Dissolved Gases

Lecture by Jens Daniel Müller
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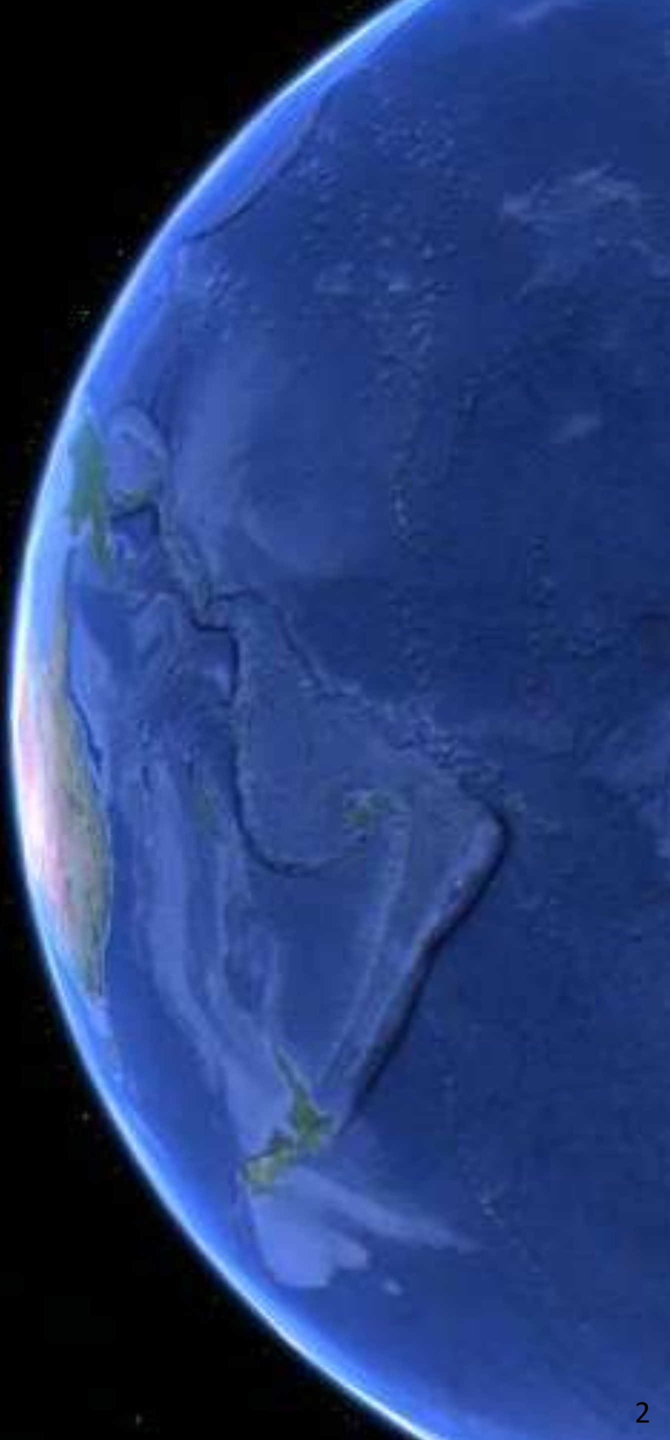
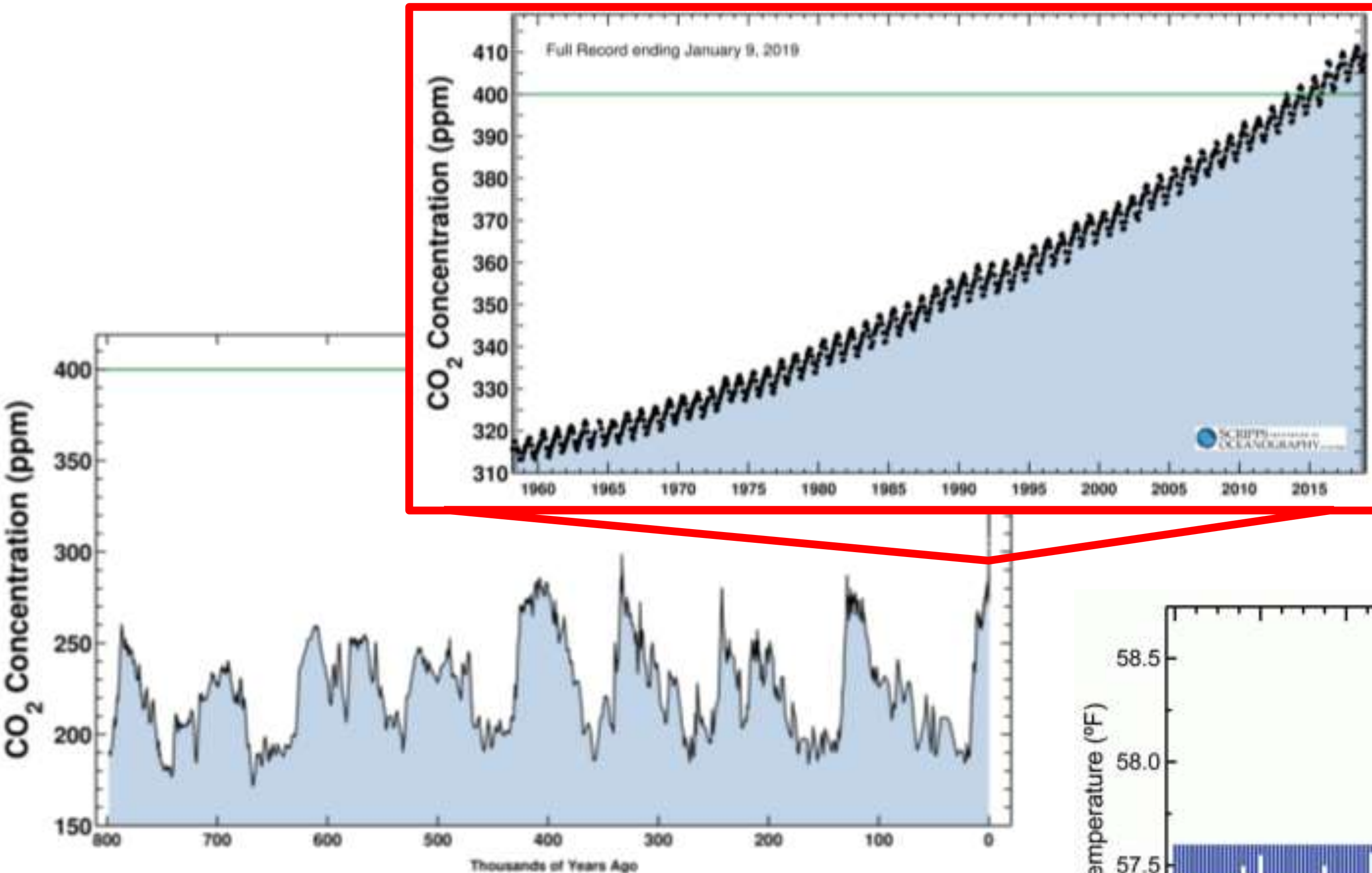
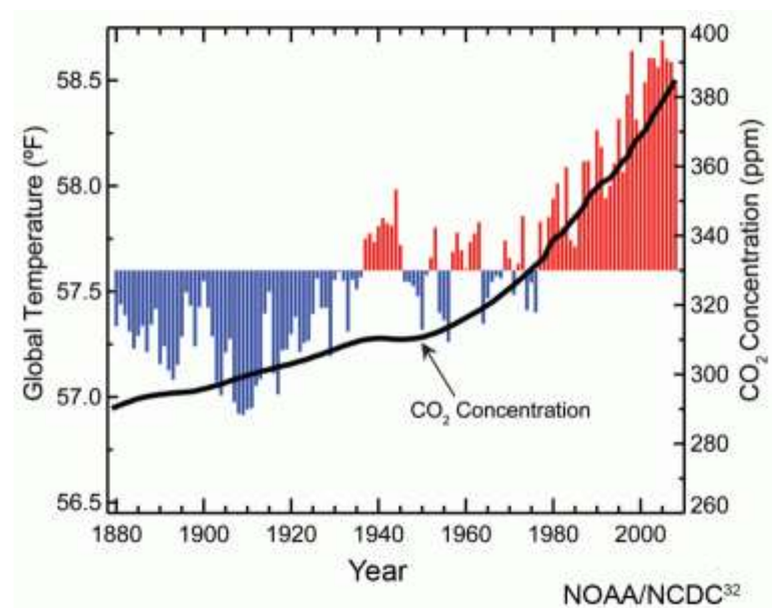
Outline

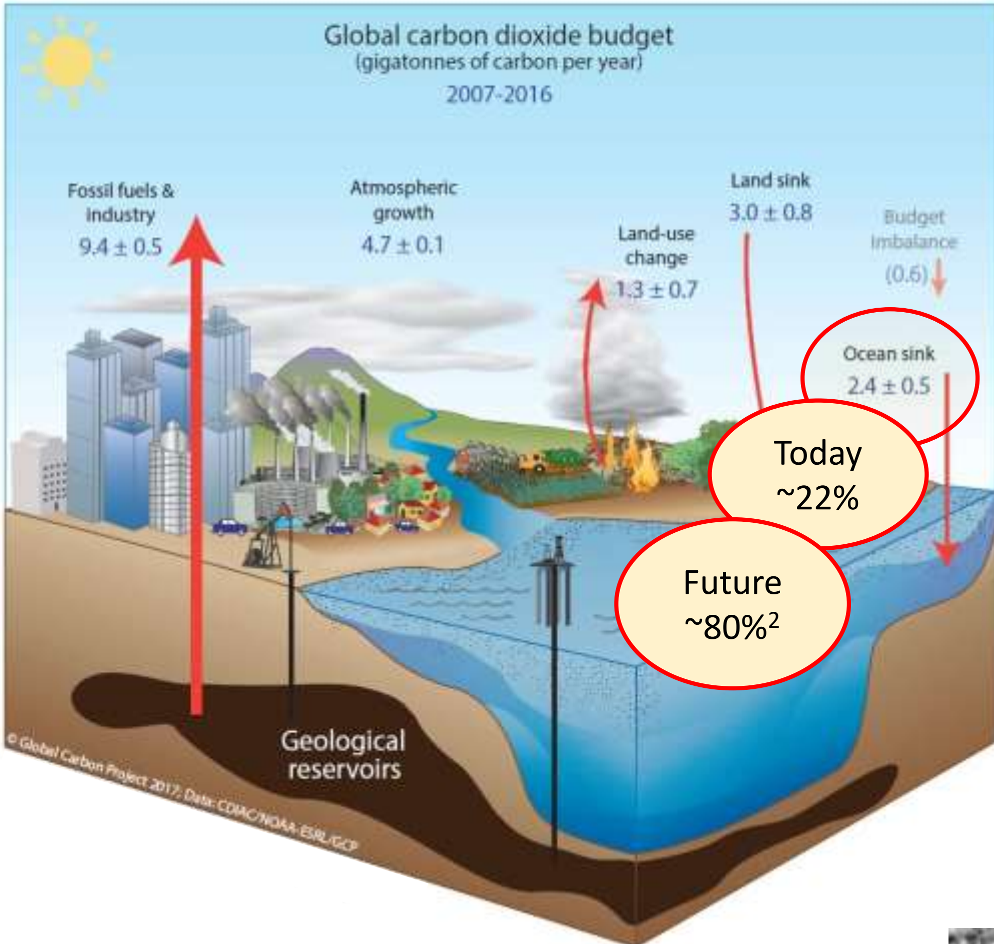
- Motivation
- Solubility of gases
- O_2 and CO_2 in the global ocean
  - Physical and biological pumps
- Marine CO_2-system
  - Equilibrium reactions
  - Freshwater vs seawater
  - Alkalinity
  - 4 measurable parameters
  - Ocean acidification
- Lake Nyos disaster

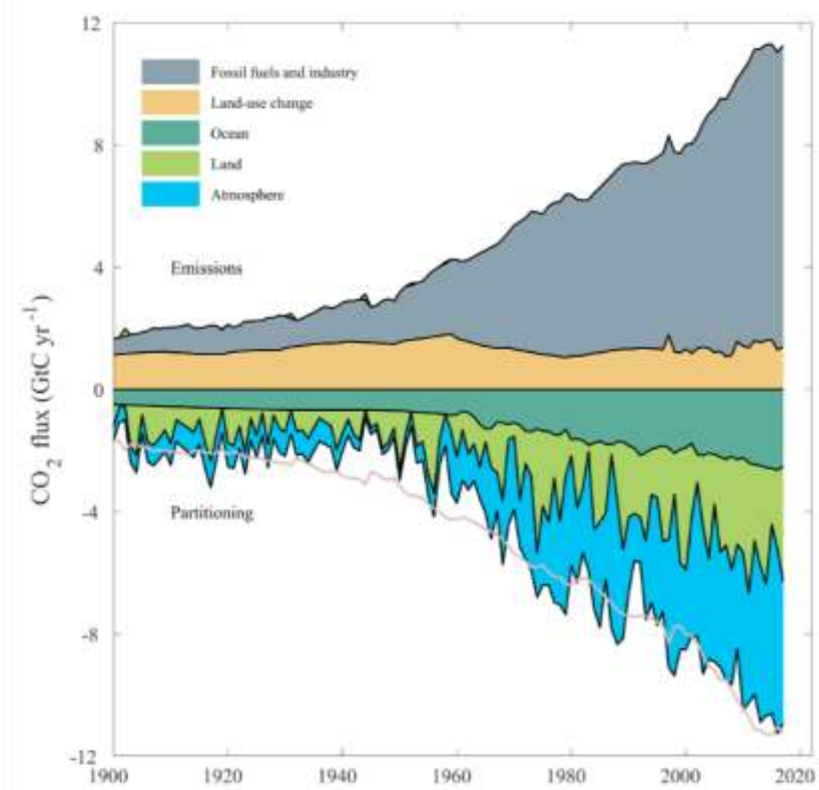


Motivation: The Oceans Role in Climate Change

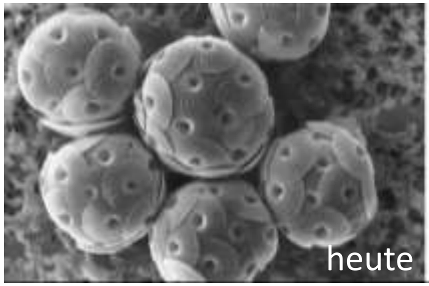


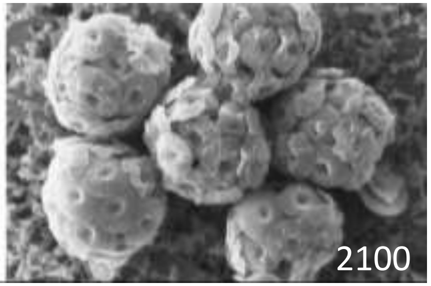




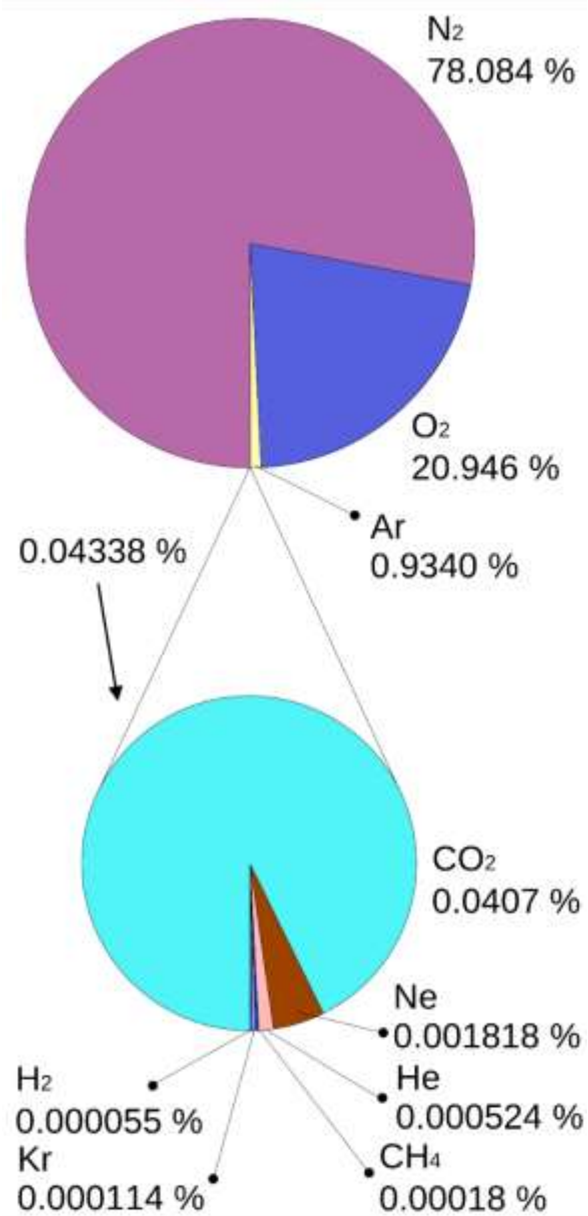


Oceanic CO_2-uptake counteracts climate change at the cost of acidification, with unpredictable consequences for marine ecosystems.
What are the chemical mechanisms involved?





John Dalton
(1766 –1844)



Dalton‘s Law for ideal gases:

$$P = \sum_{i=1}^{k} p_i$$

P = total pressure of gas mixture
p_i = partial pressure *i*-th component of mixture

Definition of partial pressure:

$$p_i = P \cdot x_i = P \cdot \frac{n_i}{\sum_{j=1}^{k} n_j}$$

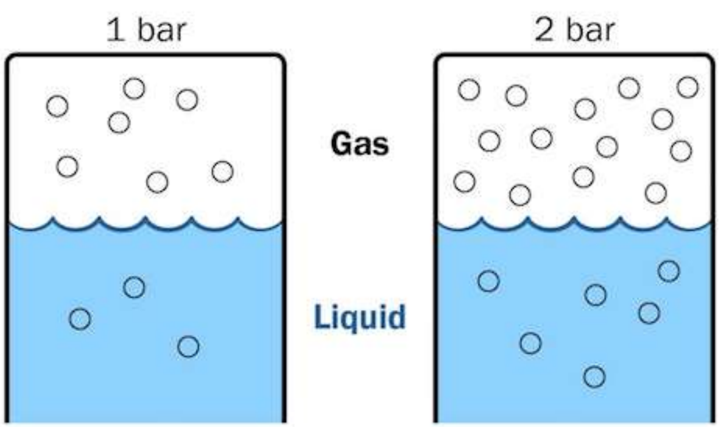
x_i = Mole fraction *i*-th component of mixture
n_i = Number of moles of *i*-th component of mixture

William Henry
(1774 - 1836)

Henry‘s Law:

$$[\mathrm{G}] = K_{\mathrm{H}} \cdot p\mathrm{G}$$

[G] = Concentration of gas G in liquid phase;
*p*G = Partial pressure of gas G in gas phase;
K_H = Henry‘s Law constant for gas G = *f*(T,S)



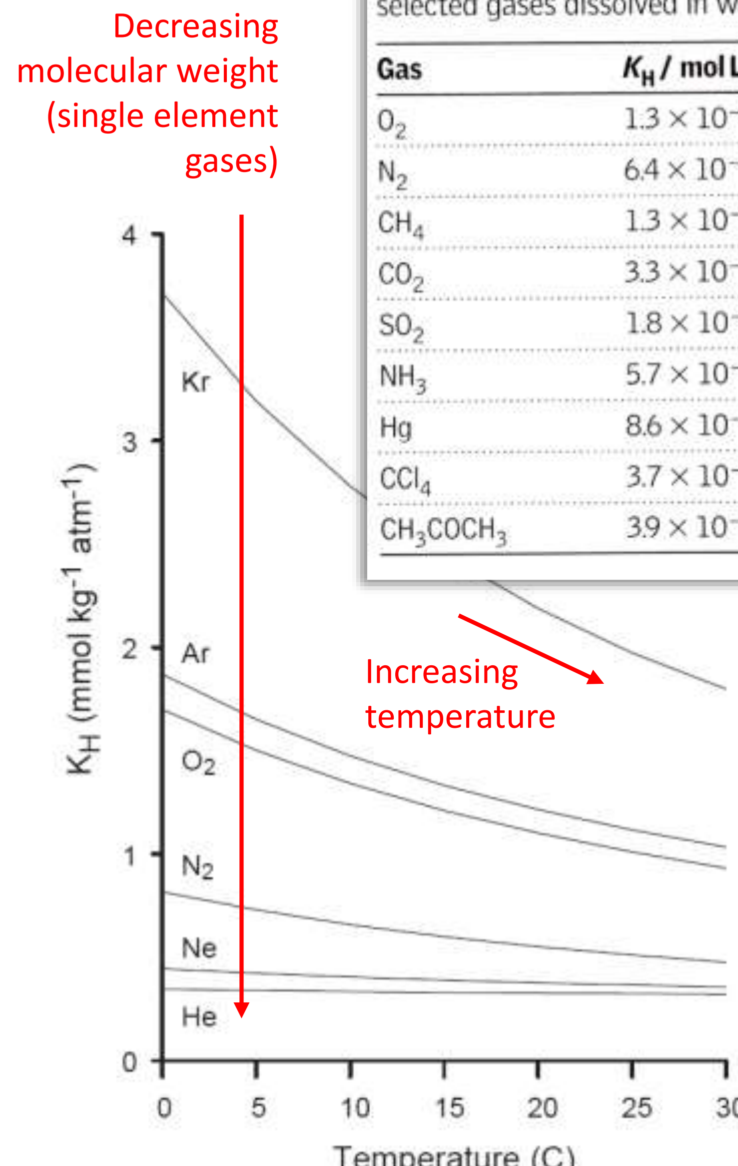
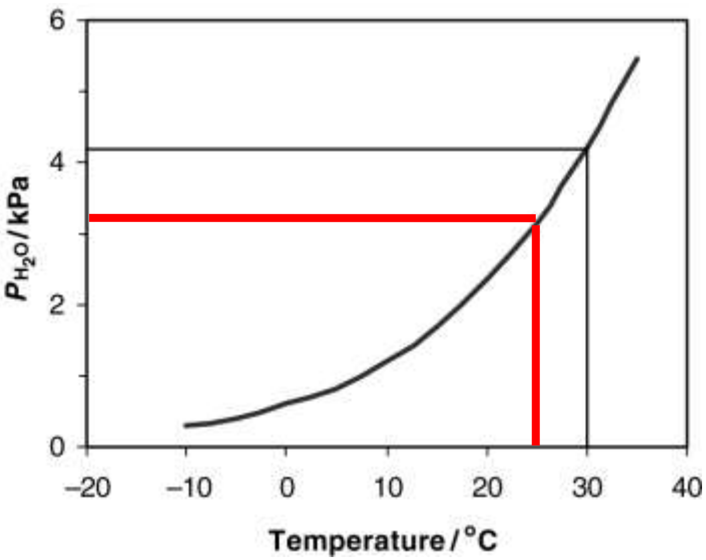


Table 11.1 Henry's law constants for selected gases dissolved in water at 25 °C.

Gas	K_H / mol L^{-1} Pa^{-1}
O_2	1.3×10^{-8}
N_2	6.4×10^{-9}
CH_4	1.3×10^{-8}
CO_2	3.3×10^{-7}
SO_2	1.8×10^{-5}
NH_3	5.7×10^{-4}
Hg	8.6×10^{-7}
CCl_4	3.7×10^{-7}
CH_3COCH_3	3.9×10^{-3}

Saturation vapor pressure H_2O



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CH_3COCH_3	3.9×10^{-3}

Oxygen

- Essential for biogeochemical processes in water, e.g. oxidation
- Consumed during mineralisation of organic matter
- Prerequisite for all higher trophic levels
- Solubility regulates O_2 concentration in ventilated water masses

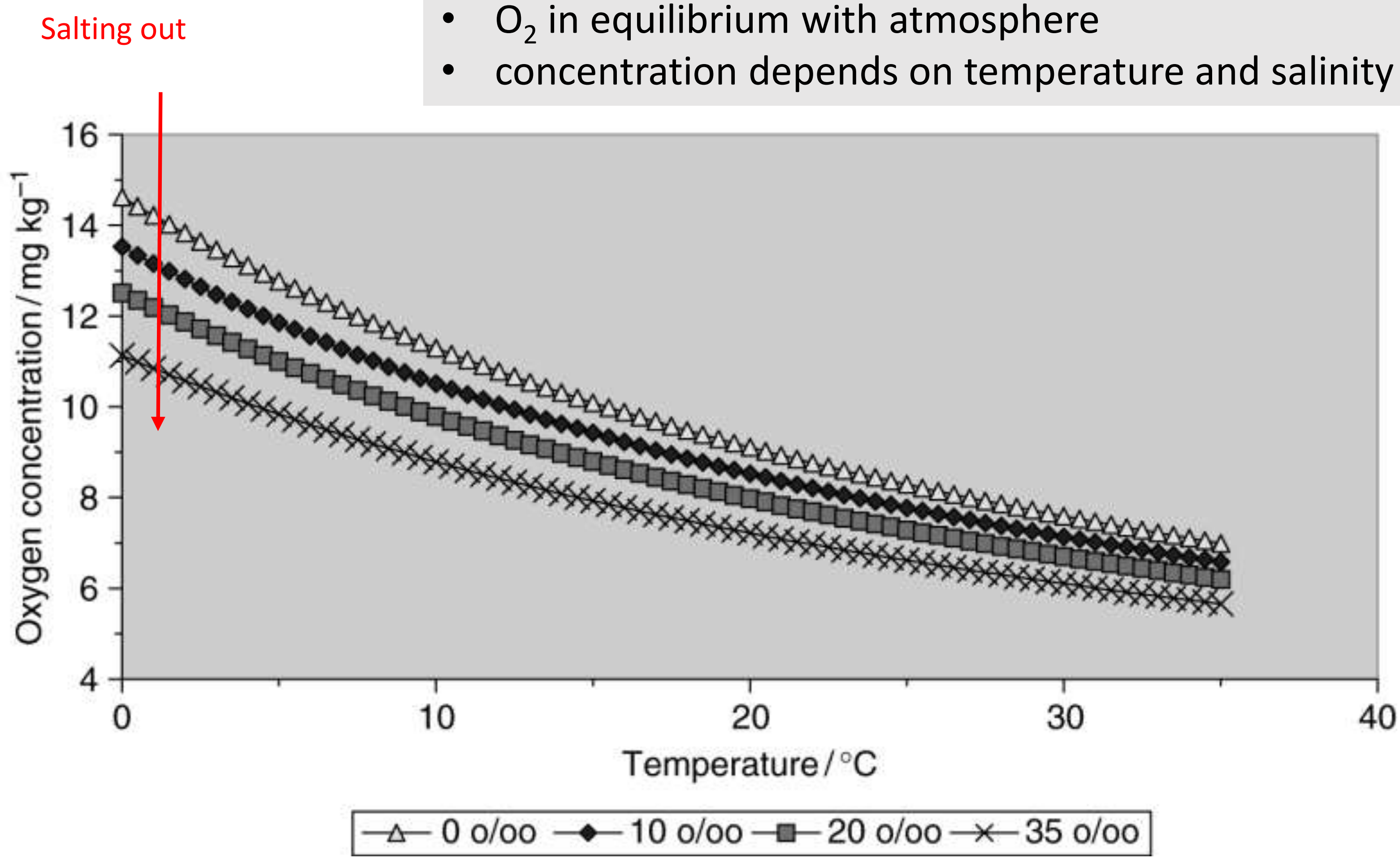
Partial pressure of oxygen at 25°C in air saturated with water vapor

$P_{O2} = (P_{total} – P_{H2O}) \times X_{O2,dry}$
$P_{O2} = (1.01 \times 10^5 - 3.2 \times 10^3)$ Pa $\times 0.209 = 2.04 \times 10^4$ Pa

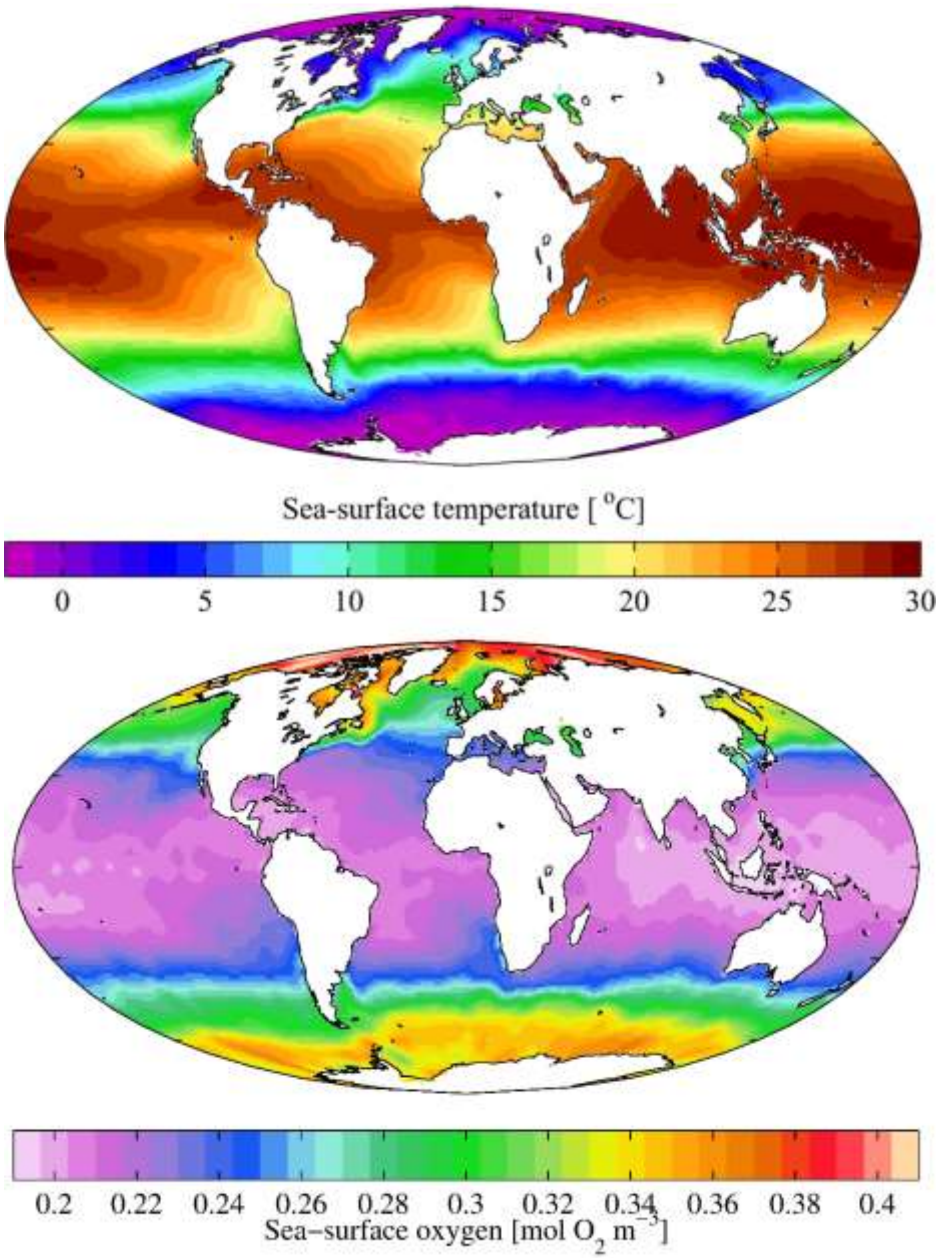
Concentration of O_2 freshwater in equilibrium with atmosphere

$[O_{2,aq}] = 1.3 \times 10^{-8}$ mol L^{-1} $Pa^{-1} \times 2.04 \times 10^4$ Pa
$= 2.7 \times 10^{-4}$ mol L^{-1}
$= 8.5$ mg L^{-1}

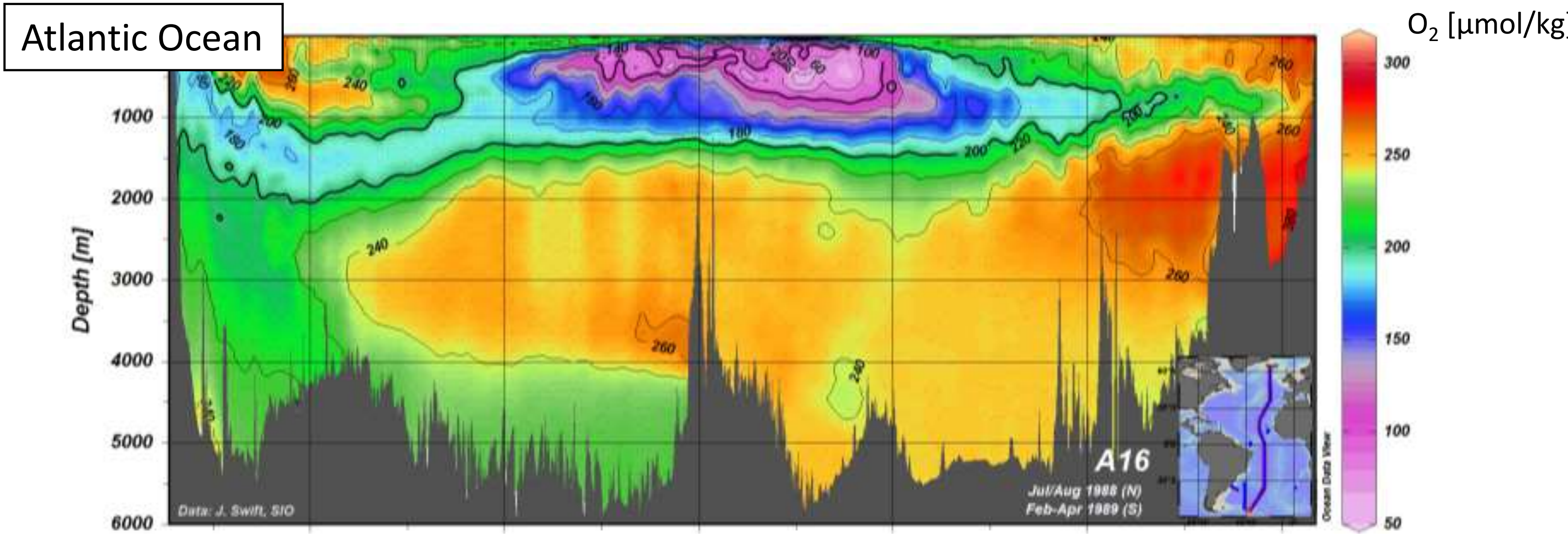
- O_2 in equilibrium with atmosphere
- concentration depends on temperature and salinity

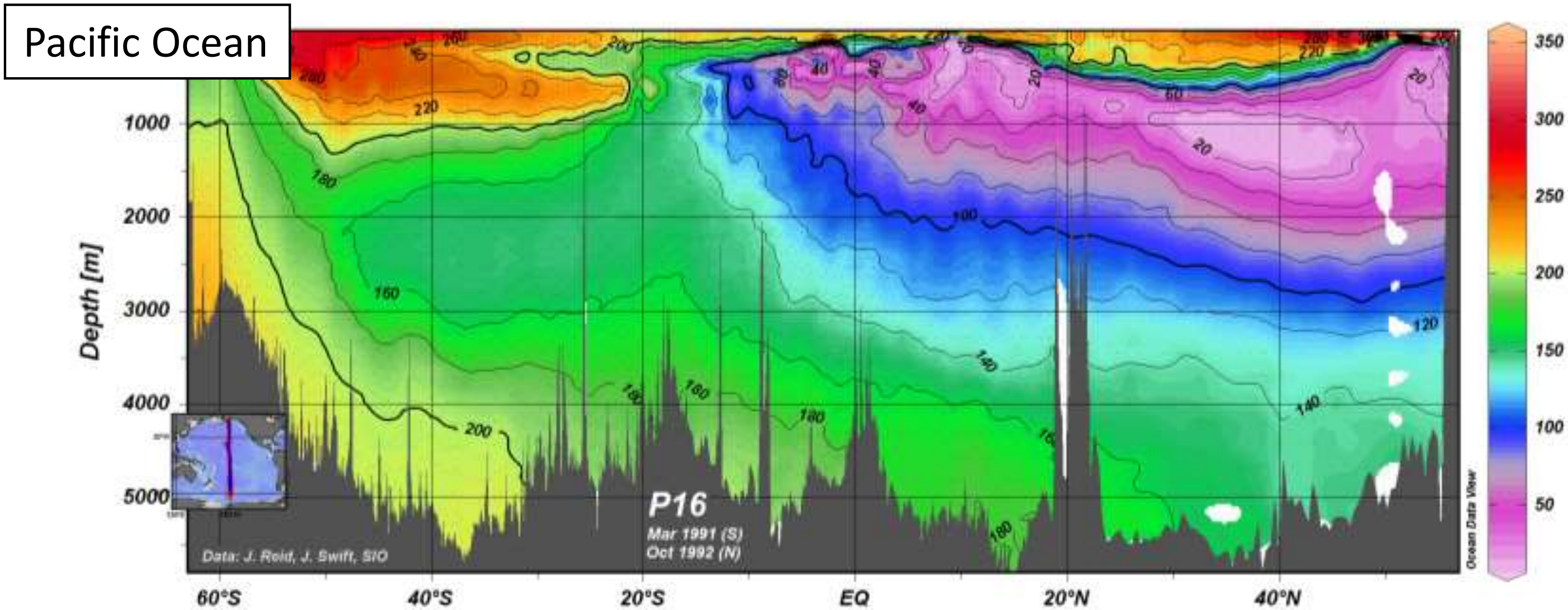


Surface Distribution of Oxygen in the Global Ocean

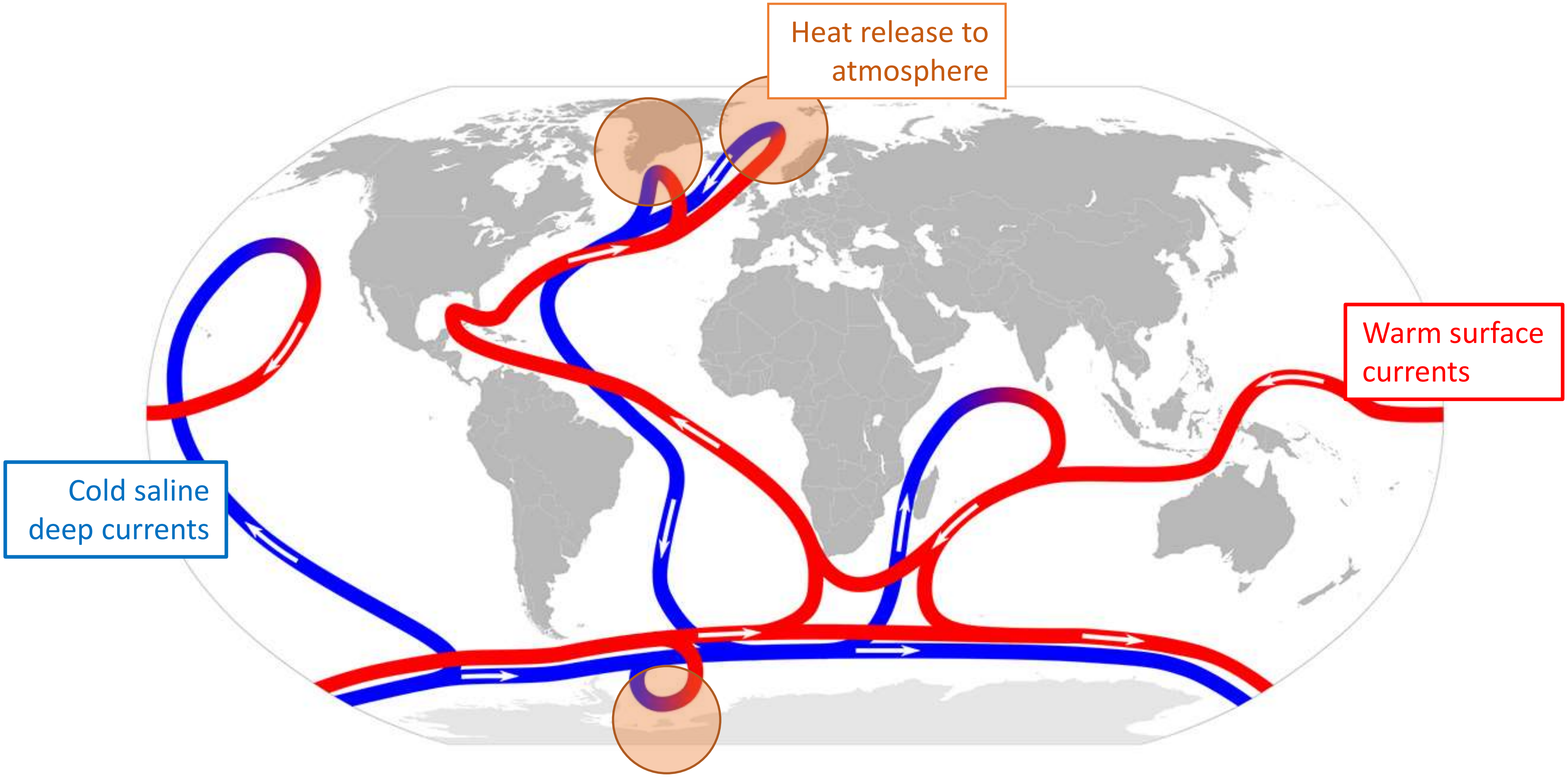


Surface distribution of O_2 in the global ocean reflects its decreasing solubility with increasing sea surface temperature (SST)

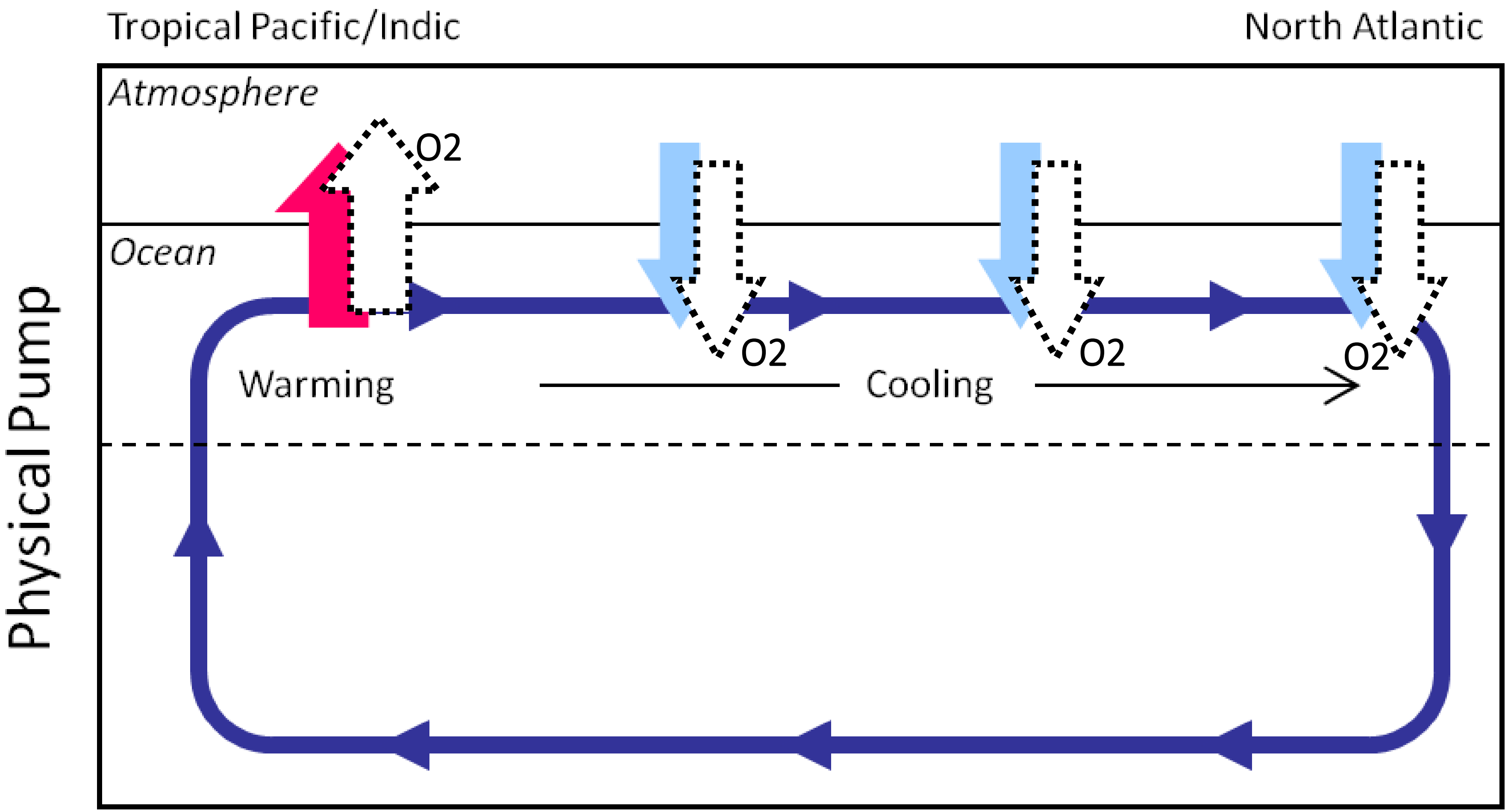

Atlantic Ocean
O$_2$ [µmol/kg]
Depth [m]
1000
2000
3000
4000
5000
6000
A16
Jul/Aug 1988 (N)
Feb-Apr 1989 (S)
Data: J. Swift, SIO
Ocean Data View
300
250
200
150
100
50


Pacific Ocean
Depth [m]
1000
2000
3000
4000
5000
P16
Mar 1991 (S)
Oct 1992 (N)
Data: J. Reid, J. Swift, SIO
Ocean Data View
60°S
40°S
20°S
EQ
20°N
40°N
350
300
250
200
150
100
50

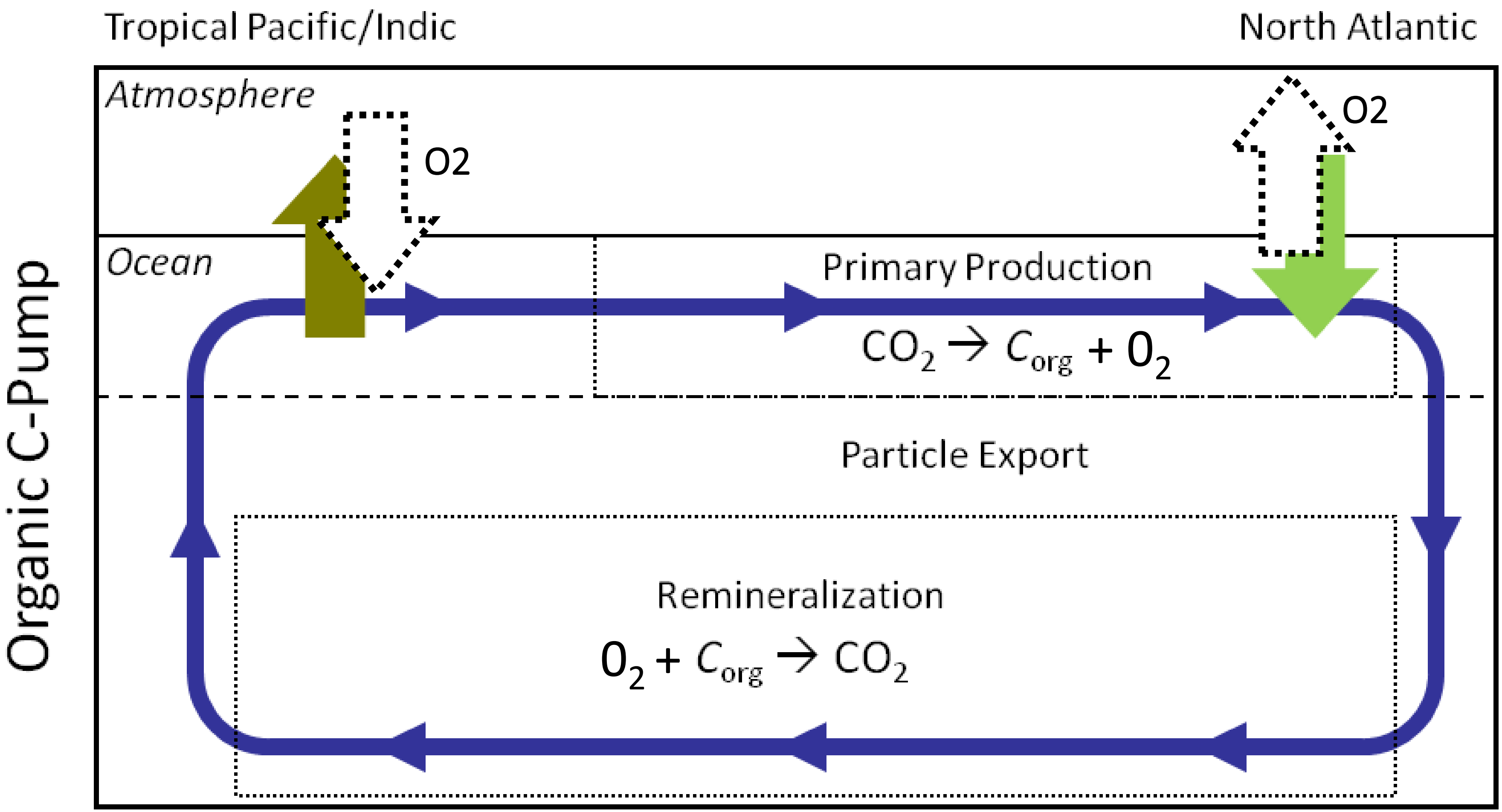
Thermohaline circulation: The Global Ocean Conveyor Belt



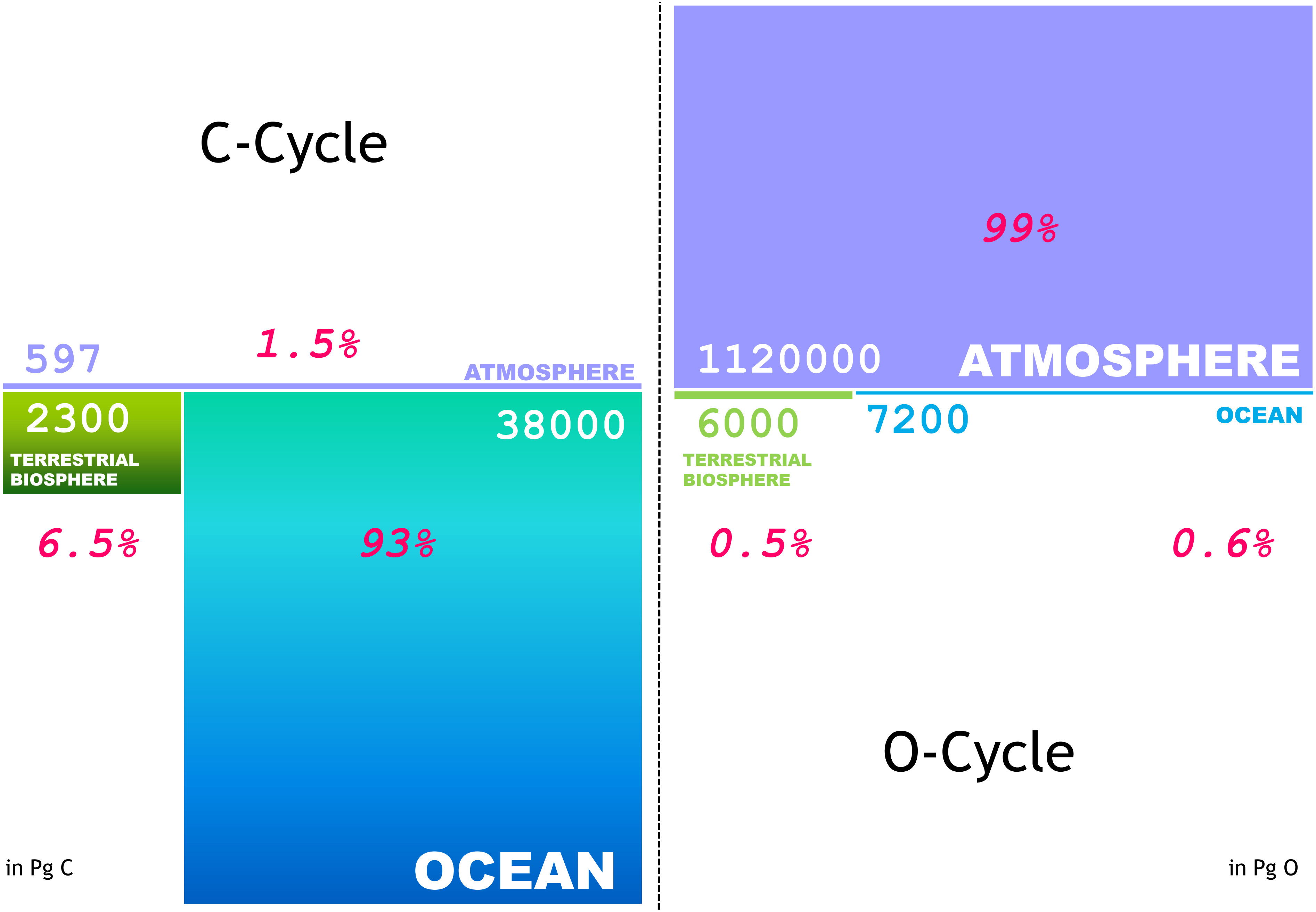
- Poleward decrease in sea surface temperature favors O_2 (white arrows) and CO_2 (colored arrows) solubility and increases seawater density
- Downwelling in the North Atlantic (e.g. Labrador Sea) ventilates ocean interior

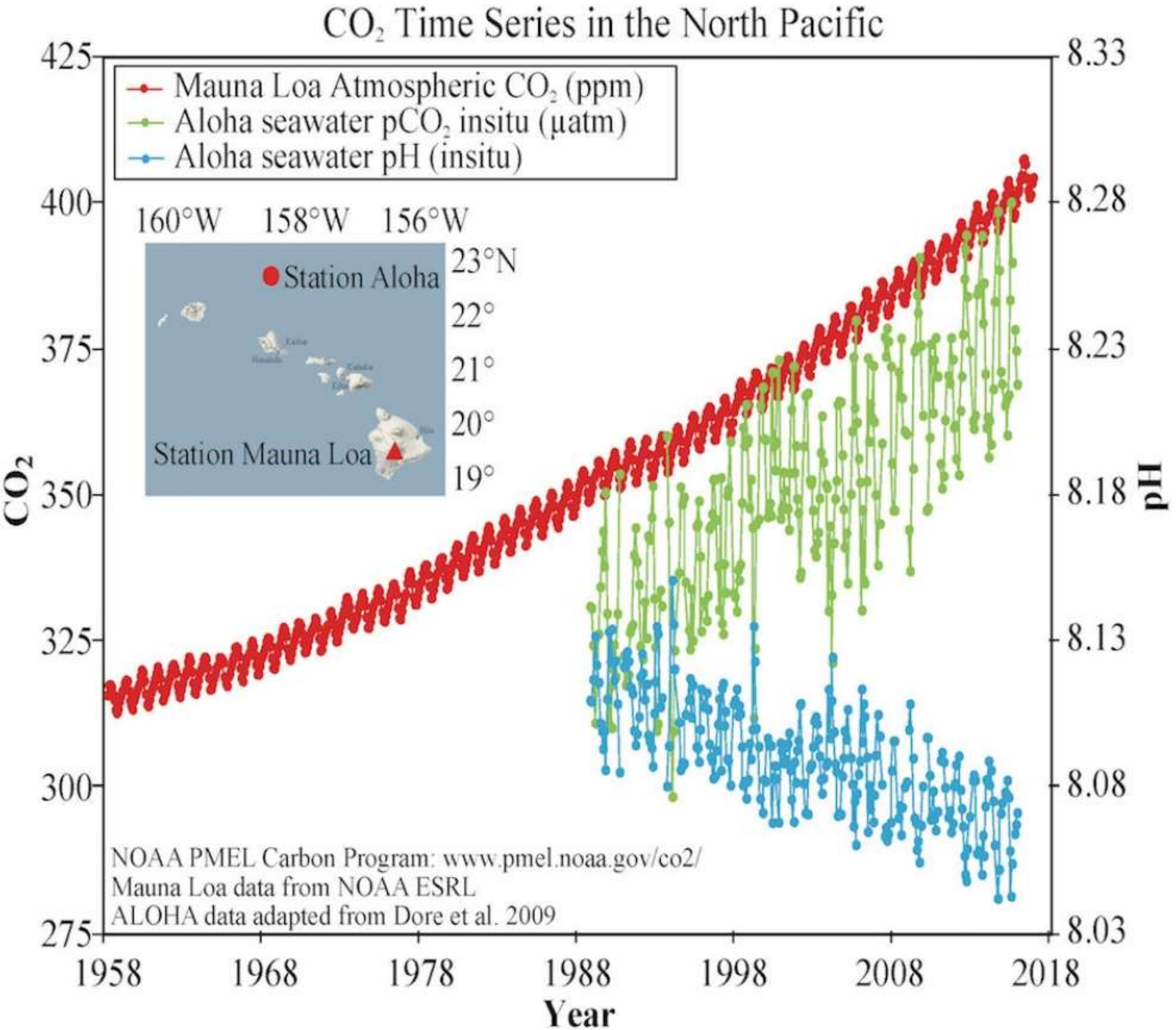


$$CO_2 + H_2O \underset{Mineralisation}{\overset{Production}{\rightleftarrows}} O_2 + CH_2O$$



Global Carbon and Oxygen Reservoirs





CO2 Time Series in the North Pacific
Mauna Loa Atmospheric CO2 (ppm)
Aloha seawater pCO2 insitu (µatm)
Aloha seawater pH (insitu)
160°W 158°W 156°W
23°N
Station Aloha
22°
21°
20°
Station Mauna Loa
19°
425
400
375
350
325
300
275
CO2
8.33
8.28
8.23
8.18
8.13
8.08
8.03
pH
NOAA PMEL Carbon Program: www.pmel.noaa.gov/co2/
Mauna Loa data from NOAA ESRL
ALOHA data adapted from Dore et al. 2009
1958
1968
1978
1988
1998
2008
2018
Year

Why is so much carbon stored in the ocean? Why does the CO_2 uptake decrease seawater pH?

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

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

$$CO_2^* = CO_2(aq) + H_2CO_3$$

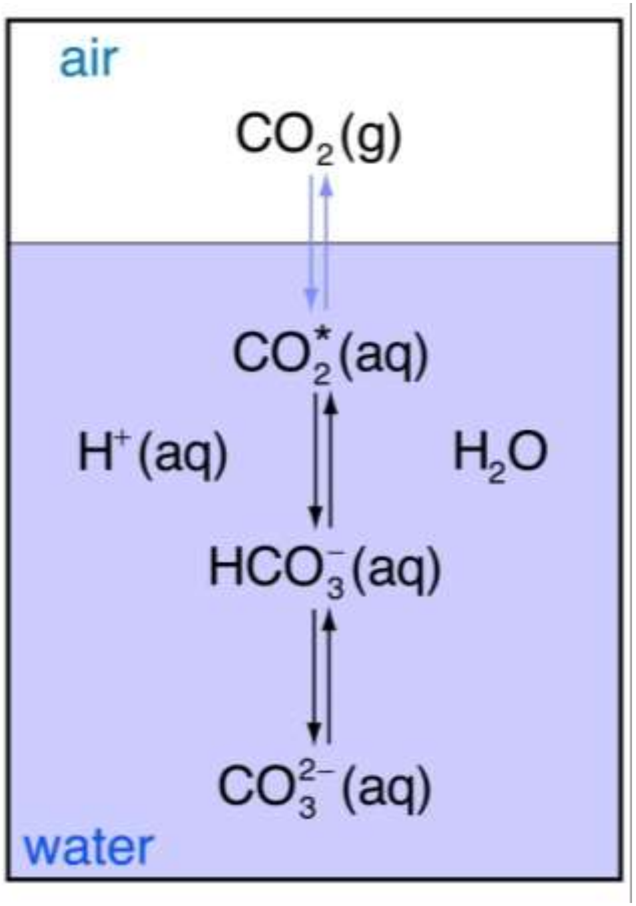
$$CO_2^* + H_2O \rightleftharpoons H^+ + HCO_3^-$$

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

$$K_H^{'} = K_0^{'} = \frac{[CO_2^*]}{pCO_2}$$

$$K_1^{'} = \frac{[HCO_3^-] \cdot [H^+]}{[CO_2^*]}$$

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



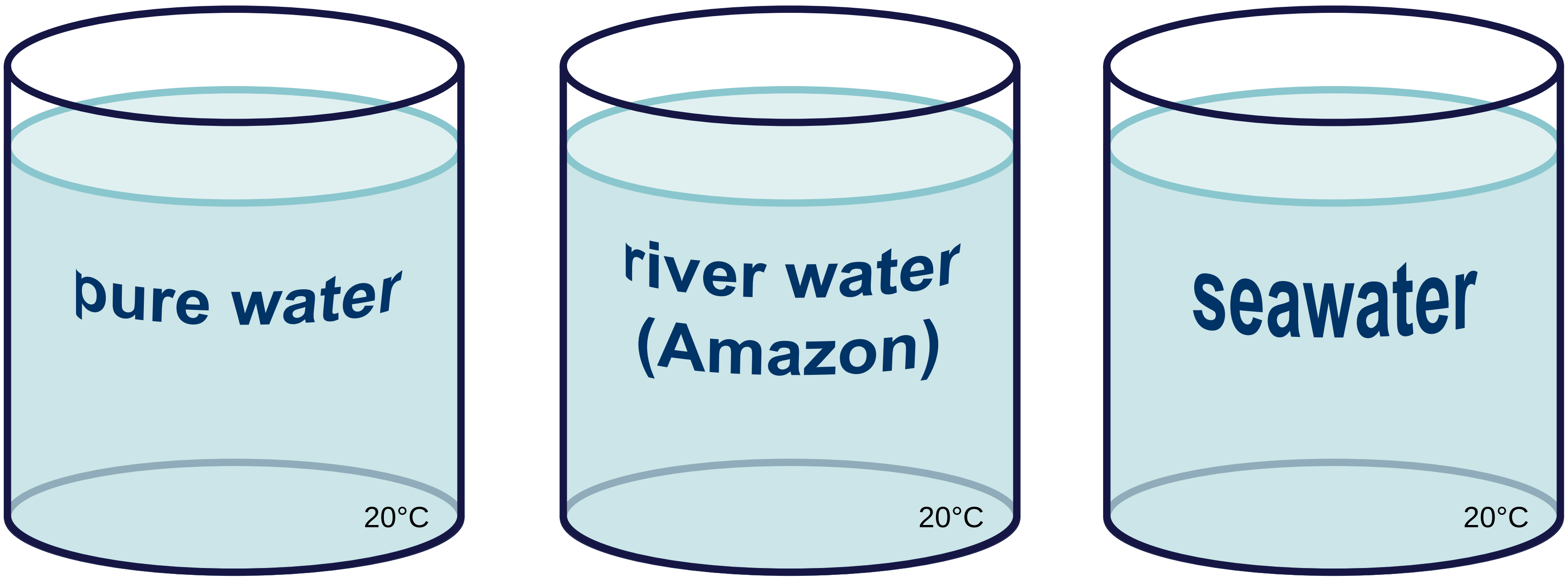
Is the ocean's CO_2 sequestration potential different?

<u>Experiment:</u>

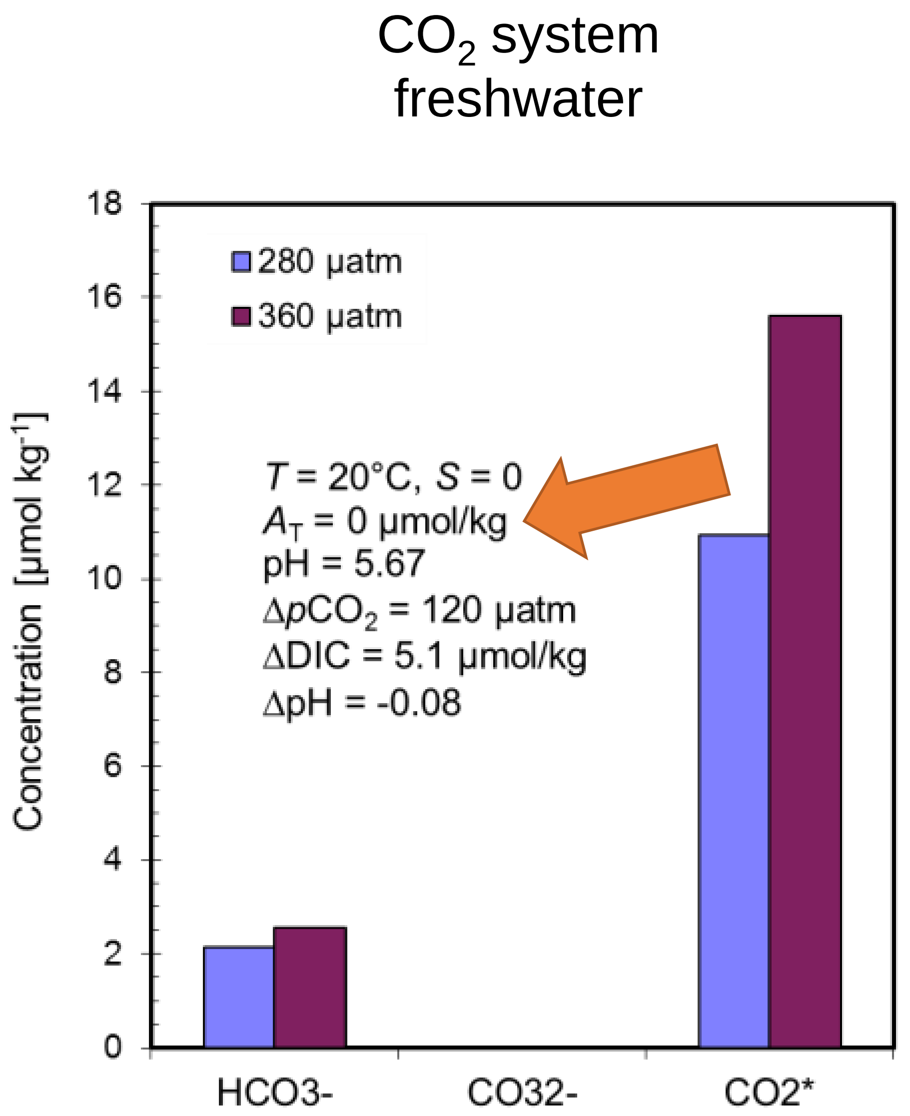
(1) Equilibrate different waters with a gas phase CO_2 concentration of 280 µatm (pre-industrial)
(2) Increase gas phase CO_2 concentration to 400 µatm (present) and re-equilibrate

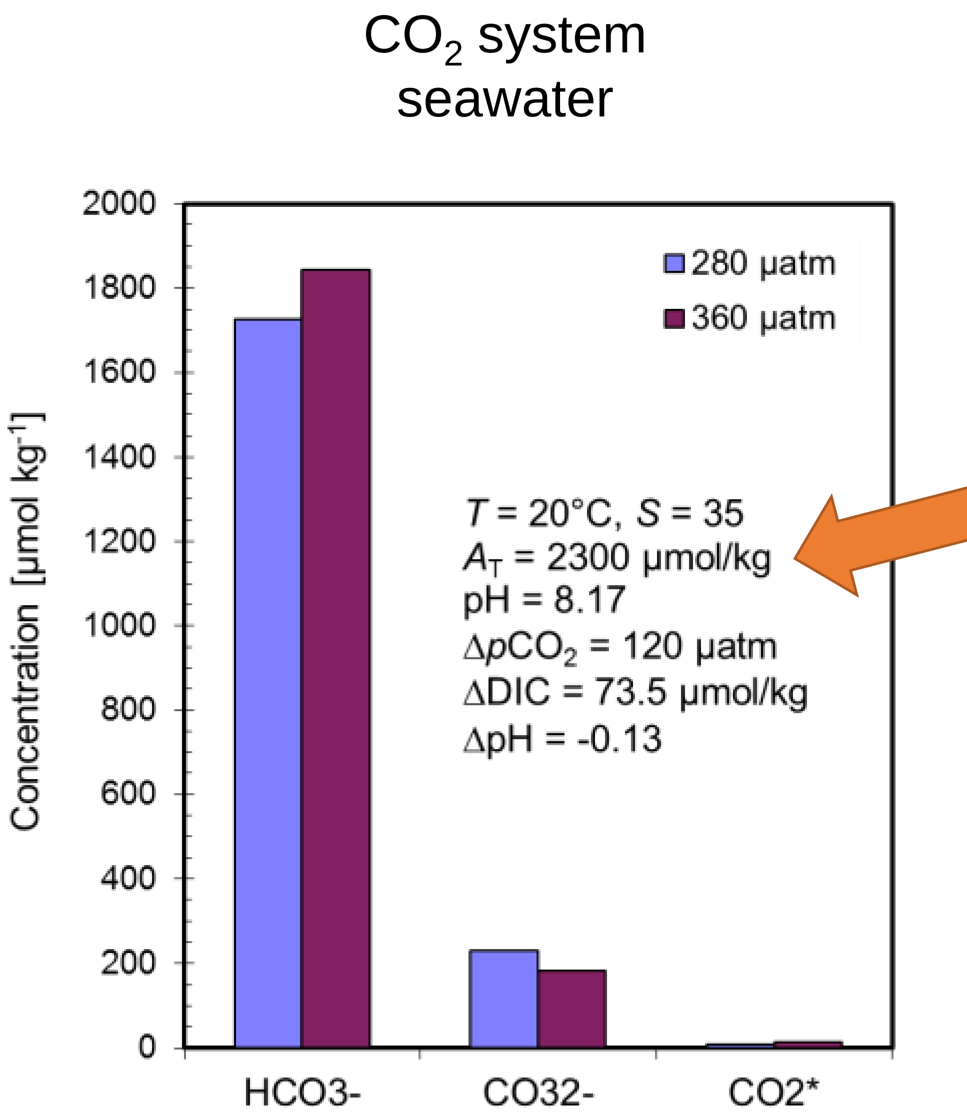
<u>Question:</u>

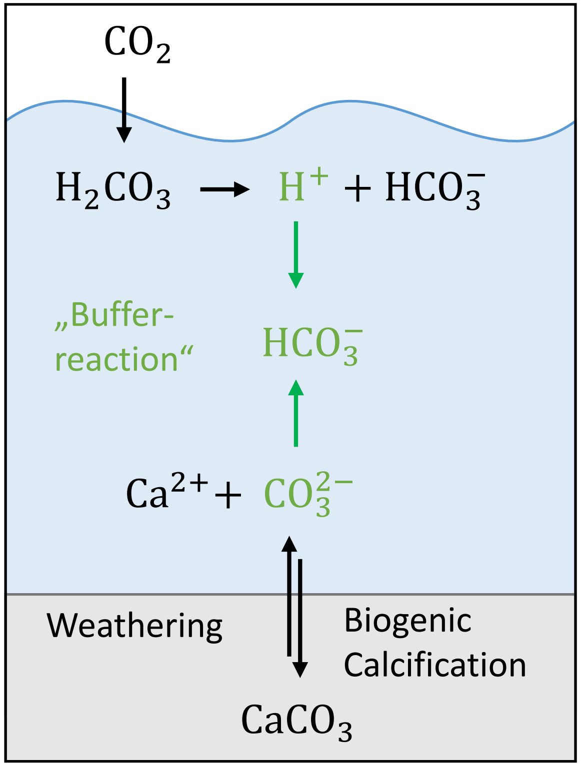
How big is the CO_2 uptake by the different types of water?
(expressed as increase in dissolved inorganic carbon concentration)



ΔDIC = 5 µmol/L	ΔDIC = 6 µmol/L	ΔDIC = 73 µmol/L
(13 → 18 µmol/L)	(607 → 613 µmol/L)	(1965 → 2038 µmol/L)

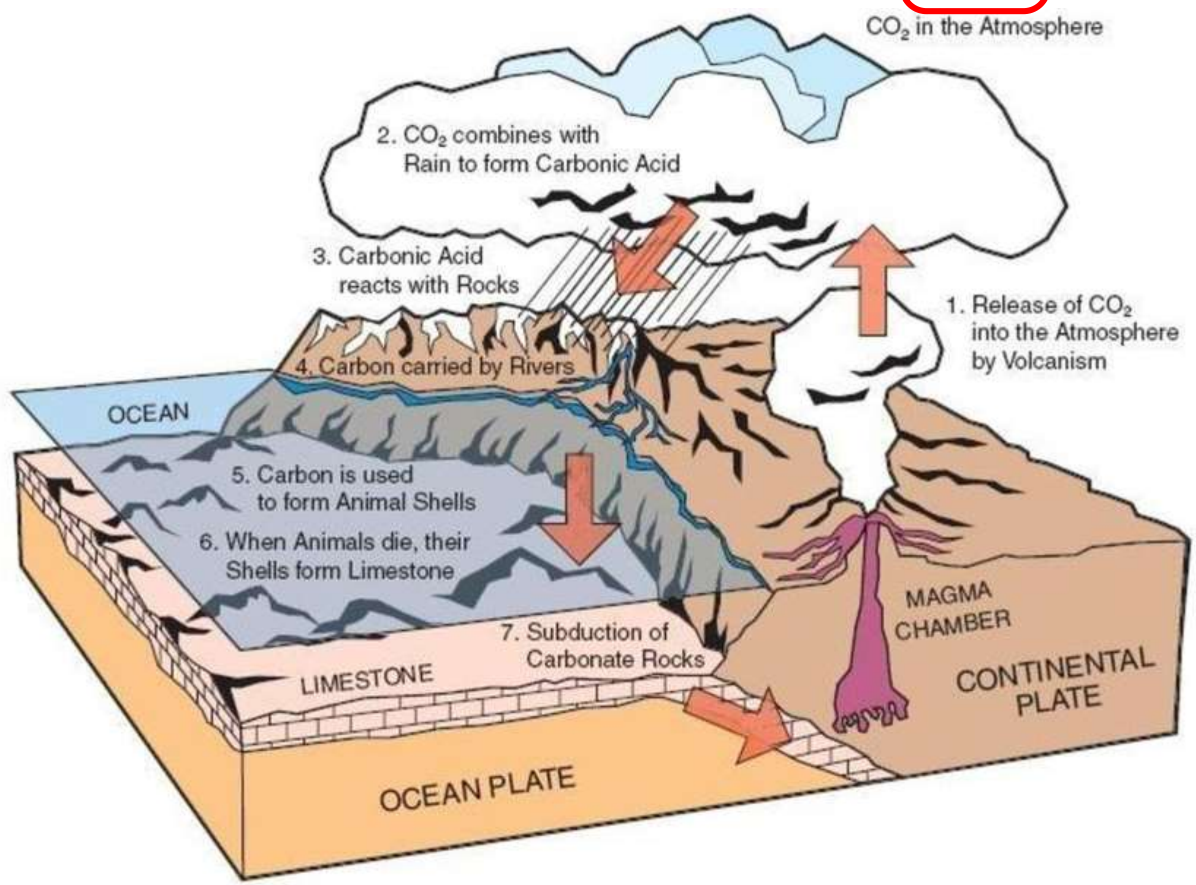

CO2 system
freshwater
18
16
14
12
10
8
6
4
2
0
Concentration [µmol kg-1]
280 µatm
360 µatm
T = 20°C, S = 0
AT = 0 µmol/kg
pH = 5.67
ΔpCO2 = 120 µatm
ΔDIC = 5.1 µmol/kg
ΔpH = -0.08
HCO3-
CO32-
CO2*


CO2 system
seawater
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Concentration [µmol kg-1]
280 µatm
360 µatm
T = 20°C, S = 35
AT = 2300 µmol/kg
pH = 8.17
ΔpCO2 = 120 µatm
ΔDIC = 73.5 µmol/kg
ΔpH = -0.13
HCO3-
CO32-
CO2*



Silicate weathering $CaSiO_3 + 2H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4$

Limestone weathering $CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$



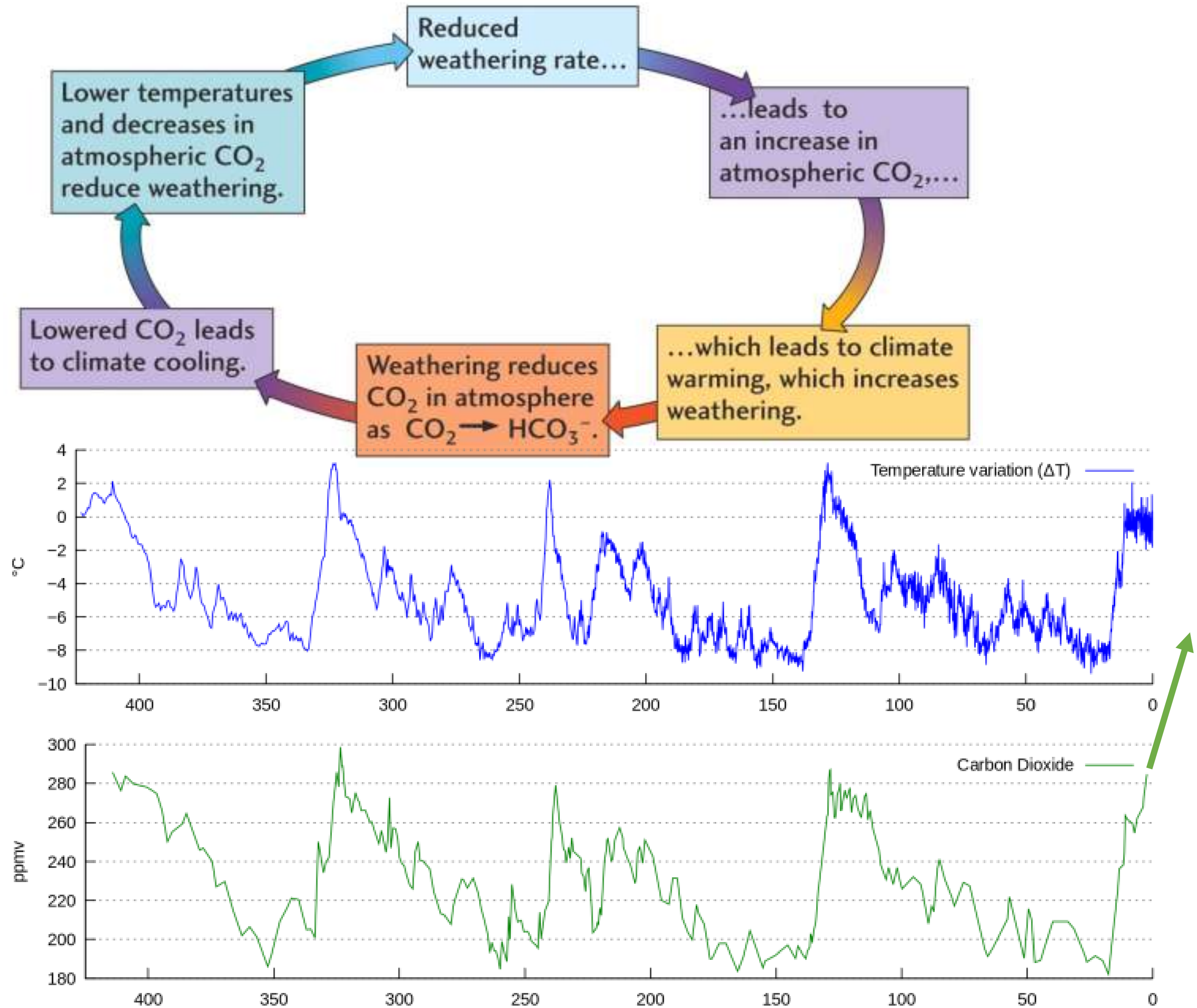
<u>Alkalinity A_T</u>

- Defined as the excess of pronton donors over proton acceptors
- Carbonate Alkalinity:

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

- Buffer reaction controls the CO_2-uptake capacity of seawater

Earth Temperature: Stabilizing CO_2 Feedback Mechanism



Now off to 400+ ppm…

Total dissolved inorganic carbon (DIC, C_T, TCO_2, ΣCO_2)

Book-keeping parameter for carbon

0.5% 88.6% 10.9%

$$\mathrm{DIC} = \left[\mathrm{CO_2(aq)}\right] + \left[\mathrm{HCO_3^-}\right] + \left[\mathrm{CO_3^{2-}}\right]$$

Total alkalinity (TA, A_T)

Booking-keeping parameter for acid-binding capacity

76.8% 18.8% 4.2% 0.2%

$$\mathrm{TA} = \left[\mathrm{HCO_3^-}\right] + 2\left[\mathrm{CO_3^{2-}}\right] + \left[\mathrm{B(OH)_4^-}\right] + \left[\mathrm{OH^-}\right] + \left[\mathrm{HPO_4^{2-}}\right] + 2\left[\mathrm{PO_4^{3-}}\right] + \left[\mathrm{SiO(OH)_3^-}\right] + \left[\mathrm{NH_3}\right] + \left[\mathrm{HS^-}\right]$$
$$- \left[\mathrm{H^+}\right] - \left[\mathrm{HSO_4^-}\right] - \left[\mathrm{HF}\right] - \left[\mathrm{H_3PO_4}\right]$$

pH

Paramater for acidity of seawater

$$p\mathrm{H} = -\log\left[\mathrm{H^+}\right]$$

Partial pressure of CO_2

Governs air-sea gas exchange

$$p\mathrm{CO_2} = \frac{\left[\mathrm{CO_2(aq)}\right]}{K_\mathrm{H}}$$

If the dissociation constants and concentrations of all acid-base species are known:
The CO_2 system is fully determined when 2 out of 4 measurable parameters are known

Formation of particulate organic matter –
Uptake of CO_2 or HCO_3^-

$$CO_2 + H_2O \Rightarrow (CH_2O)_{org} + O_2$$

$\Delta A_T = 0$ $\Delta C_T = -1$ $pH \uparrow$ $pCO_2 \downarrow$

$$HCO_3^- + H_2O \Rightarrow (CH_2O)_{org} + OH^- + O_2$$

$\Delta A_T = 0$ $\Delta C_T = -1$ $pH \uparrow$ $pCO_2 \downarrow$

Respiration of particulate organic matter

$$(CH_2O)_{org} + O_2 \Rightarrow CO_2 + H_2O$$

$\Delta A_T = 0$ $\Delta C_T = +1$ $pH \downarrow$ $pCO_2 \uparrow$

Formation of particulate calcium carbonate

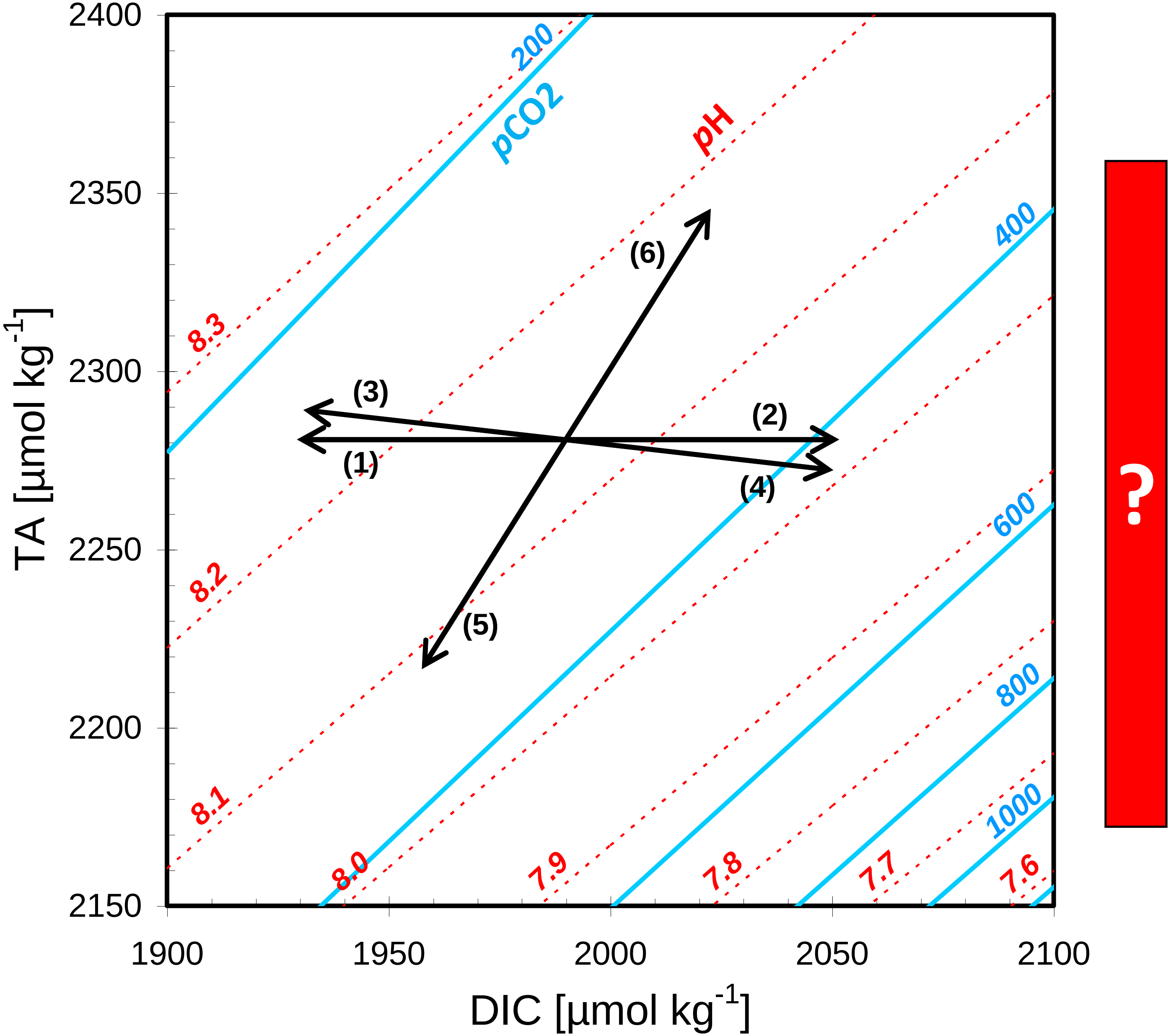
$$Ca^{2+} + 2\ HCO_3^- \Rightarrow CaCO_3\ (s) + CO_2 + H_2O$$

$\Delta A_T = -2\ \Delta C_T = -1$ *p*H ↓ *p*CO_2 ↑

Dissolution of particulate calcium carbonate

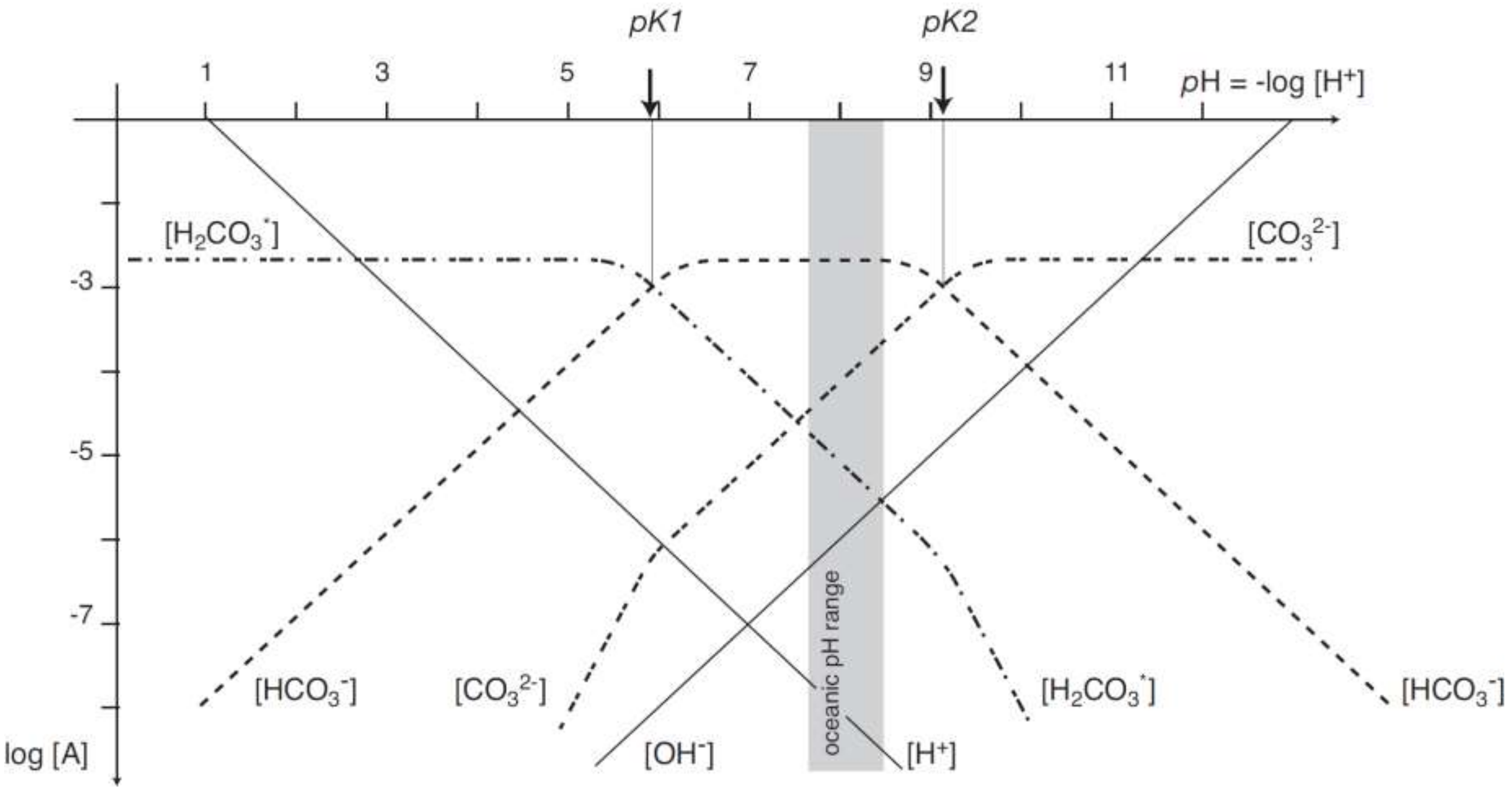
$$CaCO_3\ (s) + CO_2 + H_2O \Rightarrow Ca^{2+} + 2\ HCO_3^-$$

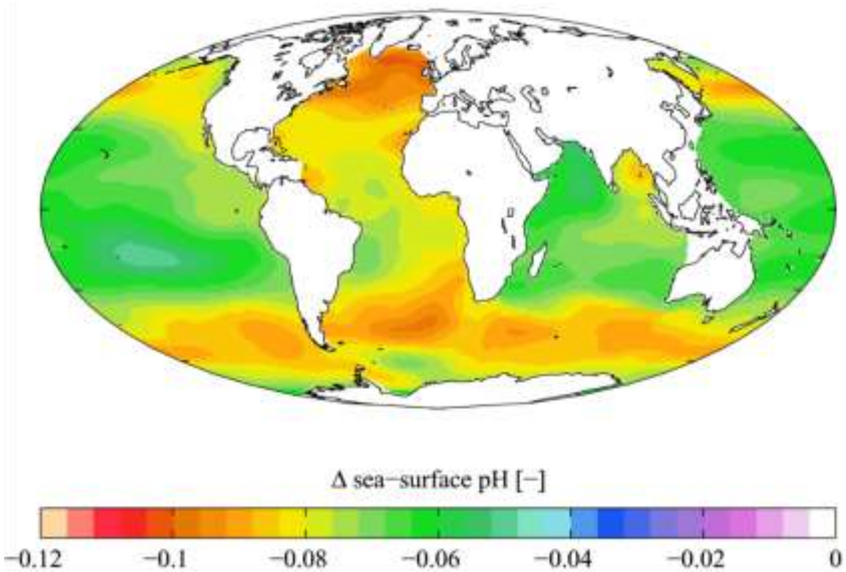
$\Delta A_T = +2 \Delta C_T = +1$ *p*H ↑ *p*CO_2 ↓

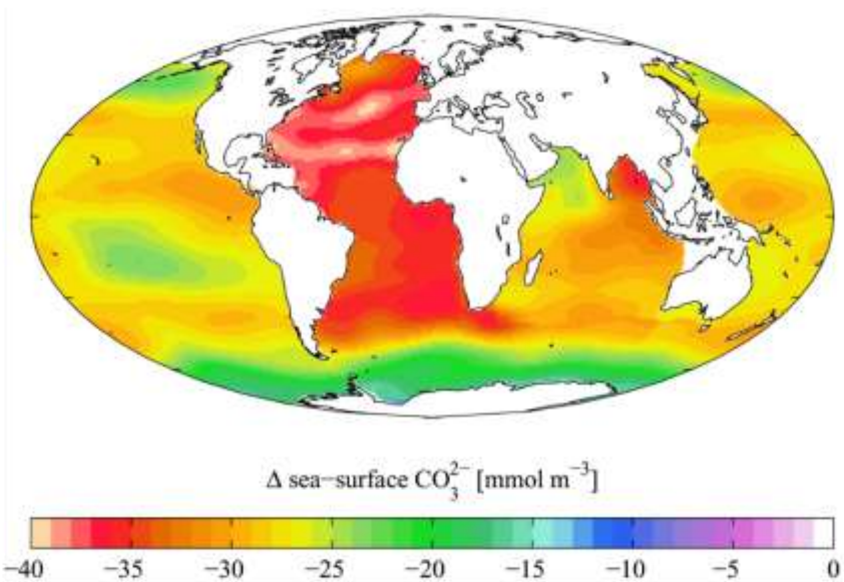


- CO_2 release to atmosphere
- CO_2 uptake from atmosphere
- Primary production
- Respiration
- Calcification
- Carbonate dissolution

Bjerrum plot of carbonic acid species in seawater

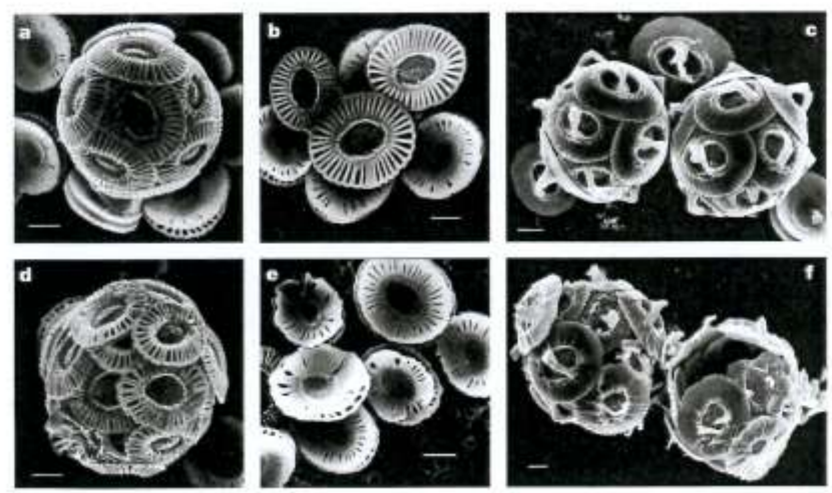




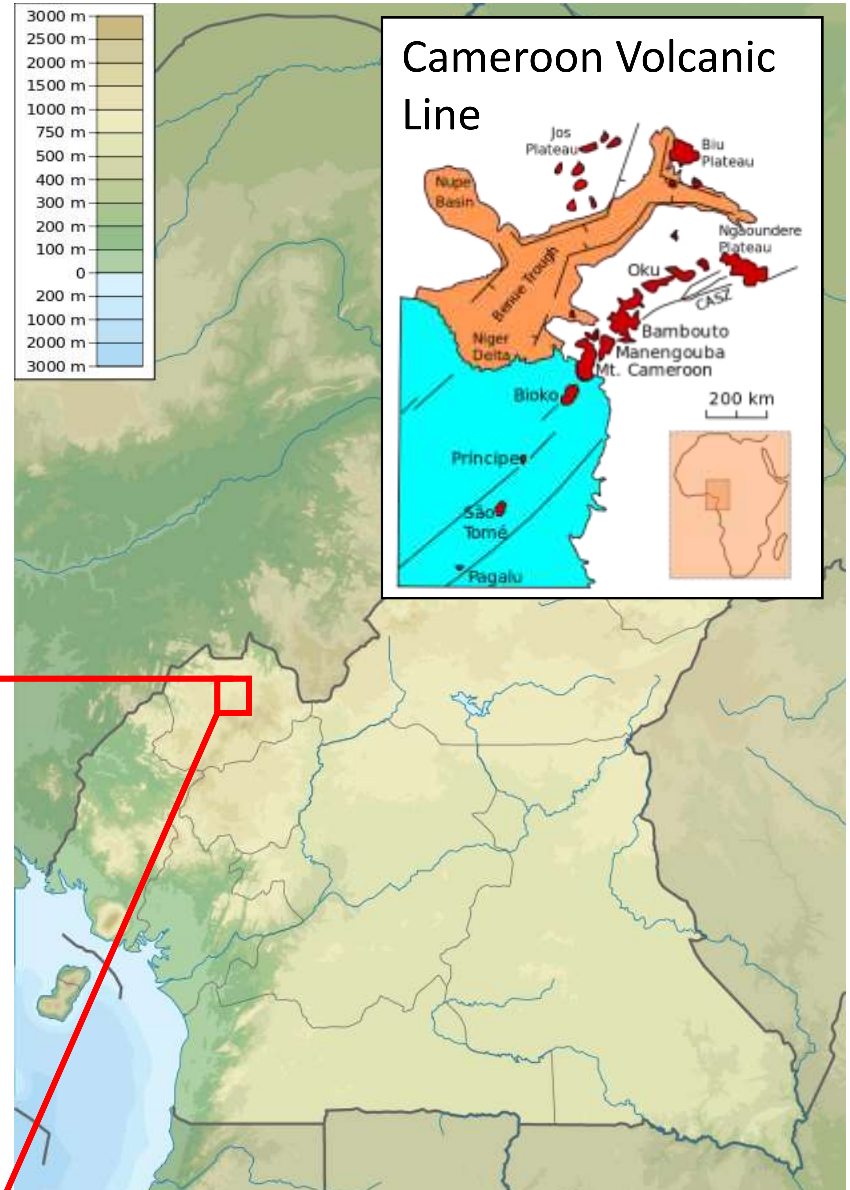


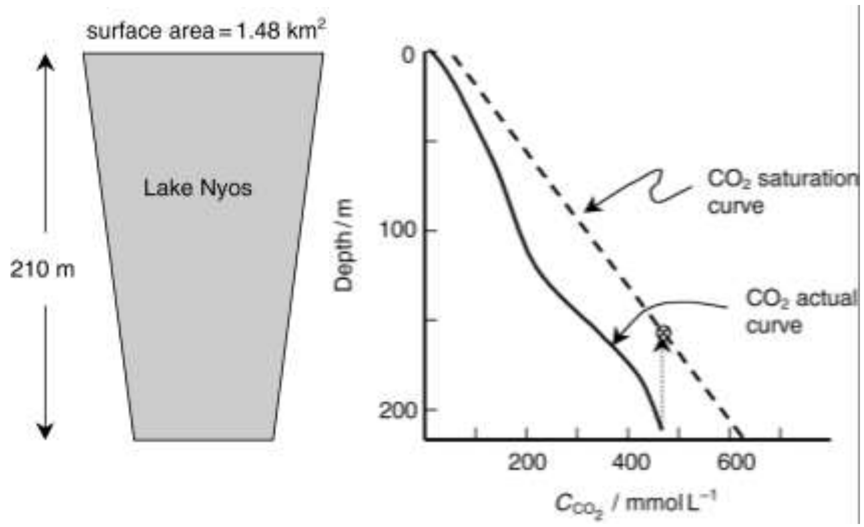
Estimated change in annual mean sea surface pH and carbonate ion (CO_3^{2-}) concentration between the pre-industrial period (1700s) and the present day (1990s).

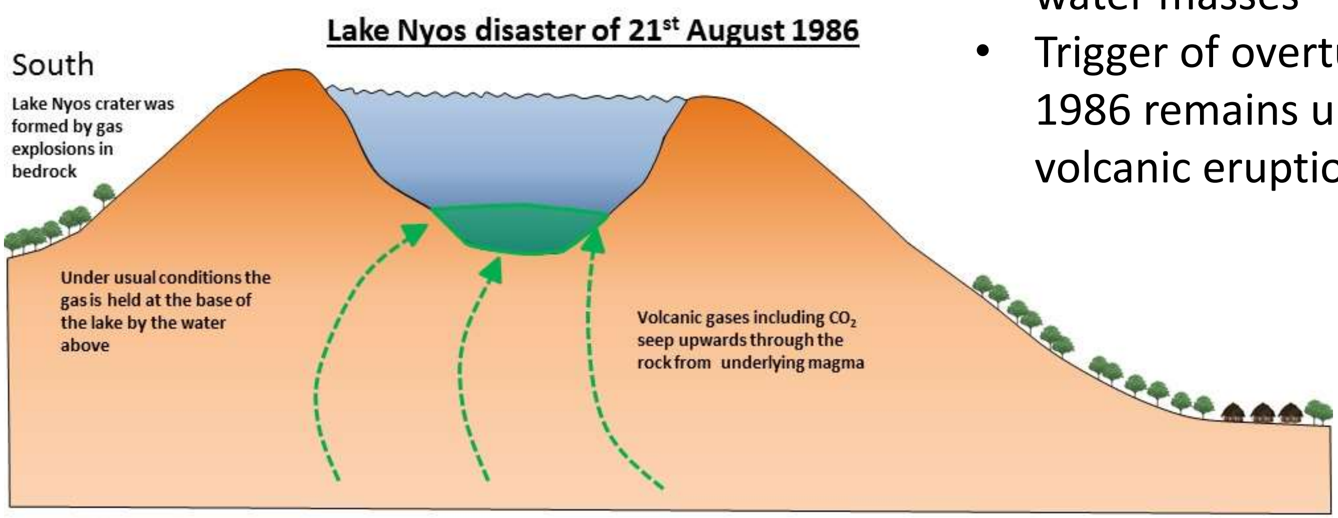
Reduced pH and carbonate ion availability impairs calcification conditions for marine calcifiers such as the phytoplankton species Emiliania Huxleyi.



- Lake Nyos in NW Cameroon with max. depth of 210 m
- 21 August 1986: sudden release of about 100,000–300,000 tons of carbon dioxide
- Gas cloud initially rose 100m high, 25m high wave hit the coast
- Being heavier than air, CO_2 descended onto nearby villages, displacing air
- Around 1,700 people and 3,500 livestock killed within 25 kilometres

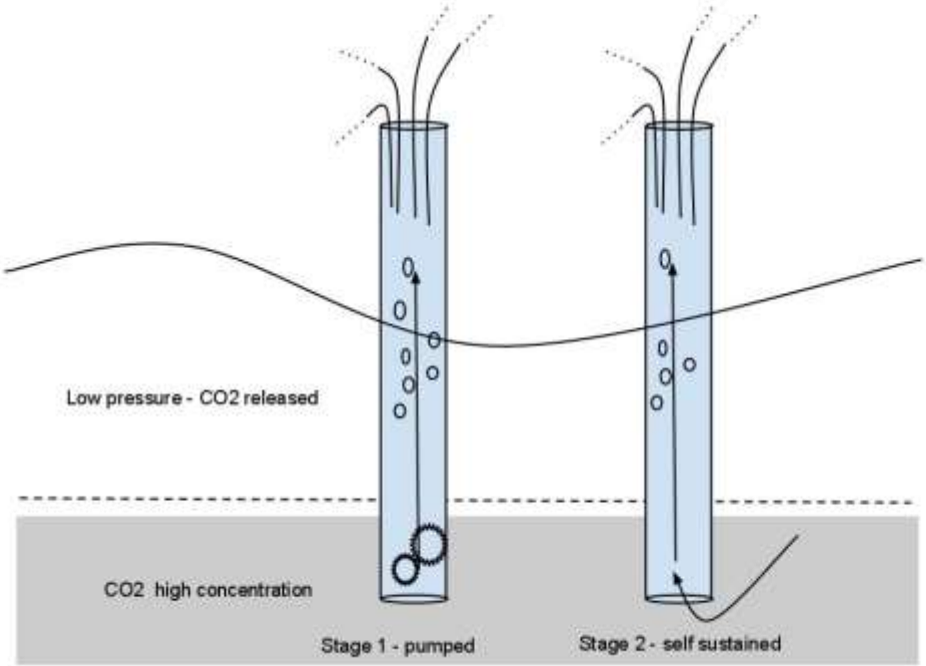






- Pocket of magma beneath lake leaks ~90.000 tons CO_2 per year into water
- Lake Nyos is thermally stratified: warm water near surface floating on colder water layers near bottom
- Saturation with CO_2 at depth
- Most of the time, stratification is stable and CO_2 remains in solution
- Uplift of water masses results in oversaturation, spontaneous degassing and self-powered uplift of additional water masses
- Trigger of overturn and outgassing in 1986 remains unknown: landslide, small volcanic eruption or cool rainwater?

- Continuous degassing of the lake since 30 January 2001
- Polyetheylene tubes (diameter 14.5 cm) lowered to the base of the lake
- Active pumping to begin rising water
- CO_2 degassing above saturation horizon causes faster rising, 50m water fountain and sucking up more water behind it
- Self-powered airlift pump



Take home messages

- Henry's law describes the solubility of gases
- Physical and biological pumps control O_2 and CO_2 in the global ocean
- Alkalinty from weathering processes causes high CO_2 storage capacity of seawater
- Ocean acidification is a major threat to marine ecosystem stability
- Lake Nyos disaster