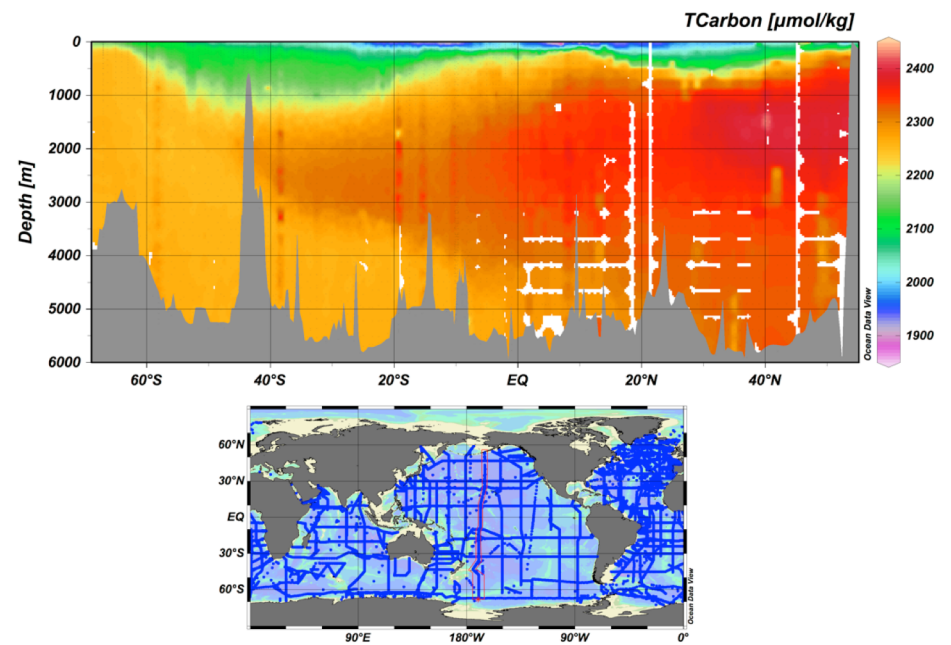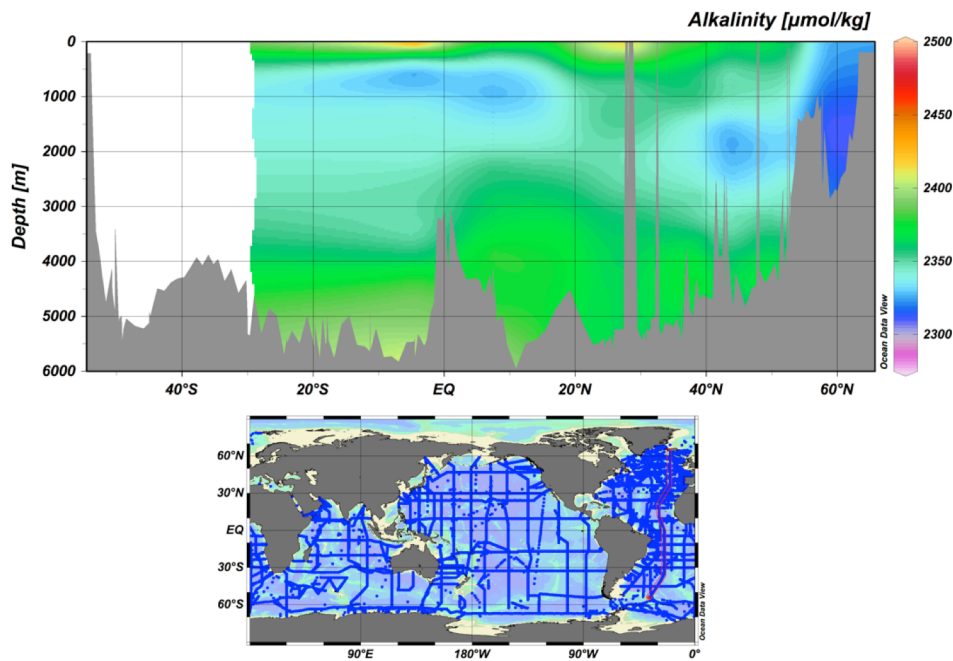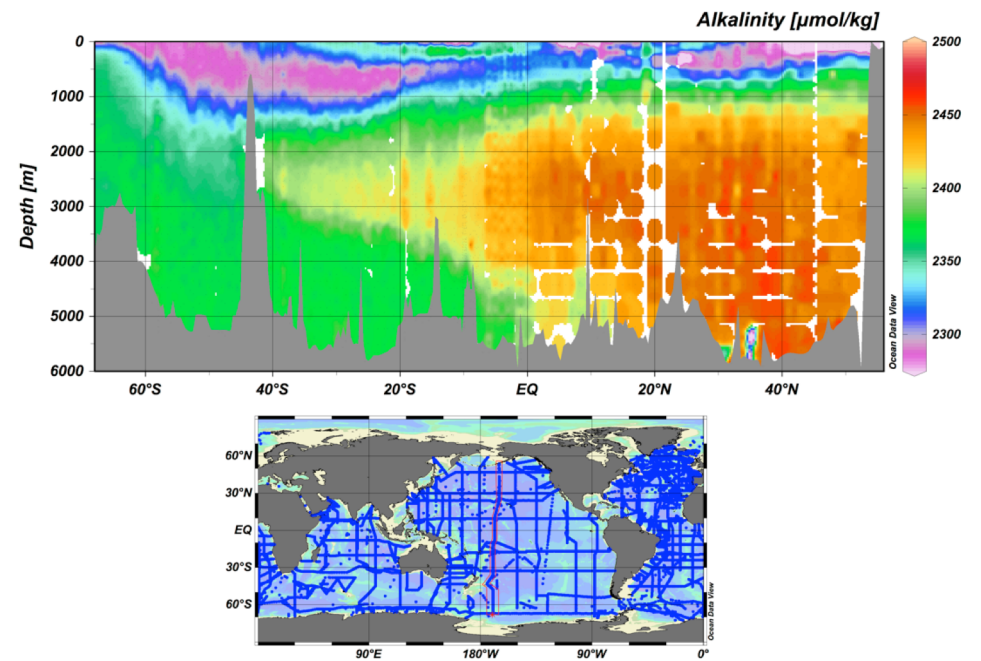The best estimate for the last few decades that ocean absorbs
CO$_2$ at the rate of about 2 PgC/year.
What regulates its spatial pattern?
Most of anthropogenic CO$_2$ remains within the top 1,000m in
the oceans. Why?

Anthropogenic CO$_2$
(μmol kg-1)
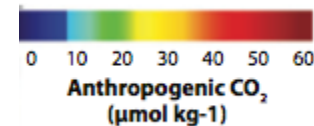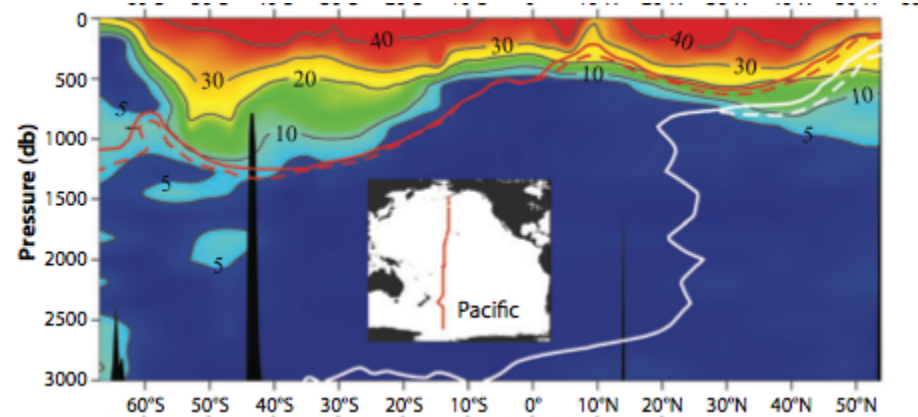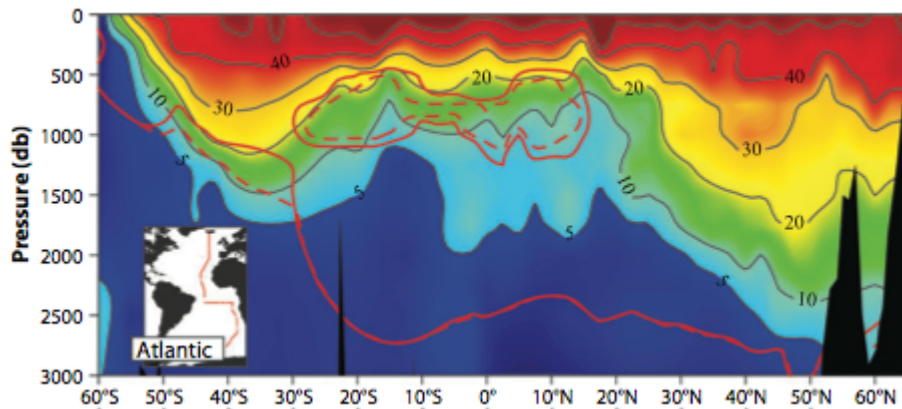
Ocean carbon uptake

- Air-sea gas transfer
  - Wind speed, solubility of CO_2

- Chemical reaction driving the CO_2 uptake:

$$CO_2 + CO_3^{2-} + H_2O \longleftrightarrow 2HCO_3^{-}$$
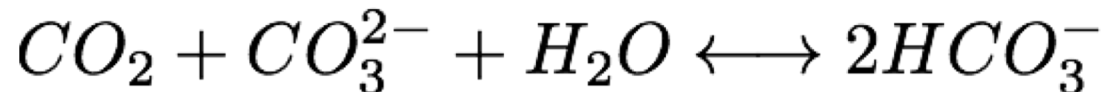
  - Carbon uptake is chemically enhanced by this reaction. $[CO_3^{2-}]$ level controls its efficiency.

Spatial distributions

(a) surface DIC (μmol kg^{-1})

DIC

1900   2000   2100

(c) surface [HCO$_3^-$] (μmol kg^{-1})   HCO$_3^-$ ~ 2DIC-Alk

1600   1700   1800   1900   2000   2100

(a) surface total alkalinity (μmol kg^{-1})

Alk

2200   2300   2400

(d) surface [CO$_3^{2-}$] (μmol kg^{-1})   CO$_3^{2-}$ ~ Alk-DIC

100   150   200   250   300

Williams_Fig. 6.4c,d
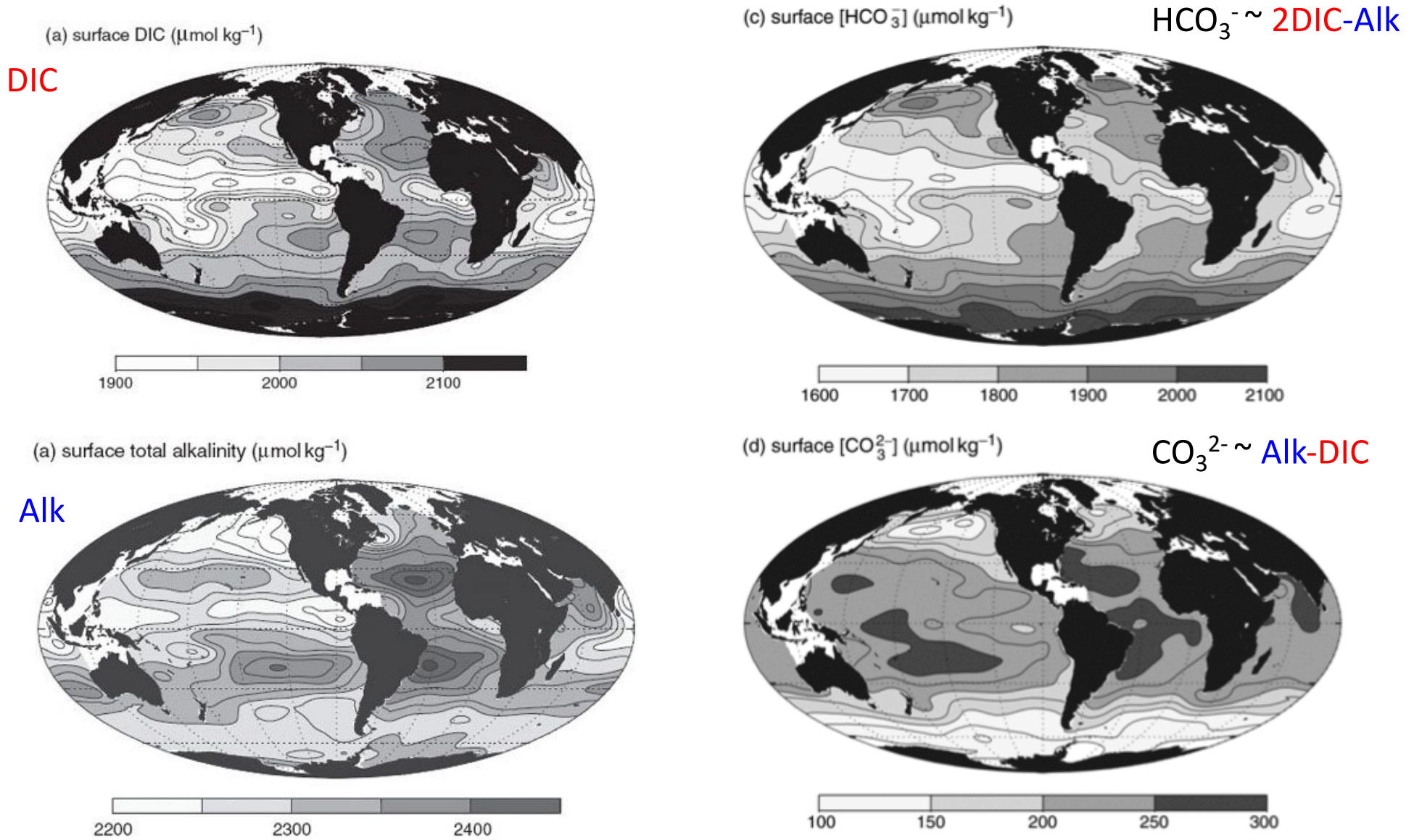
Is CO2 more soluble at high latitudes?

- Yes – colder SST enhances the solubility of CO_2

- Why then tropics/subtropics contain more anthropogenic CO_2 in the surface water?

  – Subtropical water has higher alkalinity due to the excess evaporation

  $\rightarrow$ Enhanced buffering capacity (higher CO_3^{2-})

  $\rightarrow$ Subject to the same $[CO_2]$ increase, subtropical water can absorb more carbon molecule than high latitudes

Revelle (Buffer) factor

- Equilibrium carbonate chemistry
  - Link between [CO_2] and DIC.
  - B is called Revelle (buffer) factor

$$\frac{\delta[CO_2]}{[CO_2]} = B\frac{\delta DIC}{DIC}$$

  - B is about 10 in tropics/subtropics
  - B is about 18 in polar ocean
  - Anthropogenic CO_2 increase leads to different DIC response depending on the value of B

$$B \approx \frac{[HCO_3^-]}{[CO_3^{2-}]}$$

→ Spatial variation of both bicarbonate and carbonate ions increases B with latitude

Some numbers

- Yearly rate of atmospheric CO2 increase fluctuates year to year, but it's magnitude is about 2ppm/year. Assuming saturation at the surface, can you predict the increase in the DIC of the surface water?

Use buffer factor,

$$\frac{\delta[CO_2]}{[CO_2]} = B\frac{\delta DIC}{DIC}$$

$$\delta DIC = \frac{\delta[CO_2]}{B[CO_2]}DIC = \frac{\delta[CO_2]_{sat}}{B[CO_2]_{sat}}DIC = \frac{\delta pCO_{2atm}}{B\,pCO_{2atm}}DIC$$

$$= \frac{2,ppm}{10 \times 400,ppm} \times 2000\mu mol/kg = 1\mu mol/kg$$

Observed seasonal cycle in Hawaii

Long-term increase in oceanic DIC

Looking at the slope, the rate of increase is about 15 μmol/kg from 1988 to 2002

This is approximately about 1 μmol/kg per year!
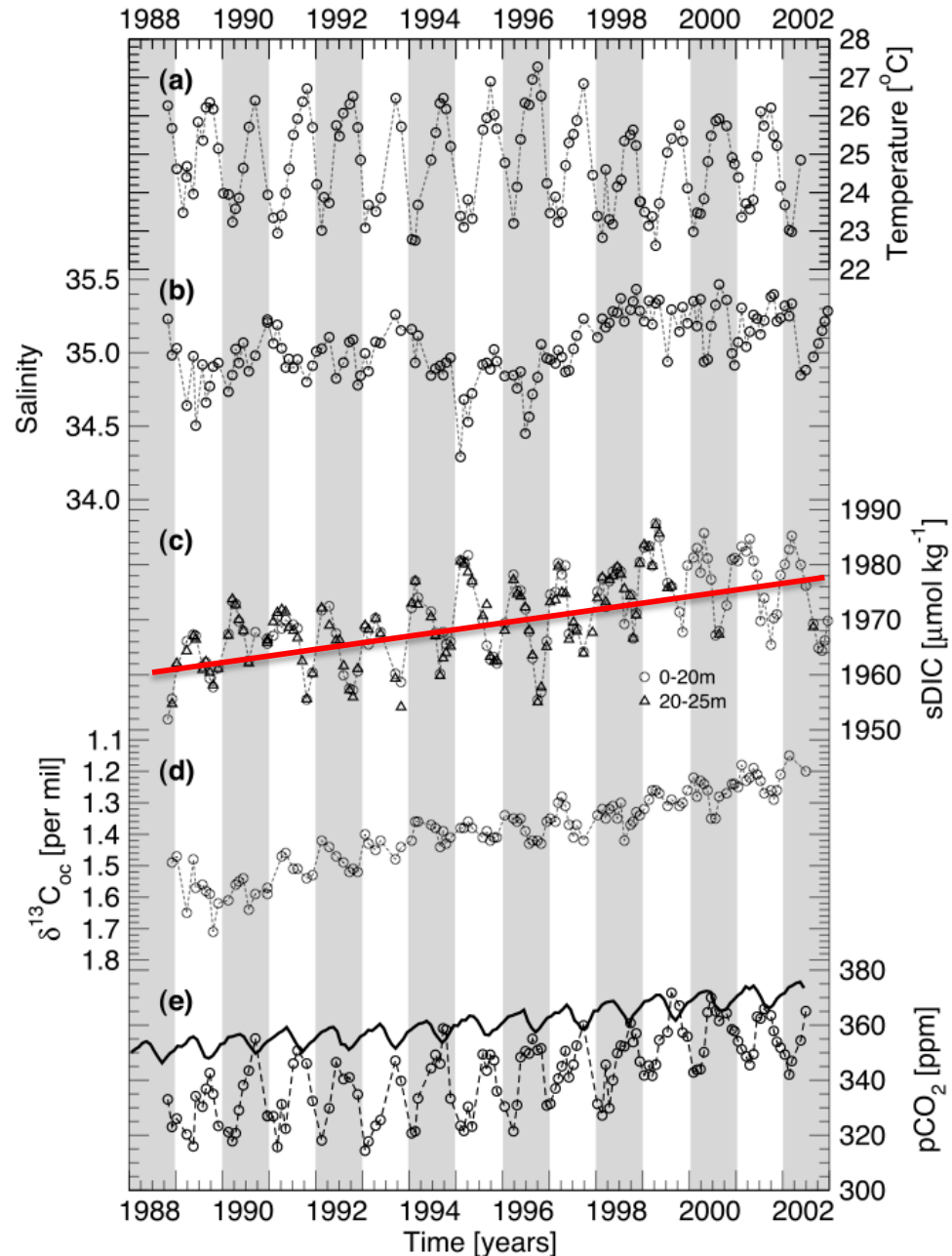
More numbers

- If the surface ocean DIC is increasing at the rate of about 1 μmol/kg per year for the surface mixed layer, what would be the yearly carbon uptake in PgC?

- Assume average MLD of 100m and the area of the global surface ocean is about 3.5 x 10^{14} m², we get:

$$\rho \, V_{ML} \, \delta DIC = (1028 \, kgm^{-3}) \times (3.5 \cdot 10^{14} m^2 \times 100m) \times (1\mu mol/kg)$$
$$= 3.5 \cdot 10^{19} \mu mol = 3.5 \cdot 10^{13} mol = 4.3 \cdot 10^{14} gC = 0.43 PgC.$$

- This is not enough to account for the ocean carbon uptake of 2 PgC/year.

Circulation, timescale of ventilation and the carbon sequestration

- Surface water is transported into the interior ocean
- Vertical circulation replaces subsurface water (via the ocean currents and mixing)
- Age of seawater ~ residence time of water
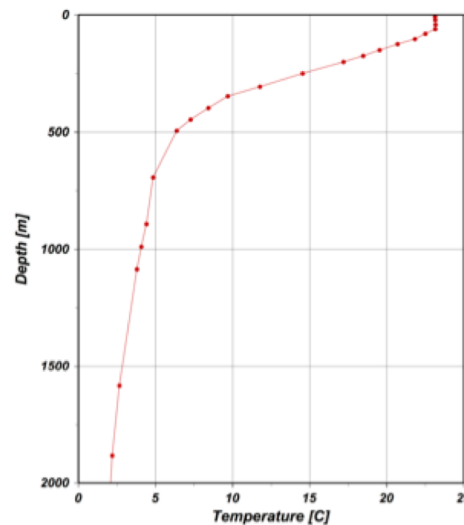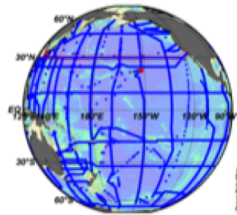
Mixed layer: ~1year

Thermocline: ~10years

Deep ocean: ~1,000 years

Water Age

- How do we define the "age of water"?
  - How long has it been since the water was in last contact with the surface?
  - Age = 0 : surface water
  - Age generally increases with depth

- How can we measure it?

Observations of water age

- Carbon-14 (^{14}C, radiocarbon)
  - Half life of 5,730 years
  - Natural C-14 is useful for deep waters
  - Bomb C-14 issues
- Tritium-Helium tracer
  - Half life of 12.43 years $\quad ^{3}H \longrightarrow {}^{3}He$
  - Most useful for thermocline waters
- Transient tracers
  - CFC-11, -12, -113, SF$_6$ are typically used
  - Increasing trend in the atmosphere ➜ ocean
  - Ocean concentration lags behind the atmosphere
  - Most useful for thermocline waters

Observed C-14 age

- Matsumoto et al., 2007, JGR-Ocean
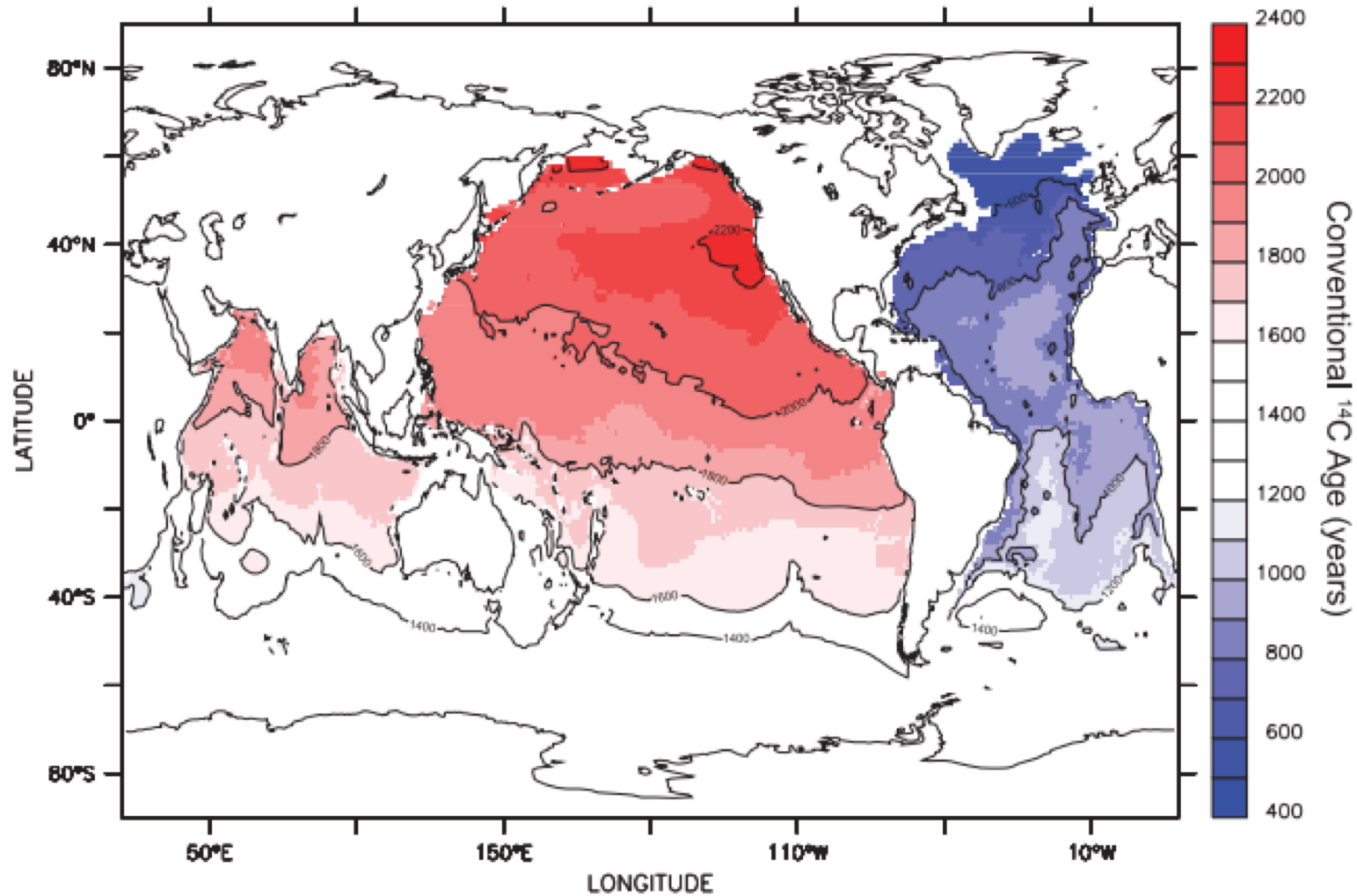
Figure 1. An objectively mapped conventional ^{14}C age of natural radiocarbon below 1500 m, following *Matsumoto and Key* [2004]. Unit is years.

Issues with C-14 age

- The surface C-14 is not at equilibrium with the atmosphere

- Air-sea exchange of carbon isotope is very slow: it takes about 10 years to equilibrate the surface mixed layer → large air-sea disequilibrium

- This is called "surface reservoir age" indicating that the newly formed deep water has non-zero (positive) age.

Corrected C-14 age

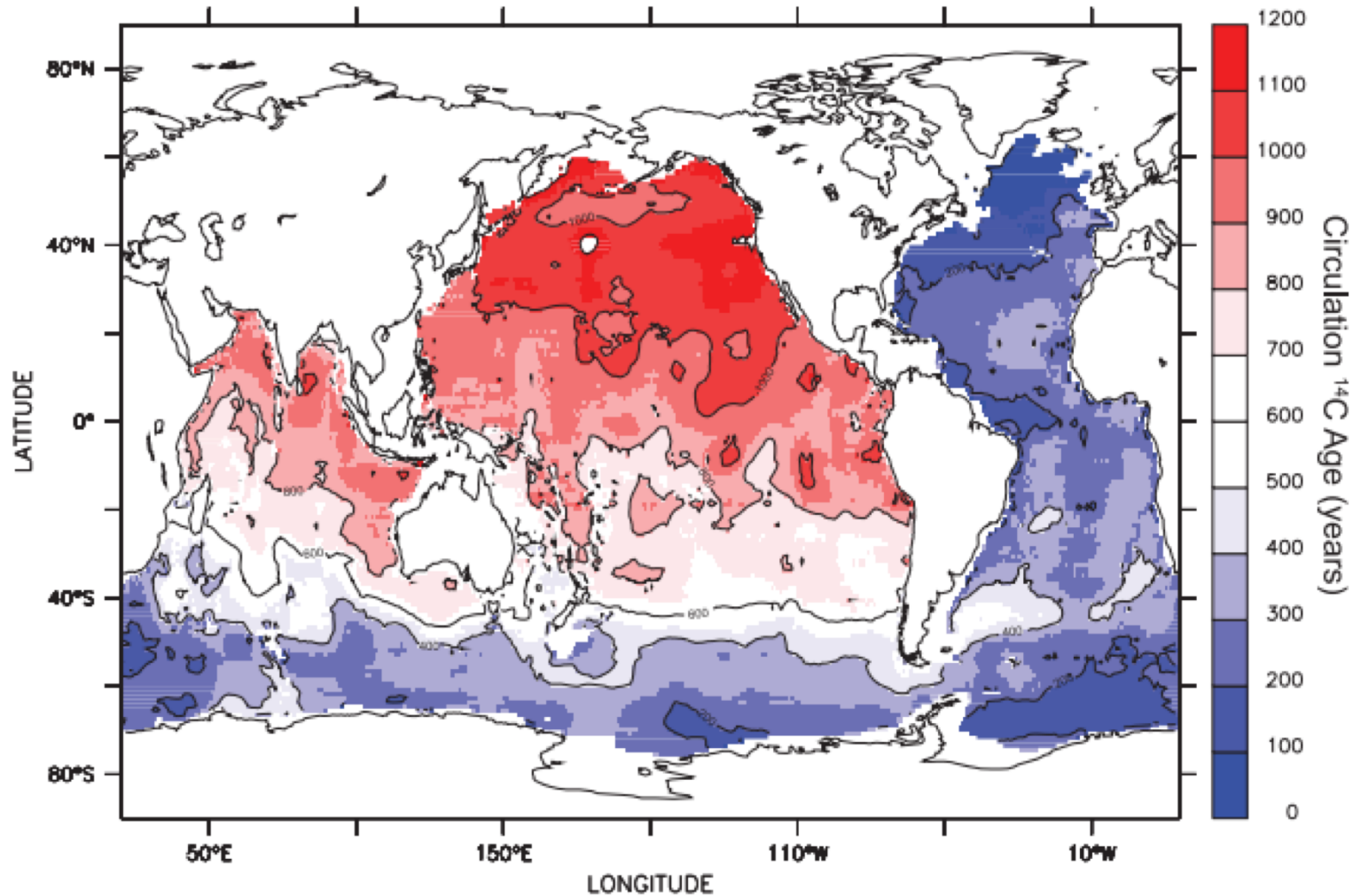**Figure 4.** A map of circulation ^{14}C age below 1500 m. This is equivalent to conventional ^{14}C age (Figure 1) but accounts for surface ocean ^{14}C reservoir age and the different sources of deep water. Unit is years.

CFC-11, -12

- Mecking et al., (2004)

(a) Atmospheric CFC concentrations
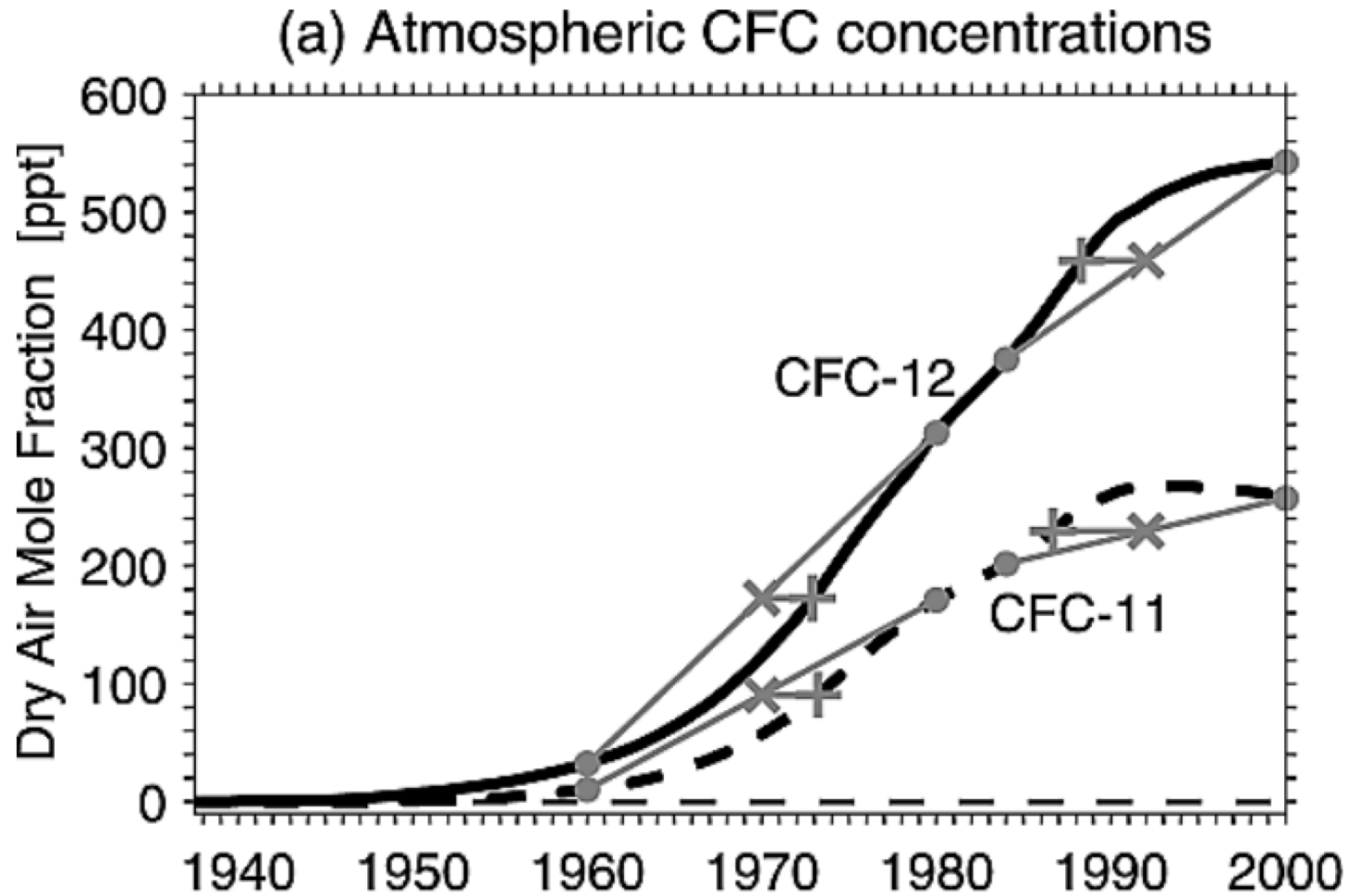
CFC-12 age in the thermocline

(d) σ_θ = 26.0: CFC-12 during WOCE (corrected to 1993)
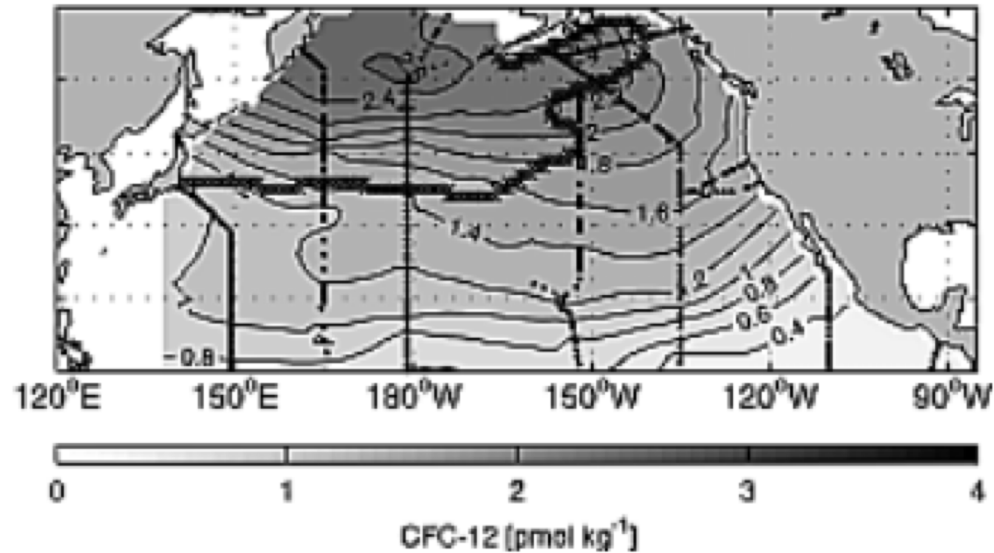
High CFC concentration means young age ➜ more recently ventilated waters

(c) σ_θ = 26.0: pCFC-12 age during WOCE (90% outcrop saturation)
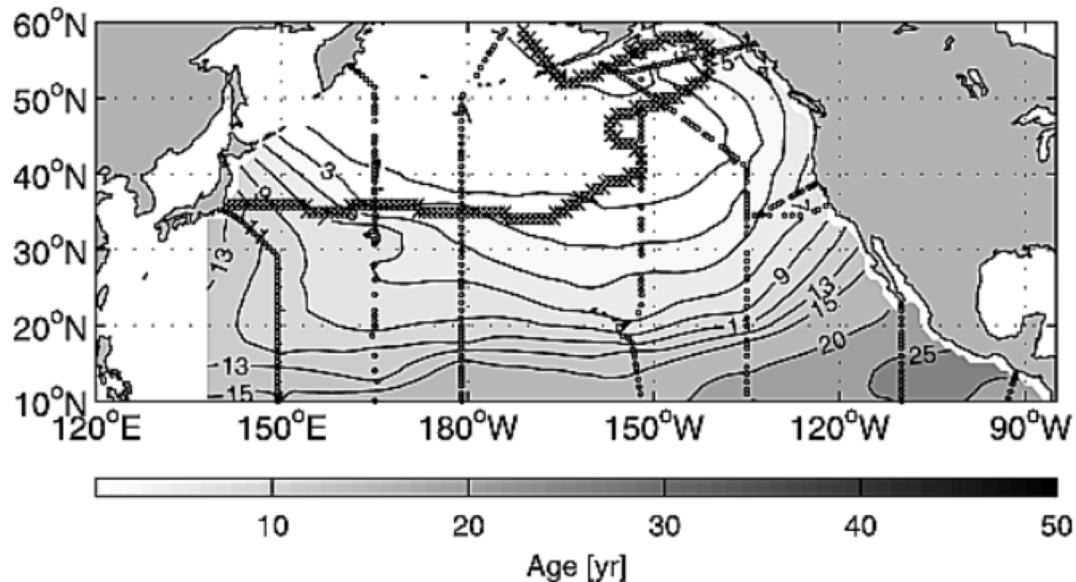
The age of waters in the upper ocean thermocline < 10 years in mid-latitudes.

The effect of mixing tends to reduce the concentration age

Ocean carbon uptake

- As the ocean absorbs fossil fuel CO_2, what would happen to $[HCO_3^-]$ and $[CO_3^{2-}]$?

  – DIC increases but Alk remains the same.

$$[HCO_3^-] \sim 2DIC - Alk \quad \uparrow$$

$$[CO_3^{2-}] \sim Alk - DIC \quad \downarrow$$

Ocean carbon uptake

- If pCO_2 increases by 1%, what would be the DIC increase under constant Alk?

  – Use the Buffer factor

  $$\frac{\delta pCO_2}{pCO_2} = B\frac{\delta DIC}{DIC}$$

  $$\frac{\delta DIC}{DIC} = \frac{1}{B} \times \frac{\delta pCO_2}{pCO_2} \sim \frac{1}{10}\%$$

Ocean carbon uptake

- As the ocean absorbs fossil fuel CO_2, what would happen to $[H^+]$ and Buffer factor?

    - $[HCO_3^-]$ increases and $[CO_3^{2-}]$ decreases...

$$[H^+] = \frac{K_2[HCO_3^-]}{[CO_3^{2-}]} \quad \uparrow$$

$$B = \frac{[HCO_3^-]}{[CO_3^{2-}]} = \frac{[H^+]}{K_2} \quad \uparrow$$

Marine CaCO$_3$ production

- Calcifiers can biologically produce CaCO$_3$. (biomineralization)

- Impacts on DIC and Alkalinity
  - 1 mol of CaCO$_3$ production **consumes** 2 mols of alkalinity and 1 mol of DIC
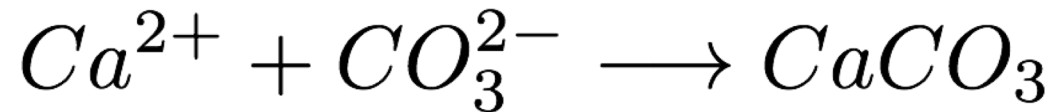
$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$$

  - Implication for [CO$_3^{2-}$] and [HCO^{3-}]?
  - Implication for pH?

CaCO$_3$ dissolution

- Their dissolution is controlled by its solubility (Ω).

$$K_{SP} = [Ca^{2+}][CO_3^{2-}] \text{ at saturation}$$

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{SP}}$$

- If Ω is less than 1, it is undersaturated and the CaCO3 dissolves in the water.

- If Ω is greater than 1, it is supersaturated.

CaCO$_3$ dissolution

- Their dissolution is controlled by its solubility (Ω).

$$K_{SP} = [Ca^{2+}][CO_3^{2-}] \text{ at saturation}$$

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{SP}}$$

- Biogenic CaCO$_3$ has two mineral forms; calcite and aragonite (K_{SP} is different between the two)
- Aragonite is more unstable than calcite (larger Ksp)
- K_{SP} increases with pressure, so naturally deep waters tend to be undersaturated → CaCO$_3$ dissolves in the deep water.

Dissolution profile

$$[CO_3^{2-}]_{sat} \equiv \frac{K_{SP}}{[Ca^{2+}]}$$

$$\Omega = \frac{[CO_3^{2-}]}{[CO_3^{2-}]_{sat}}$$

The depths of saturation horizon ~ approx 3km in the Atlantic and 1km in the Pacific.

It is shoaling approx. 1-2 m/yr

Concentration

Pressure

$\Omega > 1$

— — — — — — — — — saturation horizon

$\Omega = 1$

$\Omega < 1$

$[CO_3^{2-}]_{sat}$

$[CO_3^{2-}] = Alk - DIC$
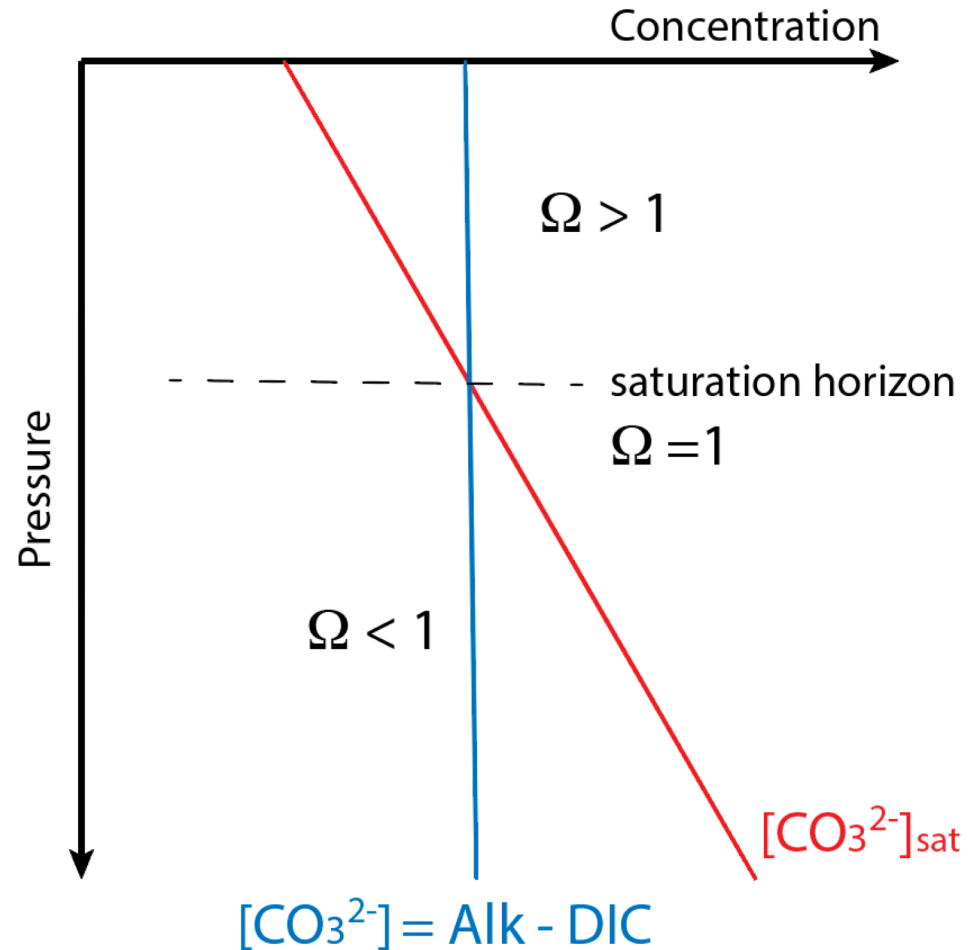
Calcium carbonate pump

- Production of sinking CaCO3 particles at the surface
  - It removes both DIC and Alk from the surface water, lowering surface $[CO_3^{2-}]$.

$$CO_2 + CO_3^{2-} + H_2O \longleftrightarrow 2HCO_3^-$$
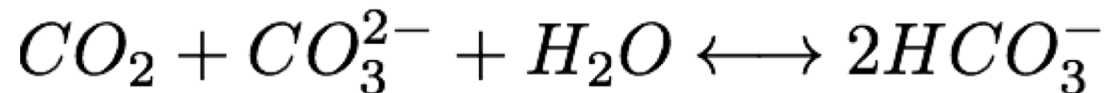
  - The balance shifts to the left in the above equation → increasing CO_2 in the surface water
  - Surface water has more $[CO_2]$, leading to de-gassing of CO2 to the atmosphere.

Carbon pumps

- Volk and Hoffert (1985)
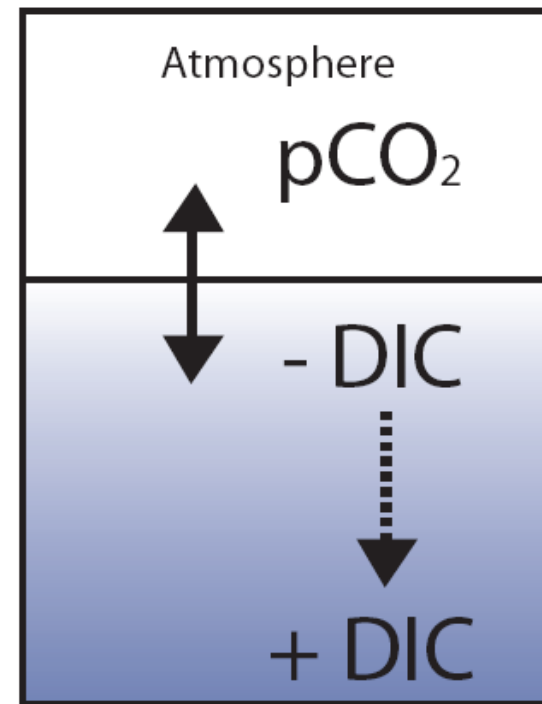 - Mechanisms that maintain vertical gradient of DIC **in a steady state**

    - Simple 1D view
      - Organic pump driven by sinking organic particle
      - Carbonate pump driven by sinking CaCO3 particles
      - Solubility pump driven by thermal stratification

Solubility pump

- Vertical temperature gradient
  - Global mean SST is about 15°C.
  - Deep water is about 2°C.
    - Deep water contains higher DIC relative to the surface

  - Considering the temperature dependence of solubility, the cooling of global ocean by 1°C leads to a lowering of atmospheric CO_2 by 10 ppm at steady state.

Biological pump

- Organic pump
  - Increases thermocline/deep nutrients and carbon. Also consumes oxygen.
  - **Decreases atmospheric CO_2**

- Carbonate ($CaCO_3$) pump
  - Increases thermocline/deep alkalinity and carbon.
  - Decreases buffering capacity at the surface, therefore **increases atmospheric CO_2**

Steady state carbon cycle

- Steady state d/dt → 0

- Atmos + Ocean C inventory is constant.

- For the 1-box atmos 2-box ocean model;

Global C mass balance

$$M_a pCO_2^{atm} + (V_s C_s + V_d C_d) = \text{(constant)}$$

Air-sea exch and carbonate chemistry

$$pCO_2^{ocn} = pCO_2^{atm}, \ C_s = f(pCO_2^{ocn}, Alk, K_i)$$

Deep ocean C balance

$$C_d = C_s + R_{C:P}(P_d - P_s)$$

Solubility pump

- Solubility pump acts through K_0 in the carbonate chemistry
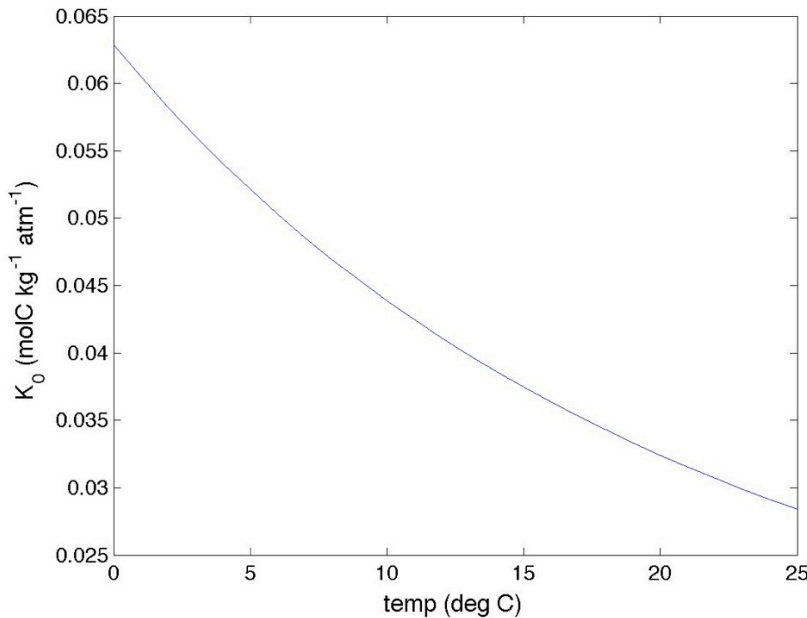- Look at a small perturbation

Global C mass balance

$$M_a \Delta pCO_2^{atm} + (V_s \Delta C_s + V_d \Delta C_d) = 0$$

Air-sea exch and carbonate chemistry

$$\Delta pCO_2^{ocn} = \Delta pCO_2^{atm}, \quad \Delta C_s = g(\Delta pCO_2^{ocn}, \Delta K_0)$$

Deep ocean C balance

$$\Delta C_d = \Delta C_s$$

K_0 decreases with T

$$\frac{\partial K_0}{\partial T} \sim -0.0015 \left[Matm^{-1} K^{-1} \right]$$

With pCO2=280ppm, Ma=1.8 x 10^{20} mol, and K_0=0.04 we get about 9ppm per 1°C warming.

$$\Delta pCO_2 = -\frac{pCO_2}{\chi K_0} \Delta K_0$$

$$\chi = \frac{BM_a pCO_2 + VC}{VC} \sim 1.2$$

Biological pump

- The 2nd term in the deep ocean DIC
- Deep ocean P is essentially a constant, so **Ps**, is the only variable (i.e. **preformed P**).

Global C mass balance

$$M_a pCO_2^{atm} + (V_s C_s + V_d C_d) = (\text{constant})$$

Air-sea exch and carbonate chemistry

$$pCO_2^{ocn} = pCO_2^{atm}, \; C_s = f(pCO_2^{ocn}, Alk, K_i)$$

Deep ocean C balance

$$C_d = C_s + R_{C:P}(P_d - P_s)$$

Biological pump

- The 2nd term in the deep ocean DIC

- Deep ocean P is essentially a constant, so **Ps**, is the only variable (i.e. **preformed P**).

Global C mass balance

$$M_a \Delta pCO_2^{atm} + (V_s \Delta C_s + V_d \Delta C_d) = 0$$

Air-sea exch and carbonate chemistry

$$\Delta pCO_2^{ocn} = \Delta pCO_2^{atm}, \ \Delta C_s = f(\Delta pCO_2^{ocn})$$

Deep ocean C balance

$$\Delta C_d = \Delta C_s - R_{C:P} \Delta P_s$$

Biological pump

- **Ps**, is measures the inefficiency of biological pump. Weaker productivity → higher surface P

$$\Delta pCO_2 = \frac{pCO_2 \, B \, R_{C:P}}{\chi C_s} \Delta P_s$$

With typical parameters, we get about 130ppm per 1μM increase in Ps

Transient carbon cycle

- Emission of fossil fuel CO_2 makes the carbon cycle off-balance.

- Modern C cycle is no longer in steady state.

- HW9 will be addressing what controls the rate of CO_2 uptake under increasing pCO_2^{atm}