Dissolved Gases

Lecture by Jens Daniel Müller
In: Analytical Chemistry 4: Environmental Chemistry
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(Slides contributed from A. Körtzinger, G. Rehder, B.Schneider)

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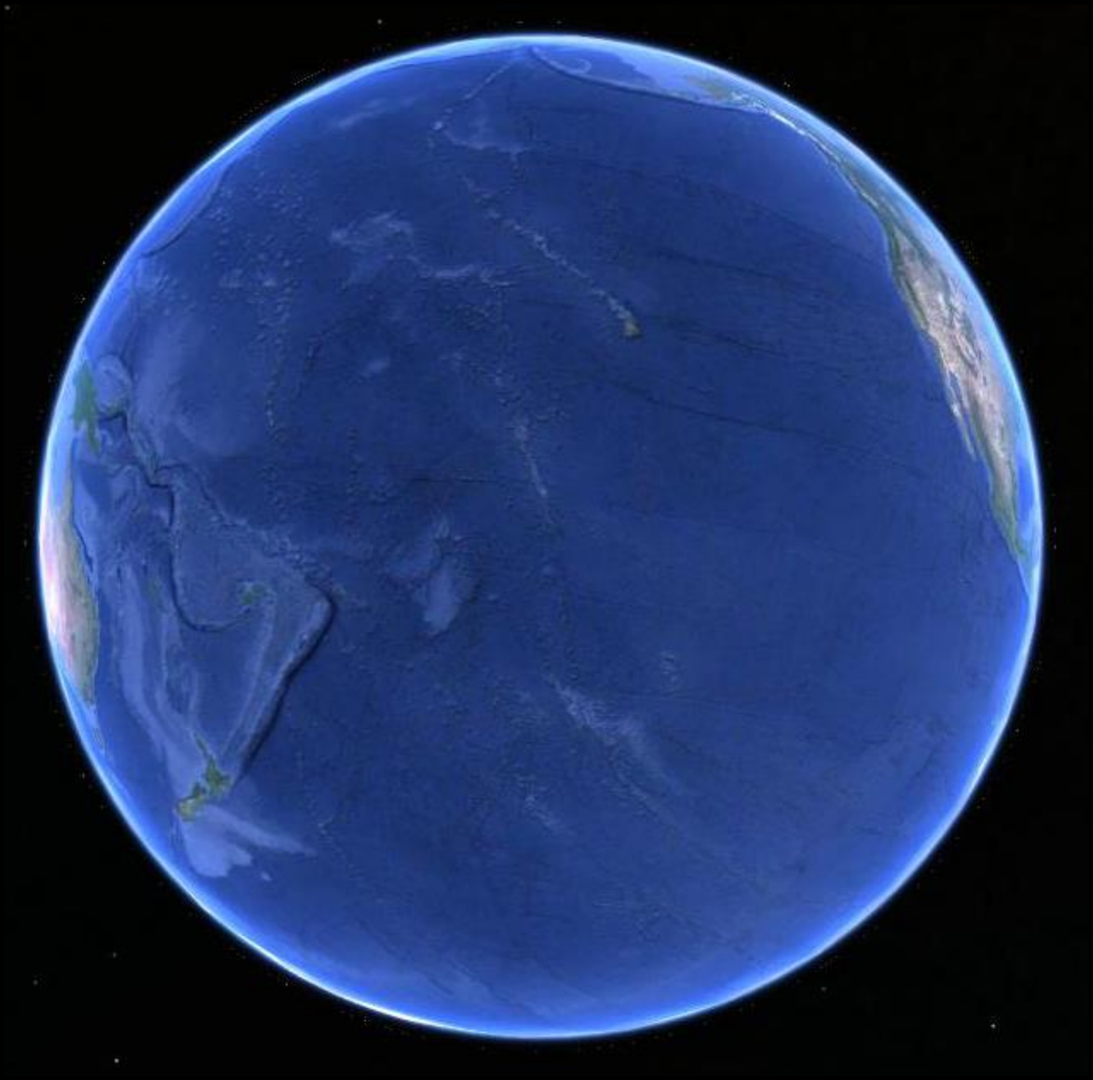
The world ocean covers 71% of the Earth‘s surface…

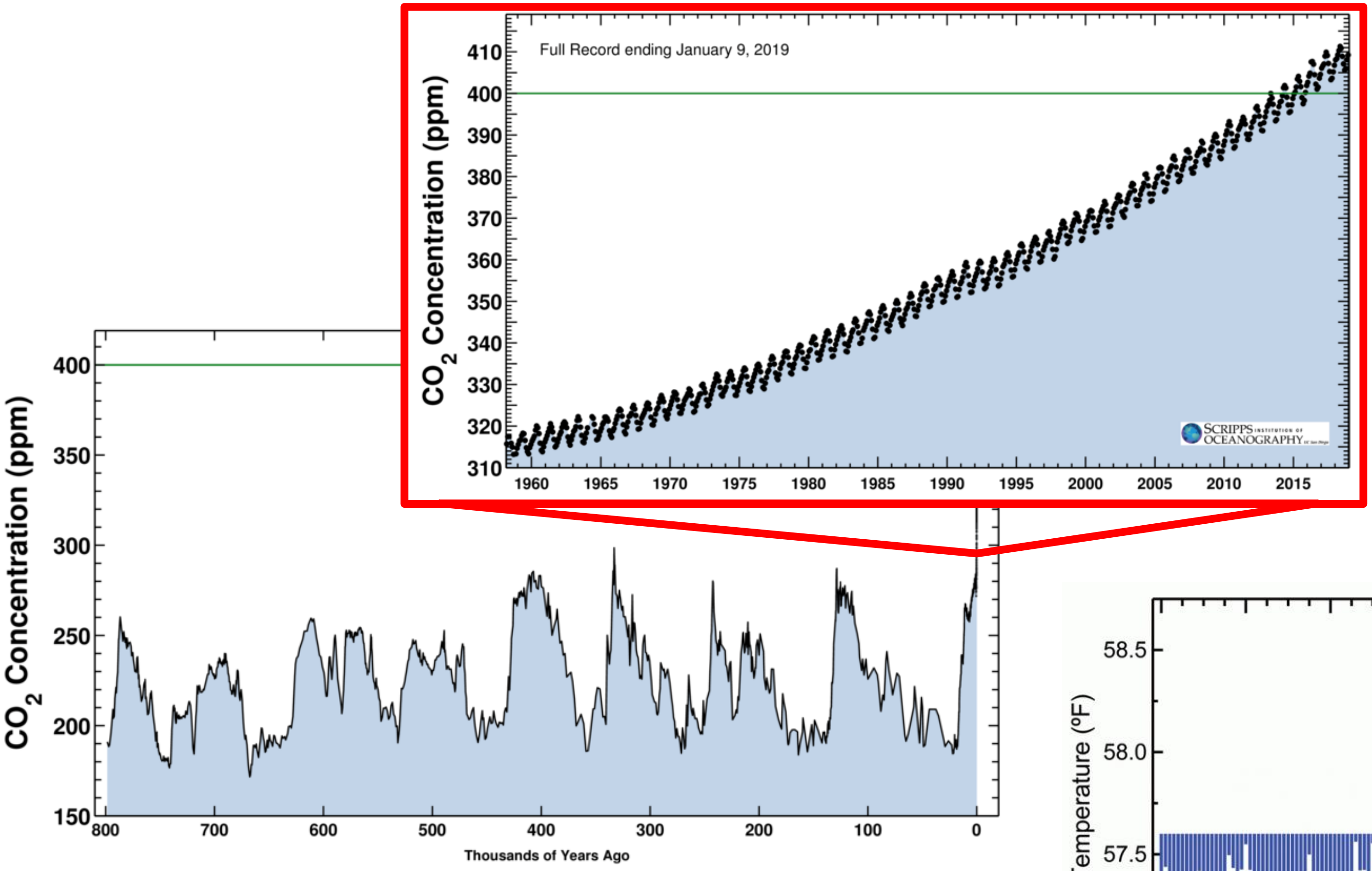


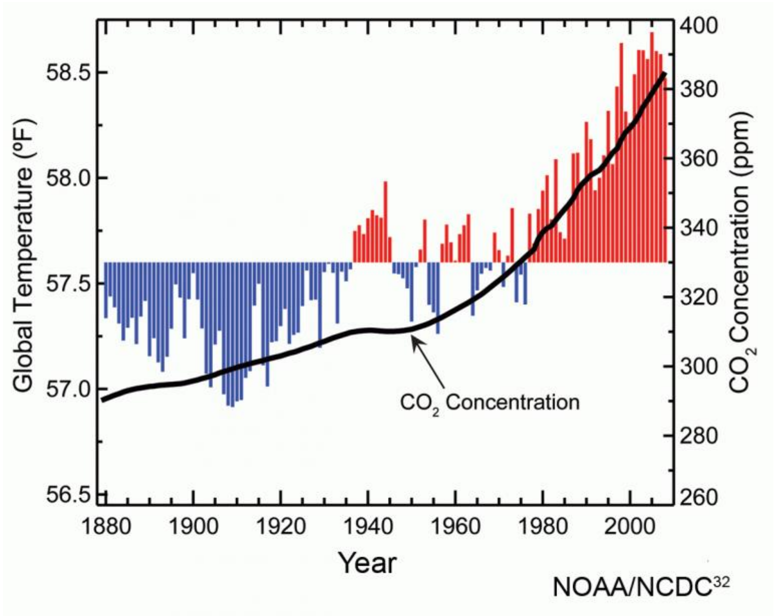
…and plays a central role in controlling the composition of its atmosphere!

Outline

- Motivation
- Solubility of gases
- Air sea gas exchange
- O_2 in the global ocean
- Marine CO_2-system
  - Equilibrium reactions
  - Freshwater vs seawater
  - Alkalinity
  - 4 measurable parameters
  - Ocean acidification

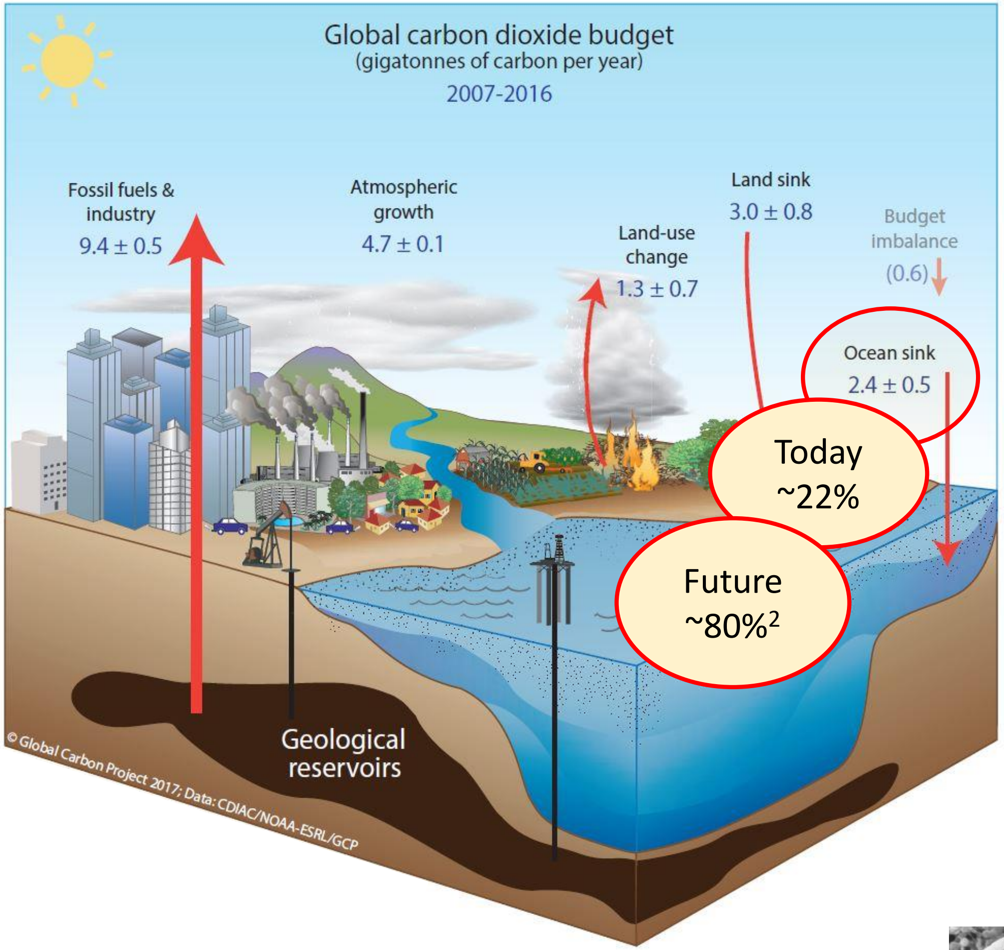
Motivation: The Oceans Role in Climate Change





https://scripps.ucsd.edu/programs/keelingcurve/

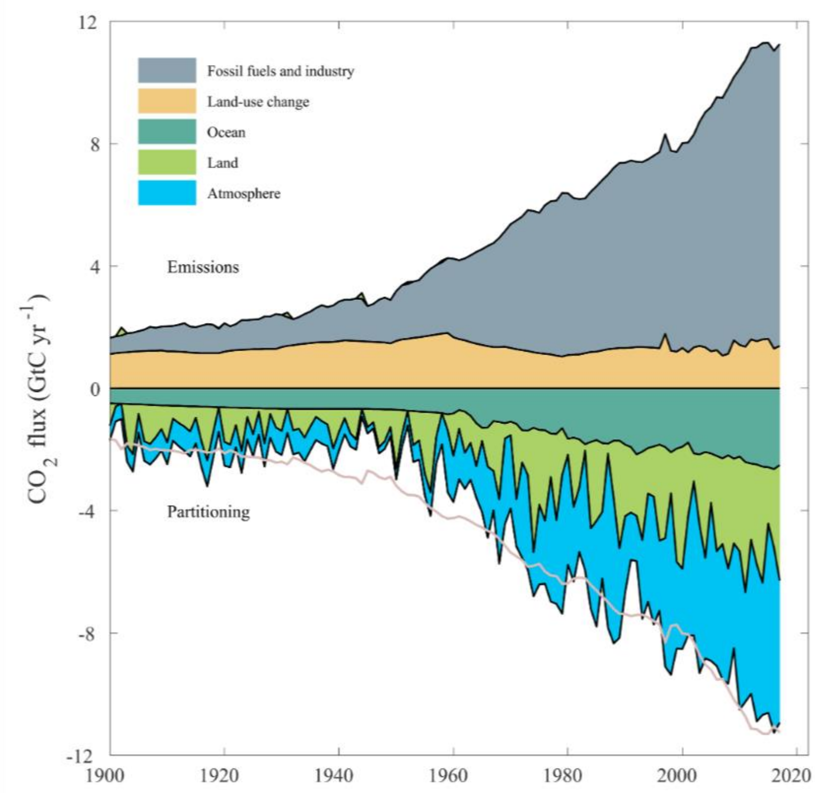
Motivation: The Oceans Role in Climate Change



© Global Carbon Project 2017; Data: CDIAC/NOAA-ESRL/GCP

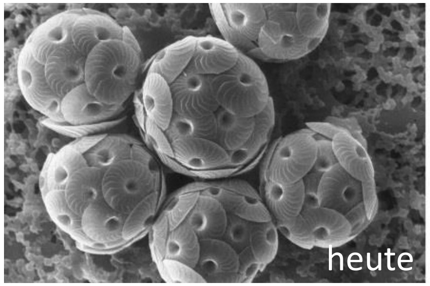
Today
~22%

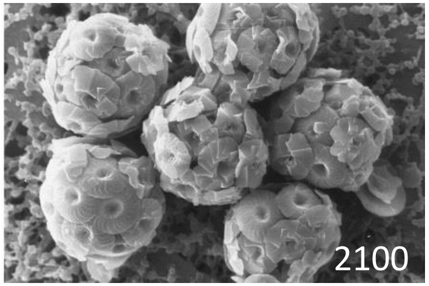
Future
~80%^{2}



Oceanic CO_2-uptake counteracts climate change at the cost of acidification, with unpredictable consequences for marine ecosystems.

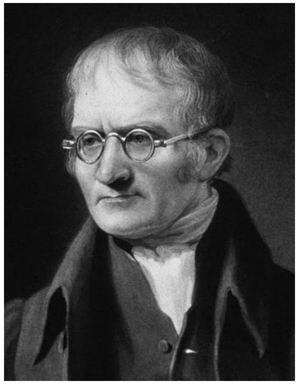
What are the chemical mechanisms involved?





Le Quéré et al. (2017), Riebesell et al. (2000)

Recap: Pressure of Gases in the Atmosphere



John Dalton
(1766 –1844)

Dalton‘s Law for ideal gases:

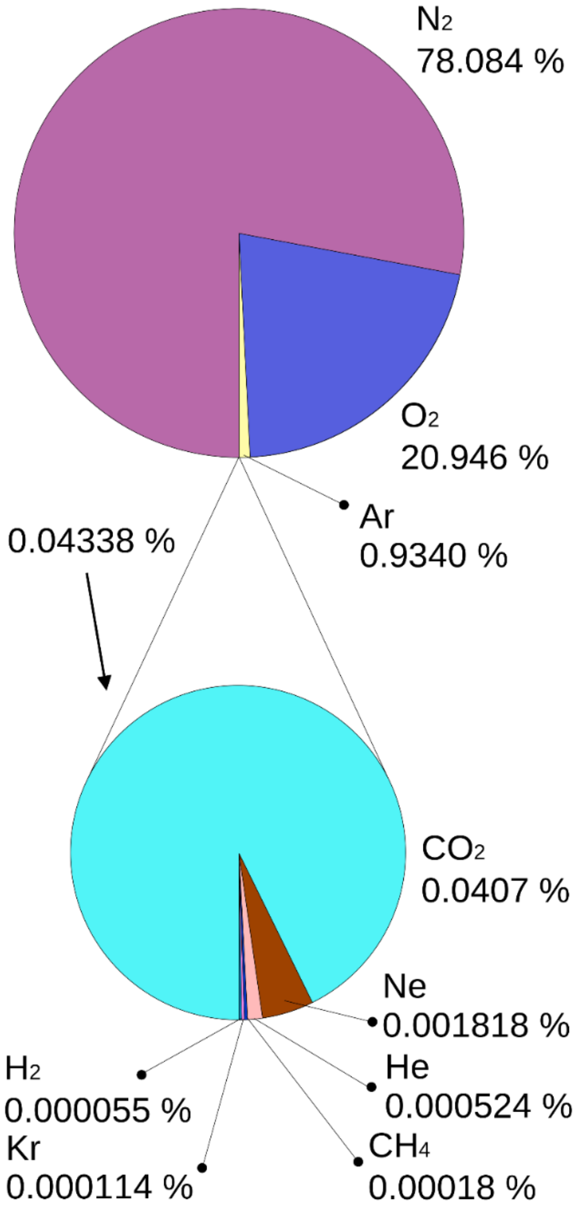
$$\boldsymbol{P = \sum_{i=1}^{k} p_i}$$

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

Definition of partial pressure:

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

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



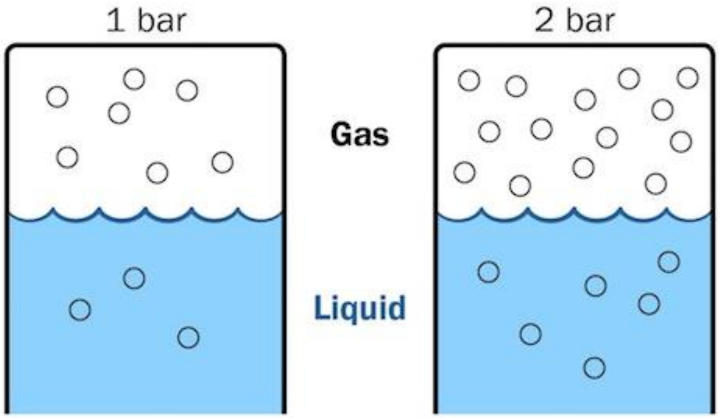
Solubility of gases in aqueous solutions

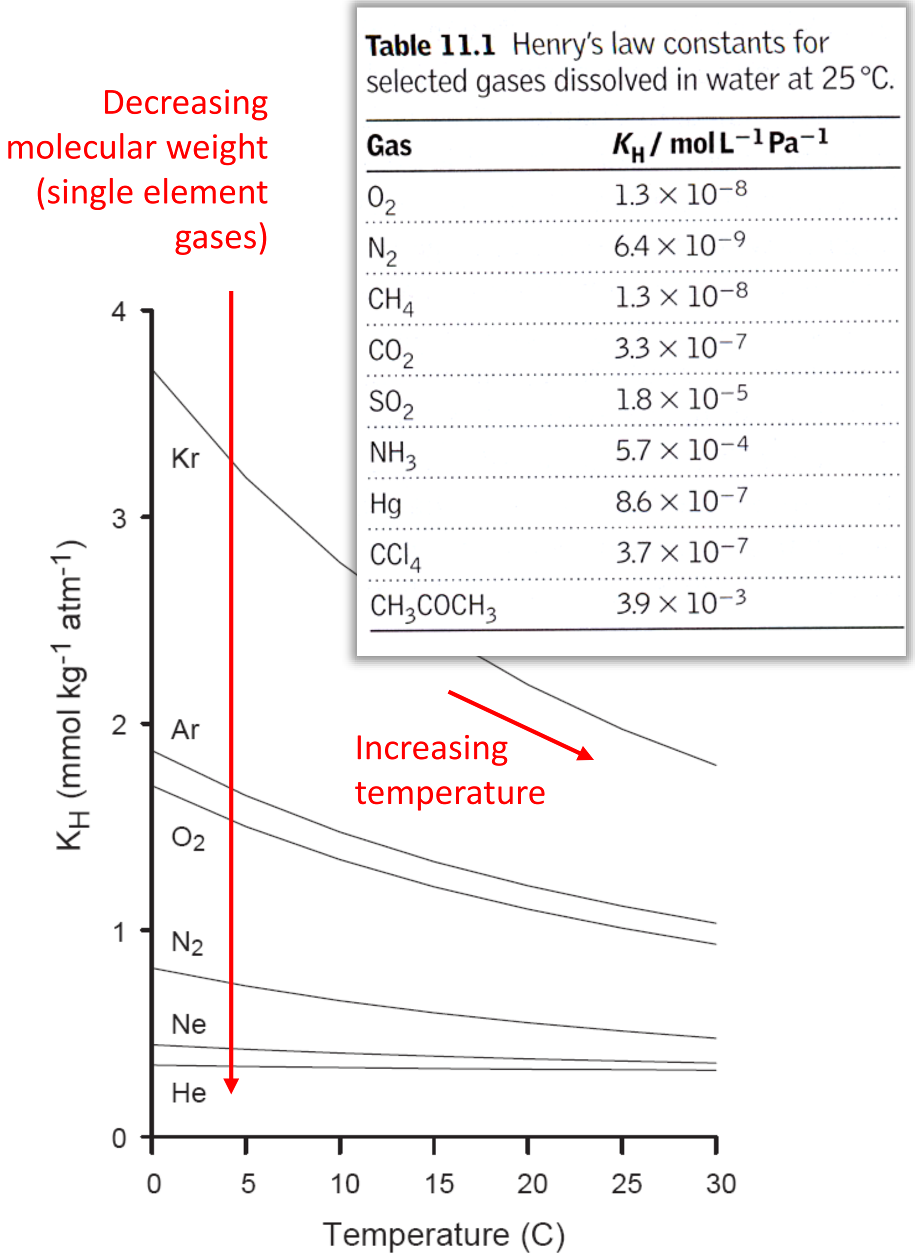
William Henry
(1774 - 1836)

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)





Decreasing molecular weight (single element gases)

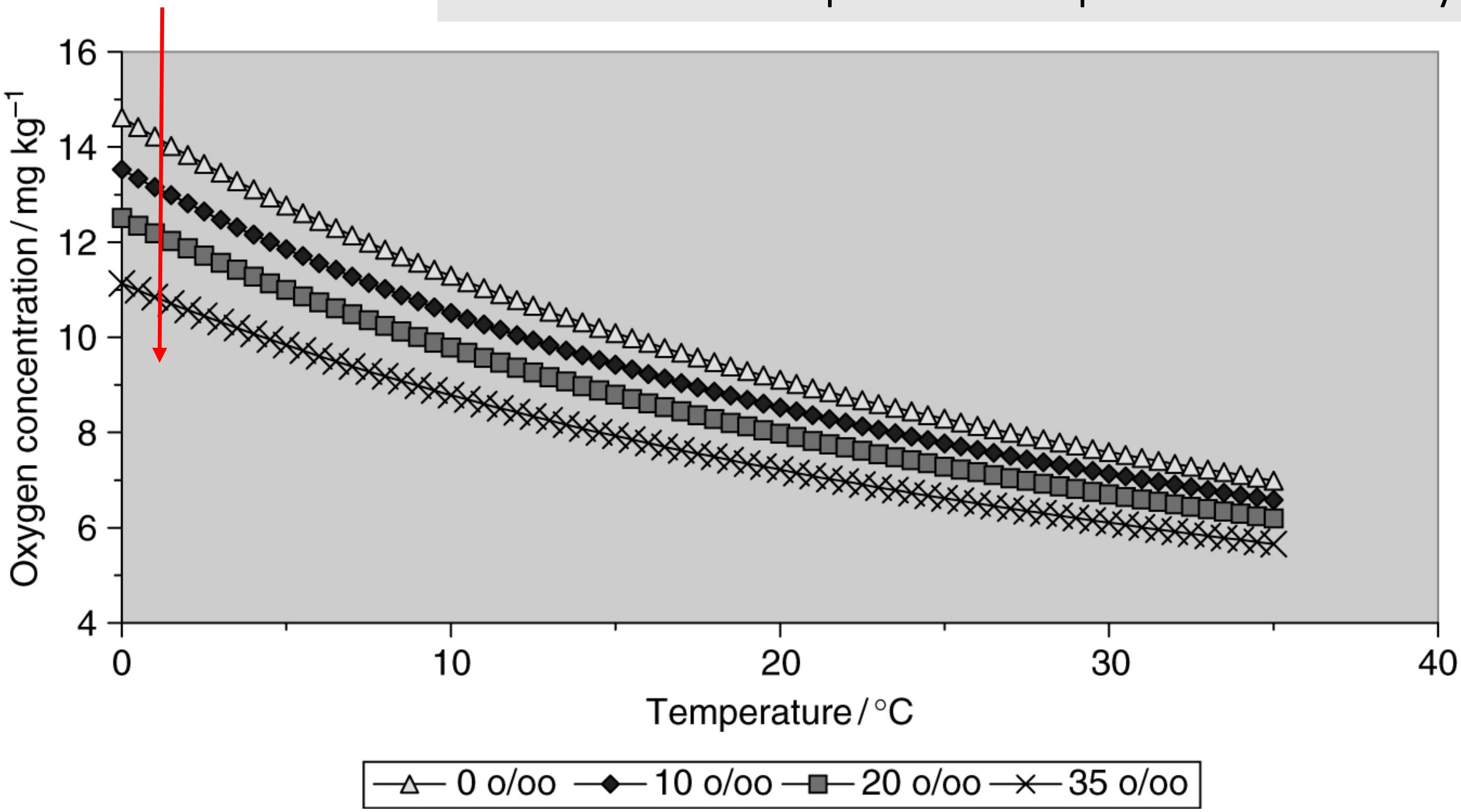
Increasing temperature

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}

Solubility of Oxygen and the Impact of Salinity

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



Solubility of Oxygen and the Impact of Salinity

So far:

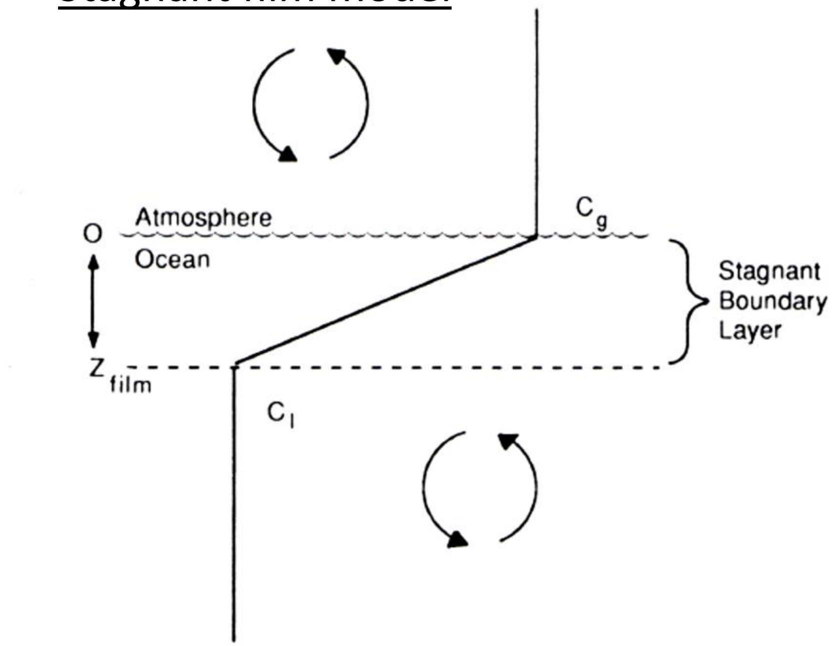
- Equilibrium considerations
- Gas specific solubility increases with
    - Decreasing temperature
    - Decreasing salinity
    - Increasing molecular weight (single element gases)

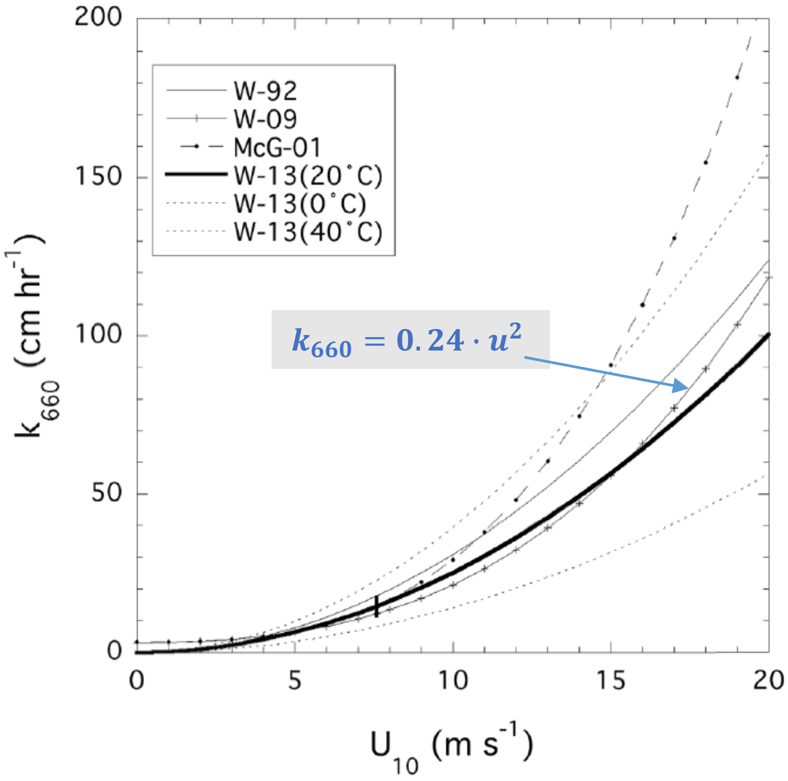
But:

- In nature, dissolved gases are rarely in equilibrium with atmosphere
- Gas exchange takes place continuously

In brief: Gas Exchange between Water and Atmosphere

Stagnant film model





$$k_{660} = 0.24 \cdot u^2$$

Air sea gas fluxes

$$F = k \cdot K_0 \cdot (pG_W - pG_a)$$

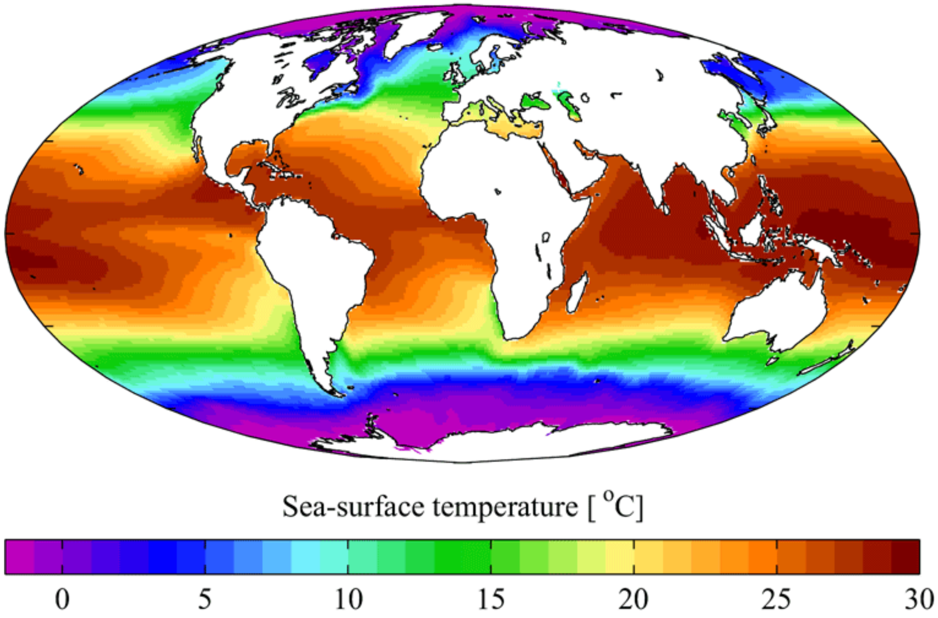
F = flux (mass area^{-1} time^{-1})
k = gas transfer velocity (length time^{-1})
pG_w = partial pressure of gas G in water
pG_a = partial pressure of gas G in air

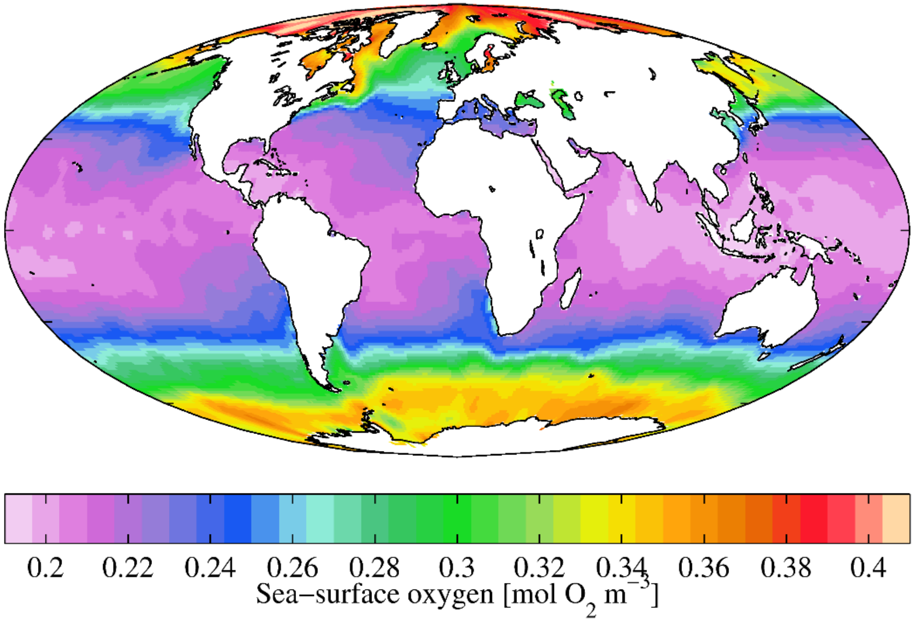
$$k = k_{660}(u) \cdot \left(\frac{660}{Sc(T,S)}\right)^{0.5}$$

k_{660} = transfer velocity normalized to Sc = 660, describes impact of wind on laminar layer
Sc = Schmidt number, gas specific (=660 for CO_2 at 20°C), ratio of viscosity to diffusion coefficient

Wanninkhof (2014)

Surface Distribution of Oxygen in the Global Ocean

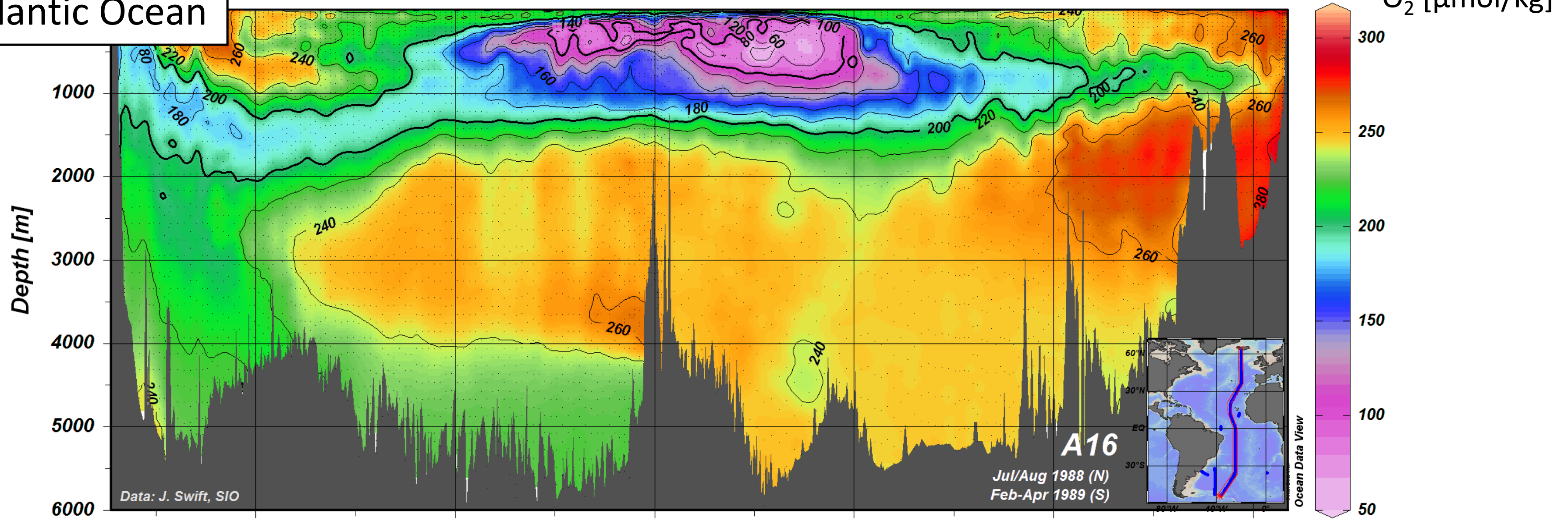




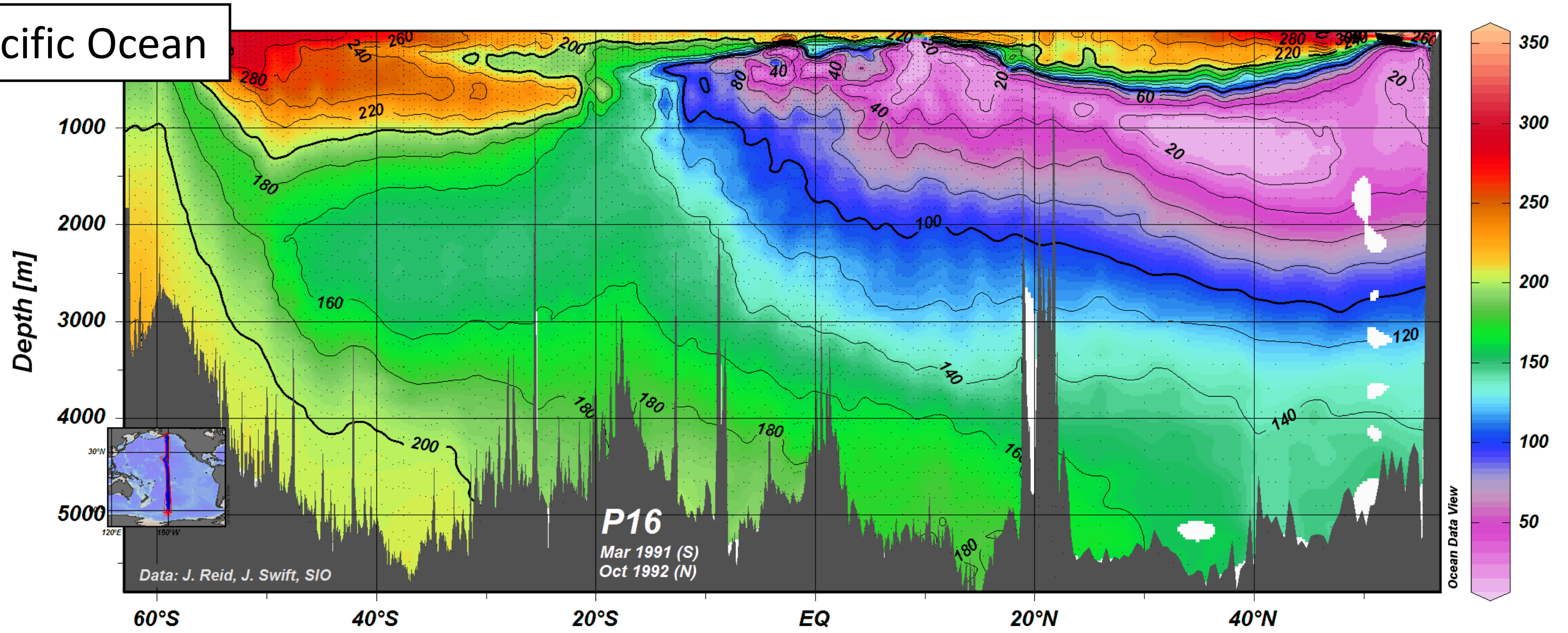
Surface distribution of O_2 in the global ocean reflects its decreasing solubility with increasing sea surface temperature (SST)

Vertical Distribution of Oxygen in the Global Ocean

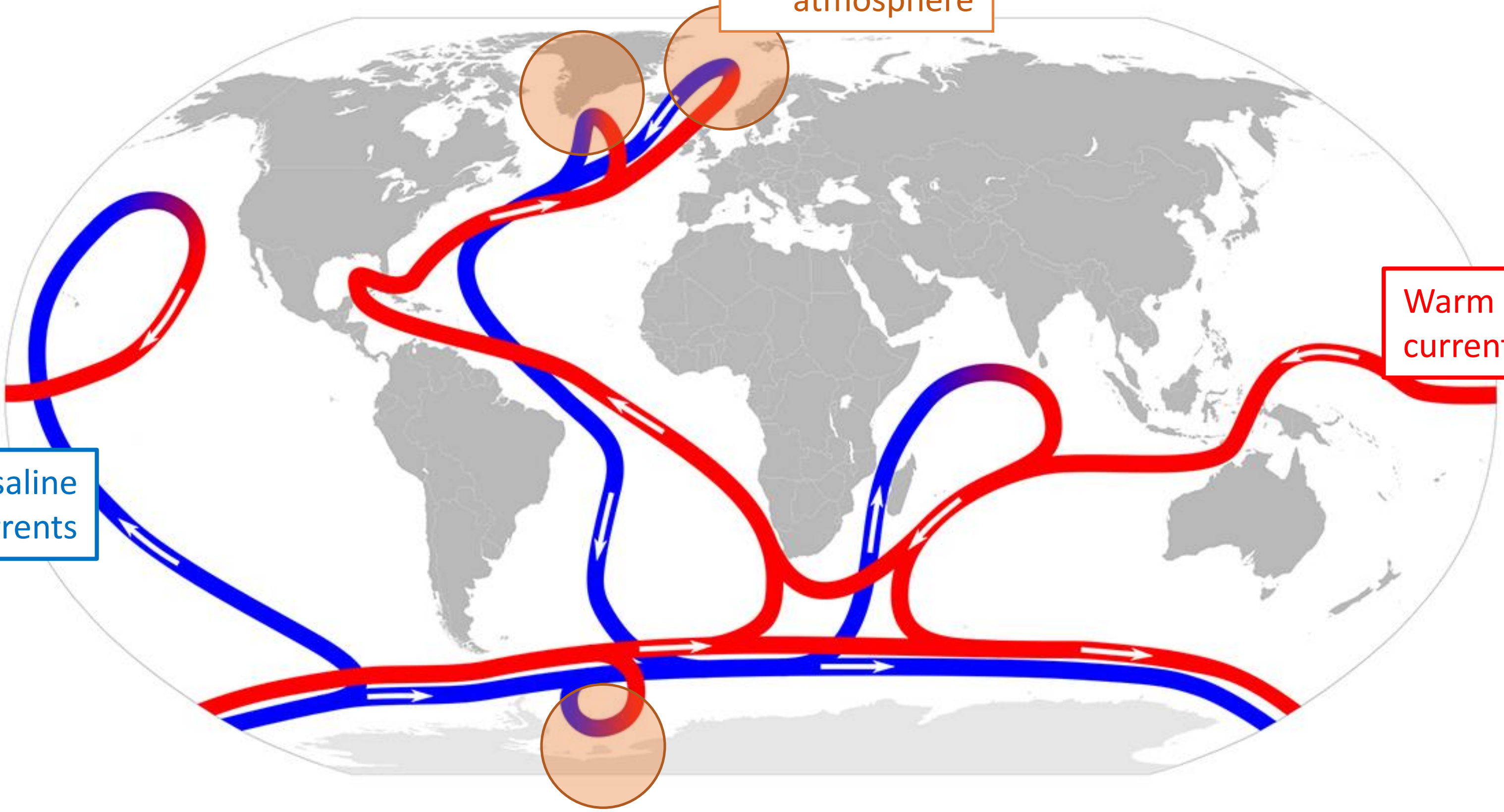
Atlantic Ocean



Pacific Ocean



Thermohaline circulation: The Global Ocean Conveyor Belt



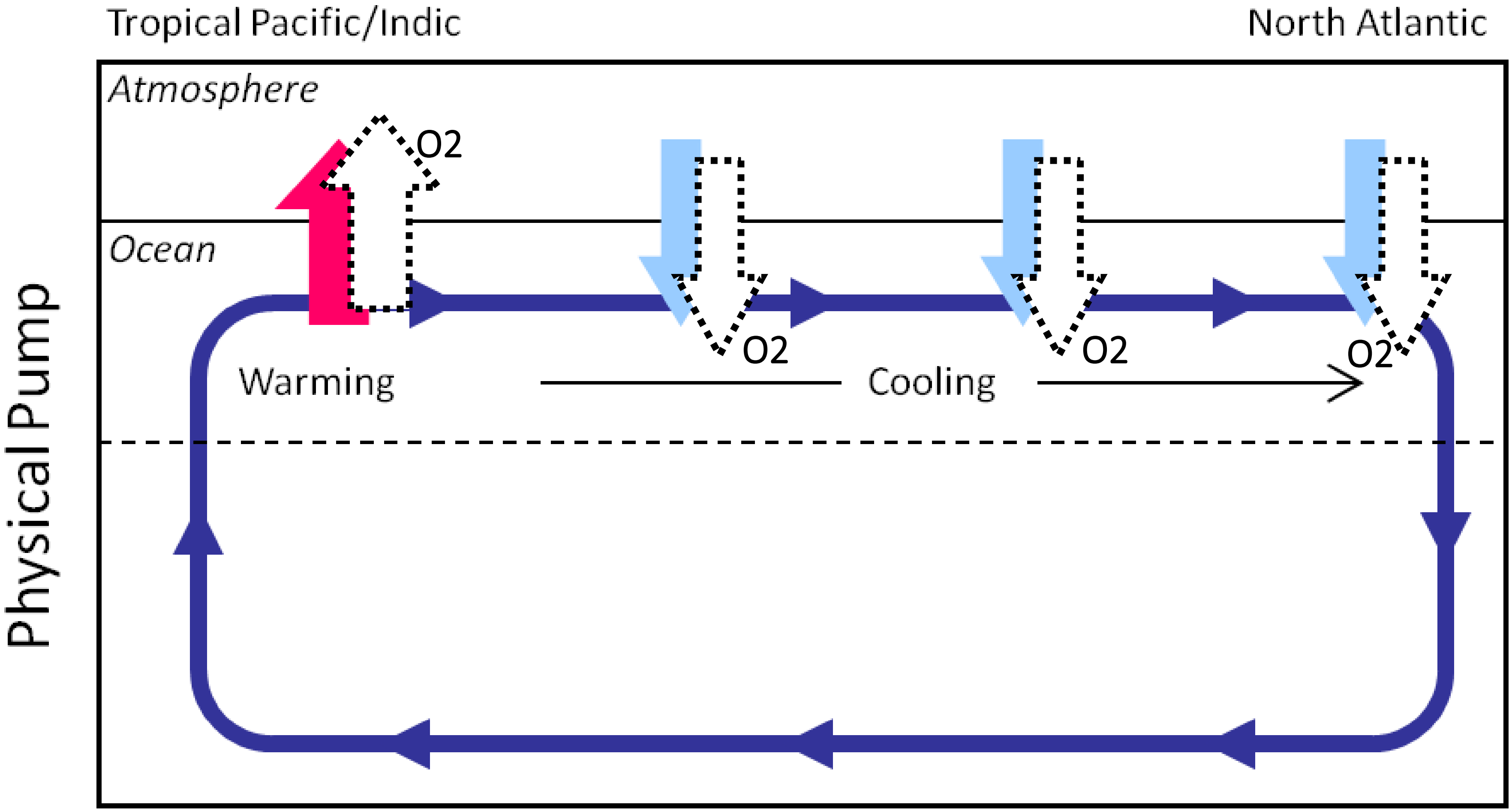
Heat release to atmosphere

Warm surface currents

Cold saline deep currents

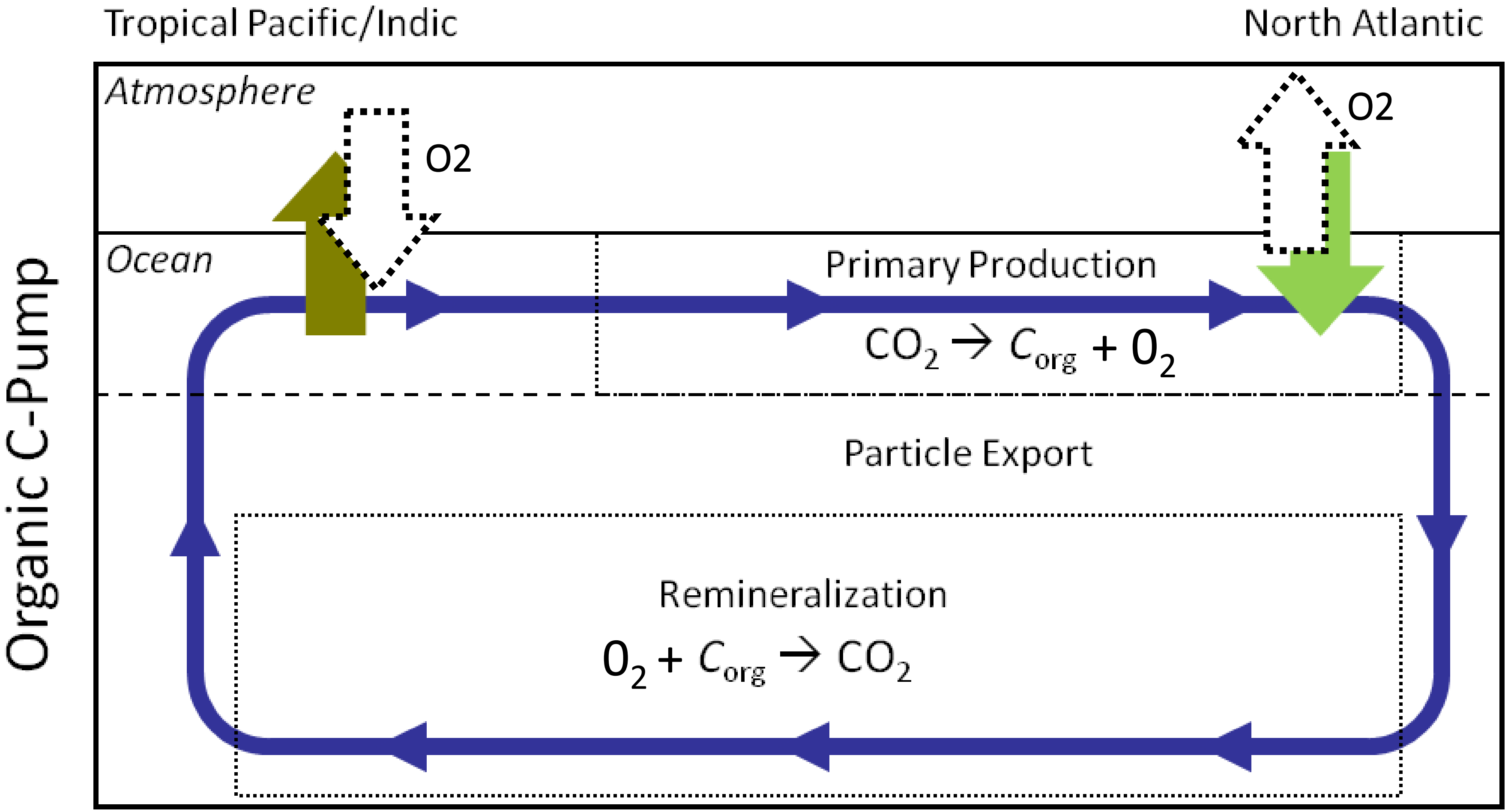
Physical Carbon Pump (aka: Solubility Pump)

- Decrease in SST favors O_2 solubility and increases density
- Downwelling in the North Atlantic (e.g. Labrador Sea) ventilates ocean interior

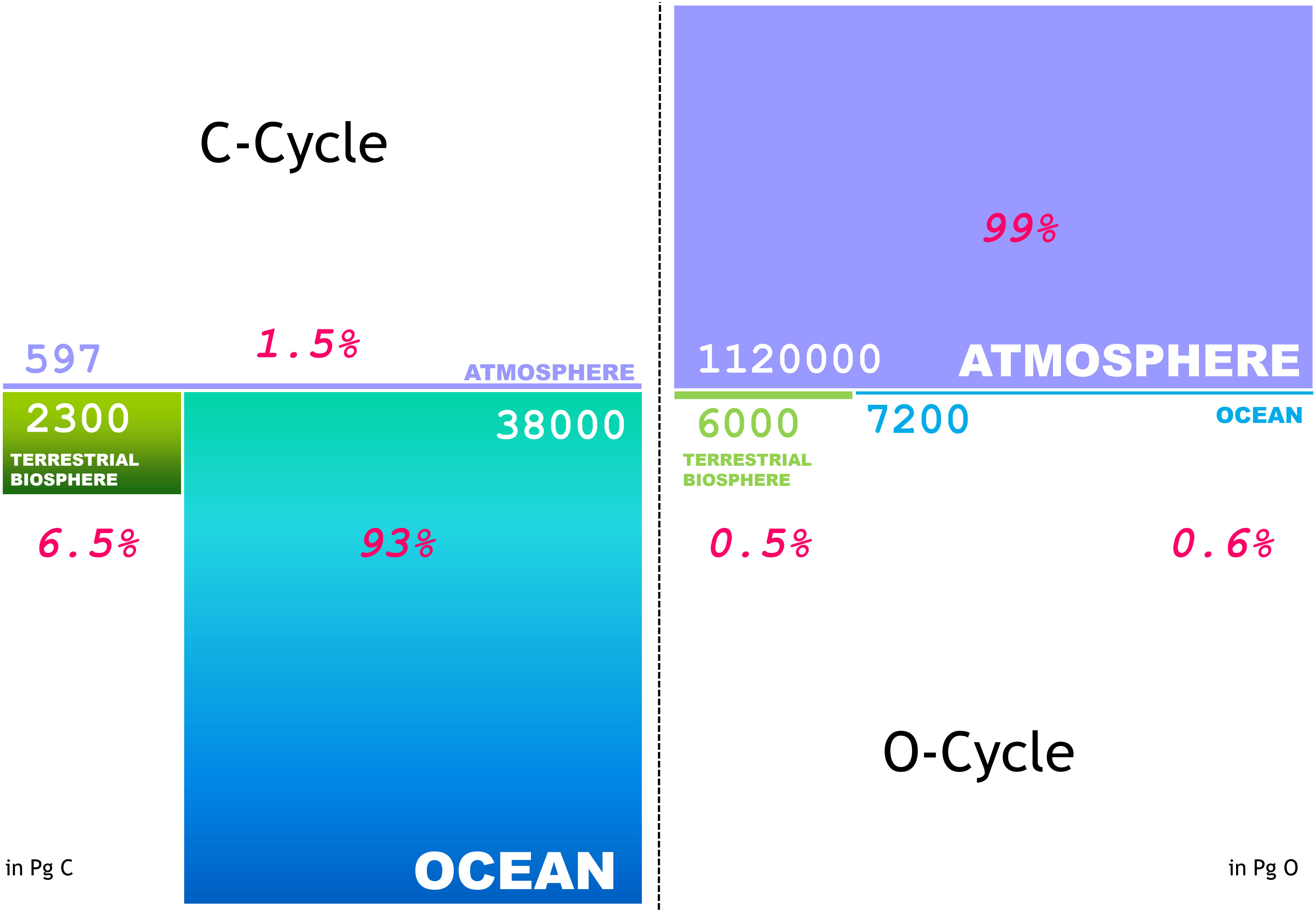


Organic Carbon Pump (aka: Soft Tissue Pump)

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



Global Carbon and Oxygen Reservoirs



C-Cycle

597

1.5%

ATMOSPHERE

2300

TERRESTRIAL BIOSPHERE

6.5%

38000

93%

OCEAN

in Pg C

O-Cycle

99%

1120000

ATMOSPHERE

6000

TERRESTRIAL BIOSPHERE

0.5%

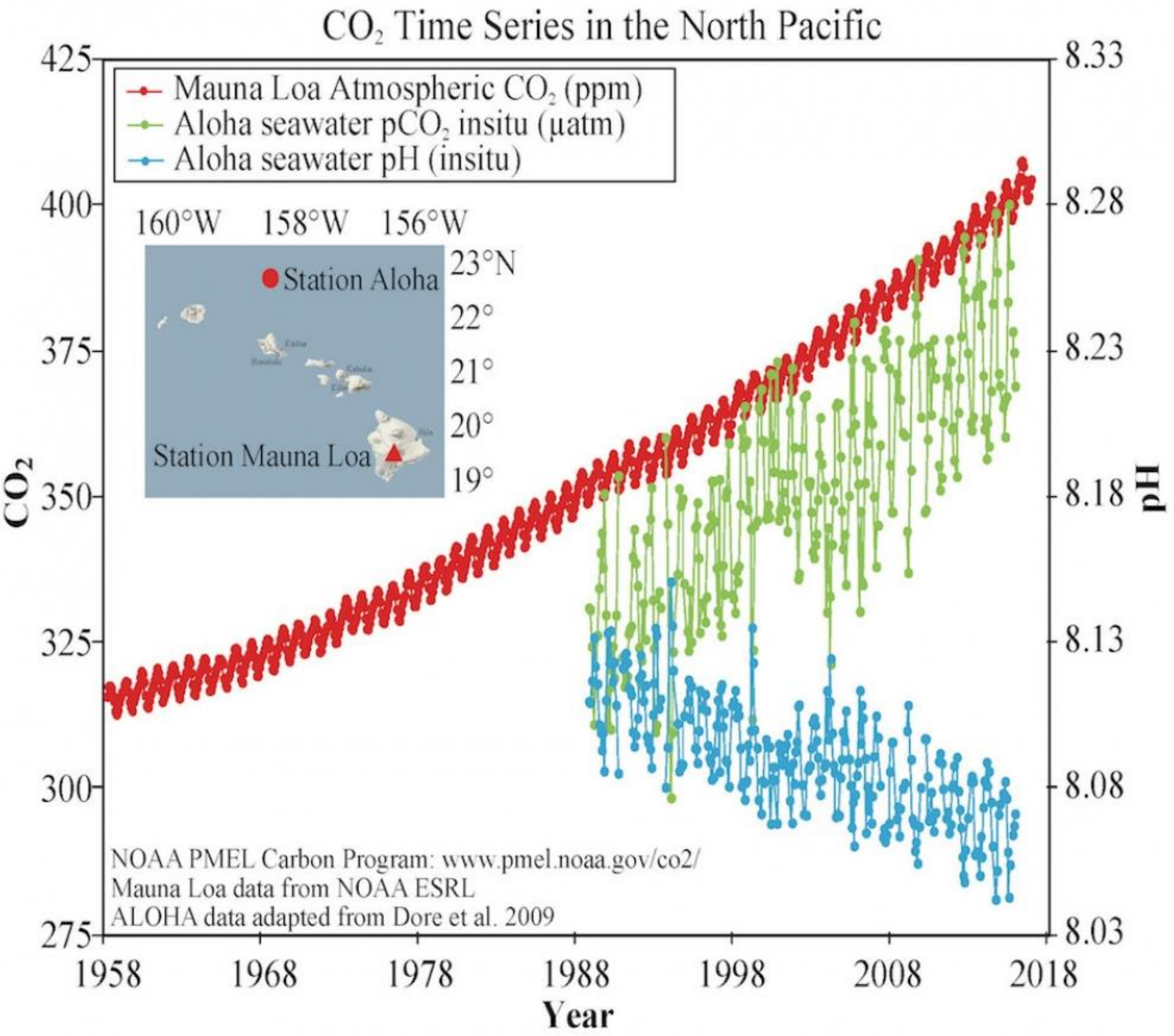
7200

OCEAN

0.6%

in Pg O

Changes in Seawater Chemistry due to Uptake of Anthropogenic CO_2



Dore et al. (2009)

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

CO_2 Equilibrium Reactions in Water

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

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

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

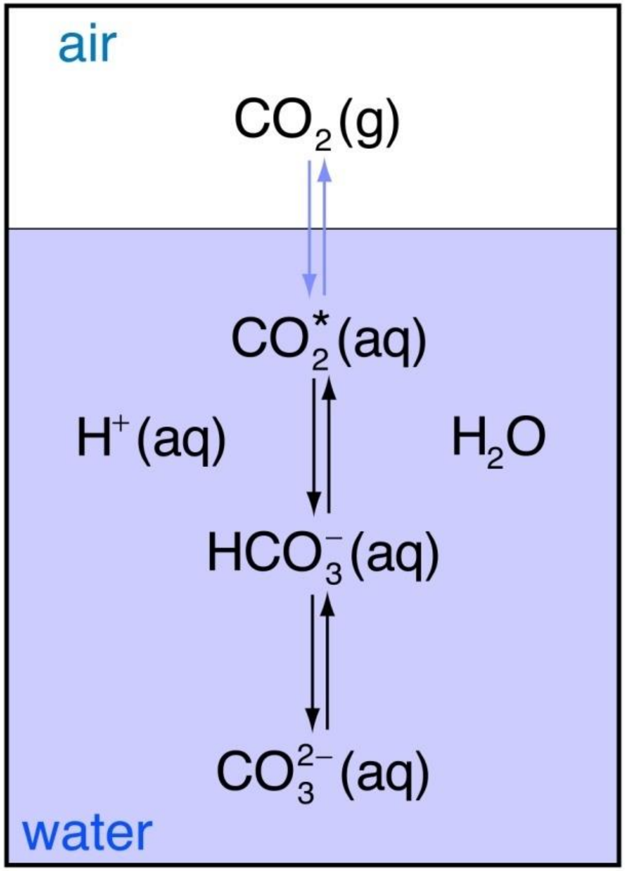
$$CO_2^* + H_2O \rightleftharpoons H^+ + HCO_3^-$$

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

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

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

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



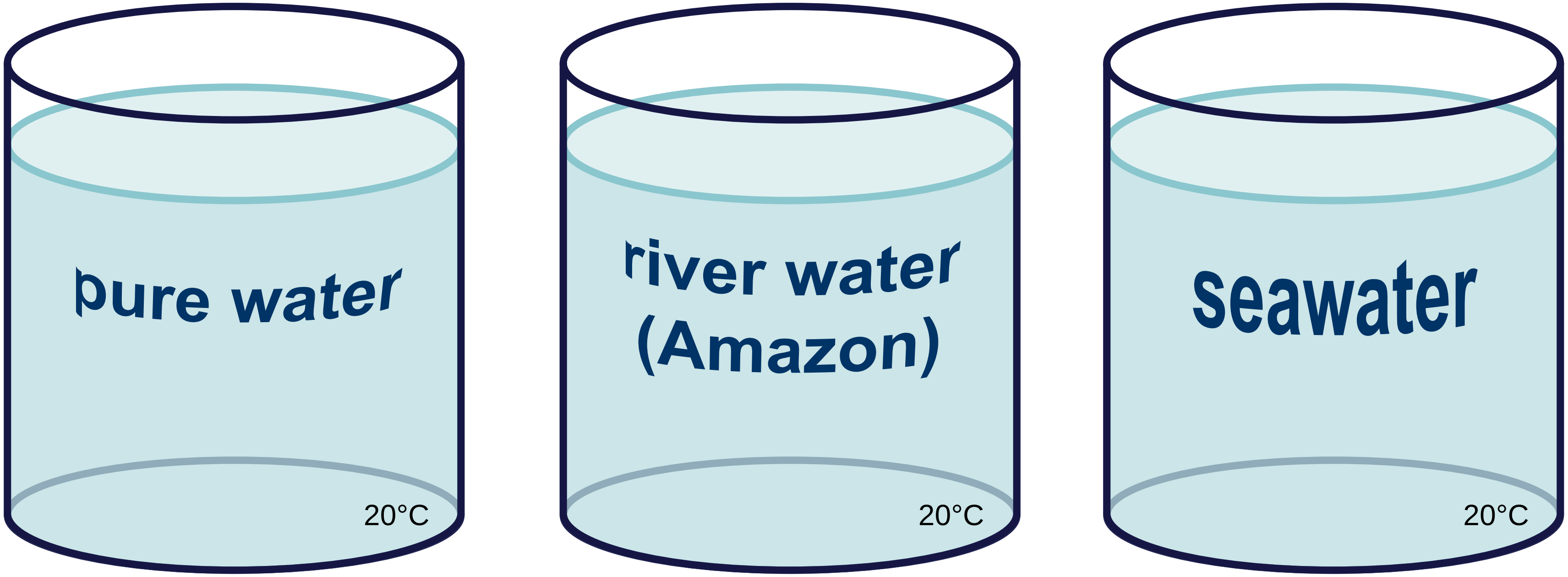
Is the ocean‘s CO_2 sequestration potential different?

Experiment:

(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

Question:

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



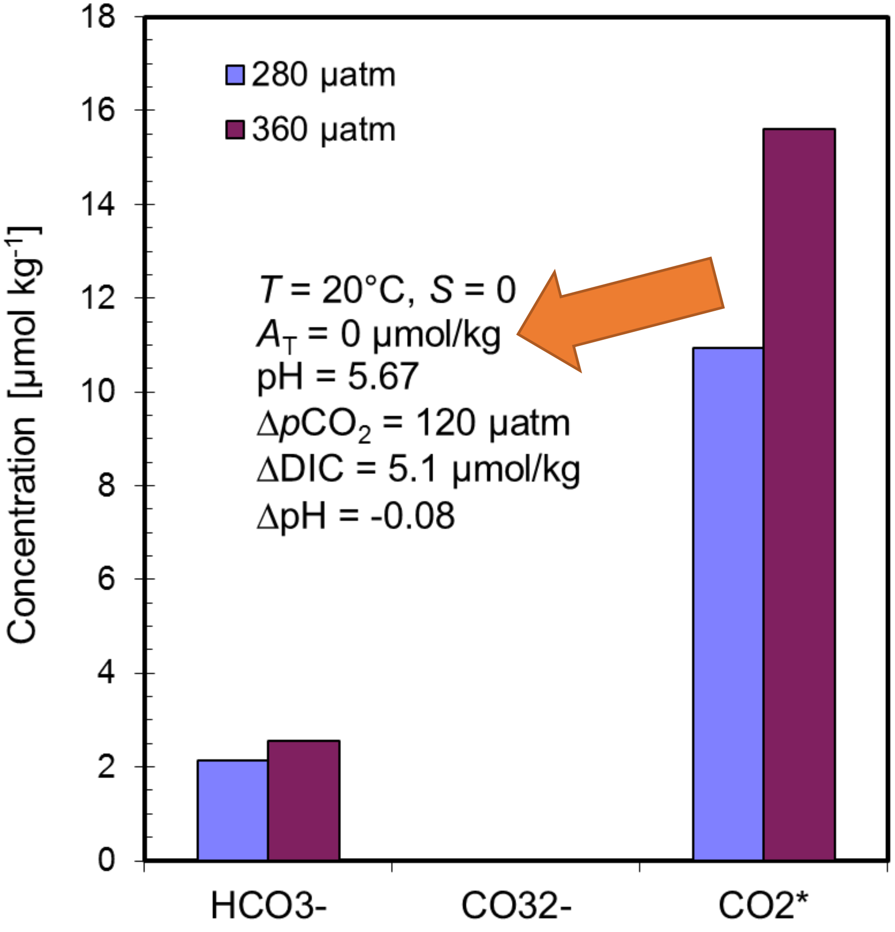
ΔDIC = 5 µmol/L
(13 → 18 µmol/L)

ΔDIC = 6 µmol/L
(607 → 613 µmol/L)

ΔDIC = 73 µmol/L
(1965 → 2038 µmol/L)

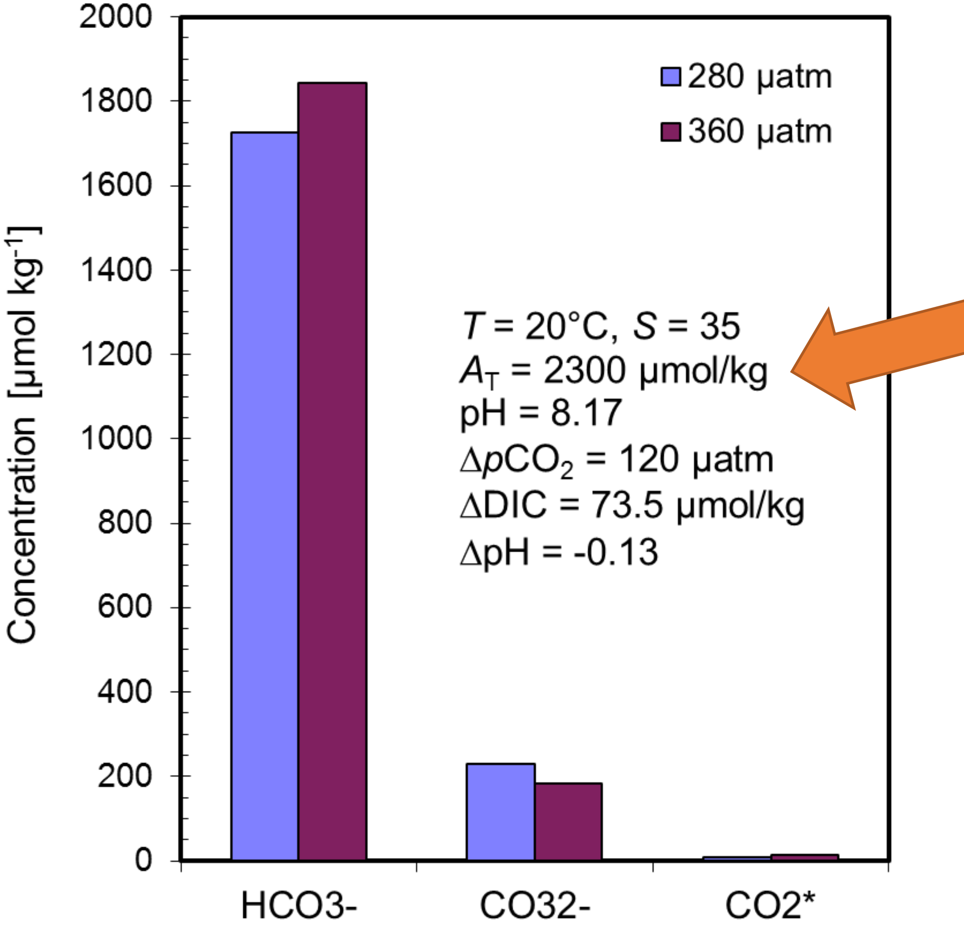
Is the ocean‘s CO_2 sequestration potential different?

CO_2 system freshwater



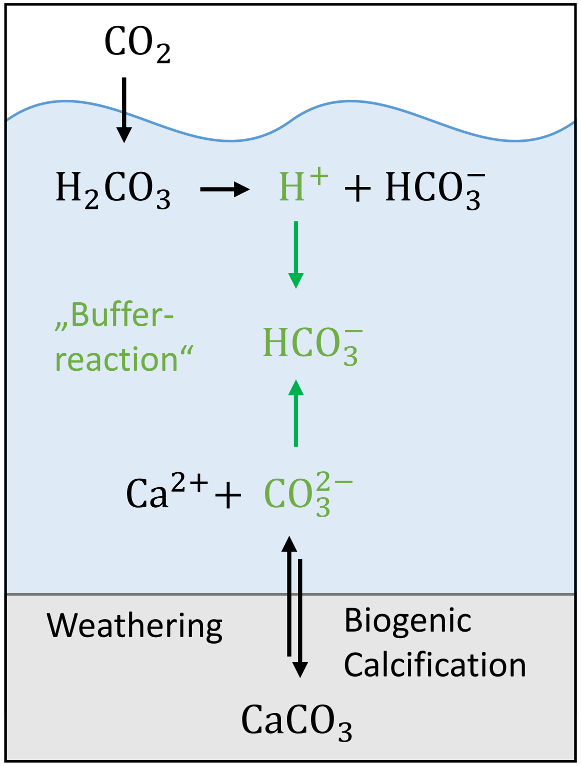
T = 20°C, S = 0
A_T = 0 µmol/kg
pH = 5.67
ΔpCO_2 = 120 µatm
ΔDIC = 5.1 µmol/kg
ΔpH = -0.08

CO_2 system seawater



T = 20°C, S = 35
A_T = 2300 µmol/kg
pH = 8.17
ΔpCO_2 = 120 µatm
ΔDIC = 73.5 µmol/kg
ΔpH = -0.13

The Alkalinity Concept



CO_2

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

„Buffer-reaction“

HCO_3^-

$Ca^{2+} + CO_3^{2-}$

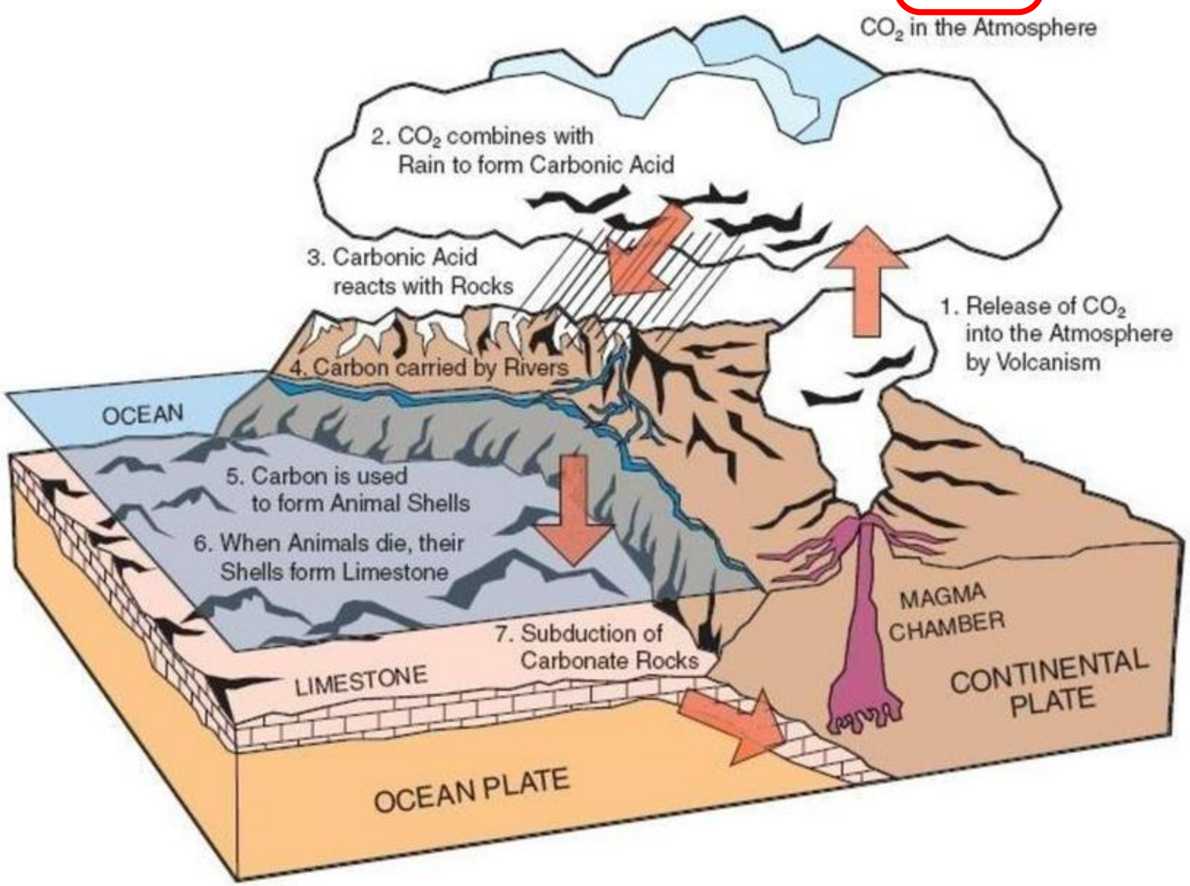
Weathering

Biogenic Calcification

$CaCO_3$

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

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

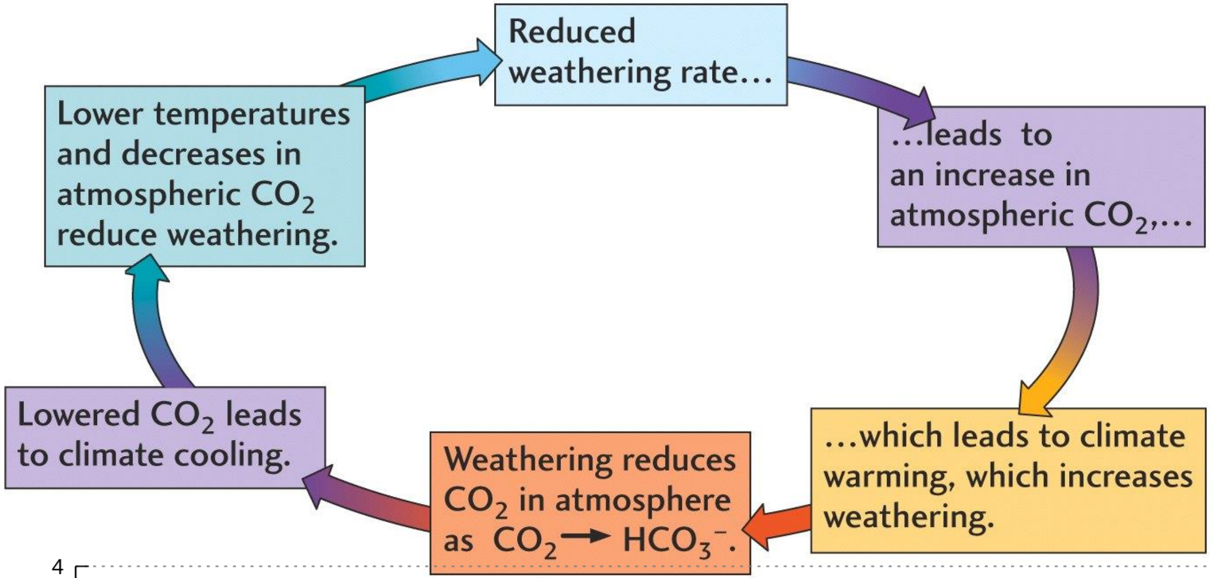


Alkalinity A_T

- Defined as the excess of proton acceptors over proton donors
- 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



Reduced weathering rate…

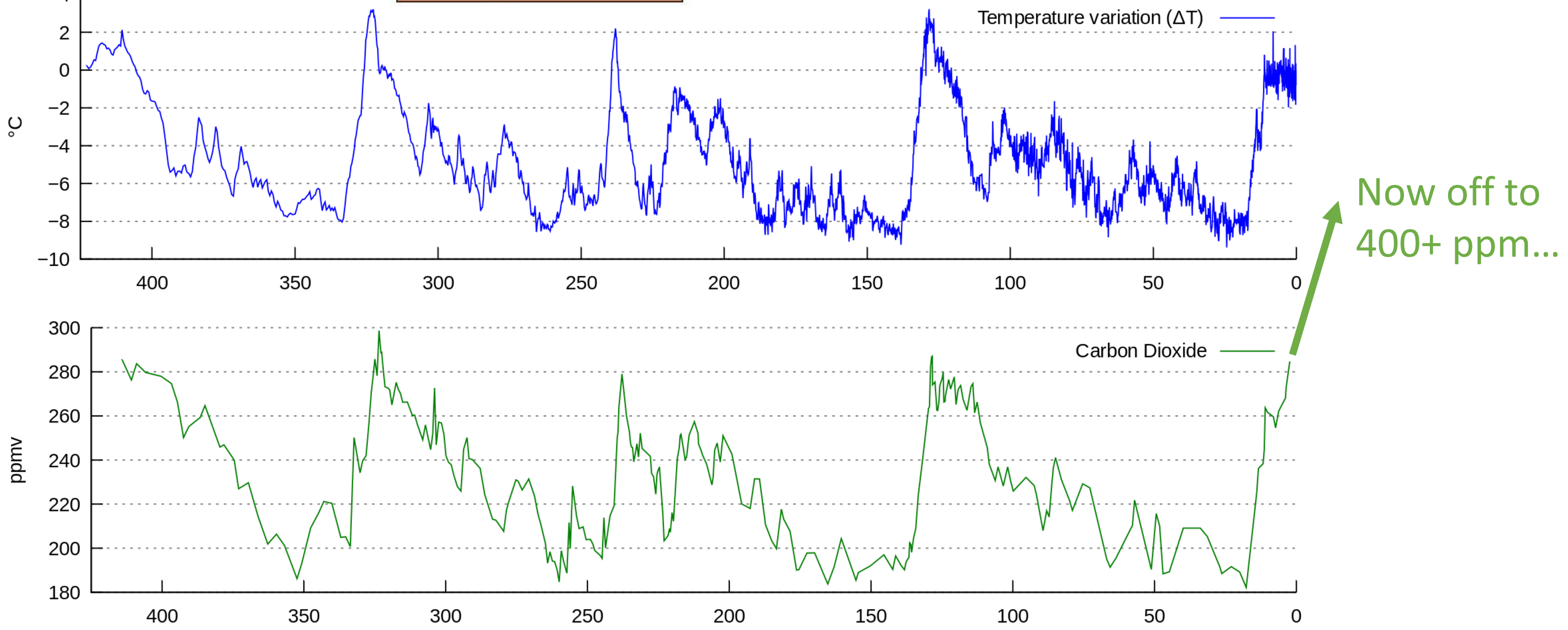
…leads to an increase in atmospheric CO_2,…

…which leads to climate warming, which increases weathering.

Weathering reduces CO_2 in atmosphere as $CO_2 \rightarrow HCO_3^-$.

Lowered CO_2 leads to climate cooling.

Lower temperatures and decreases in atmospheric CO_2 reduce weathering.



Now off to 400+ ppm…

Four measureable parameters of the CO_2 system

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

Sensitivity of the CO_2 system to major biogeochemical processes

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 ↑ pCO_2 ↓

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

$\Delta A_T = 0$ $\Delta C_T = -1$ pH ↑ pCO_2 ↓

Respiration of particulate organic matter

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

$\Delta A_T = 0$ $\Delta C_T = +1$ pH ↓ pCO_2 ↑

Sensitivity of the CO_2 system to major biogeochemical processes

Formation of particulate calcium carbonate

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

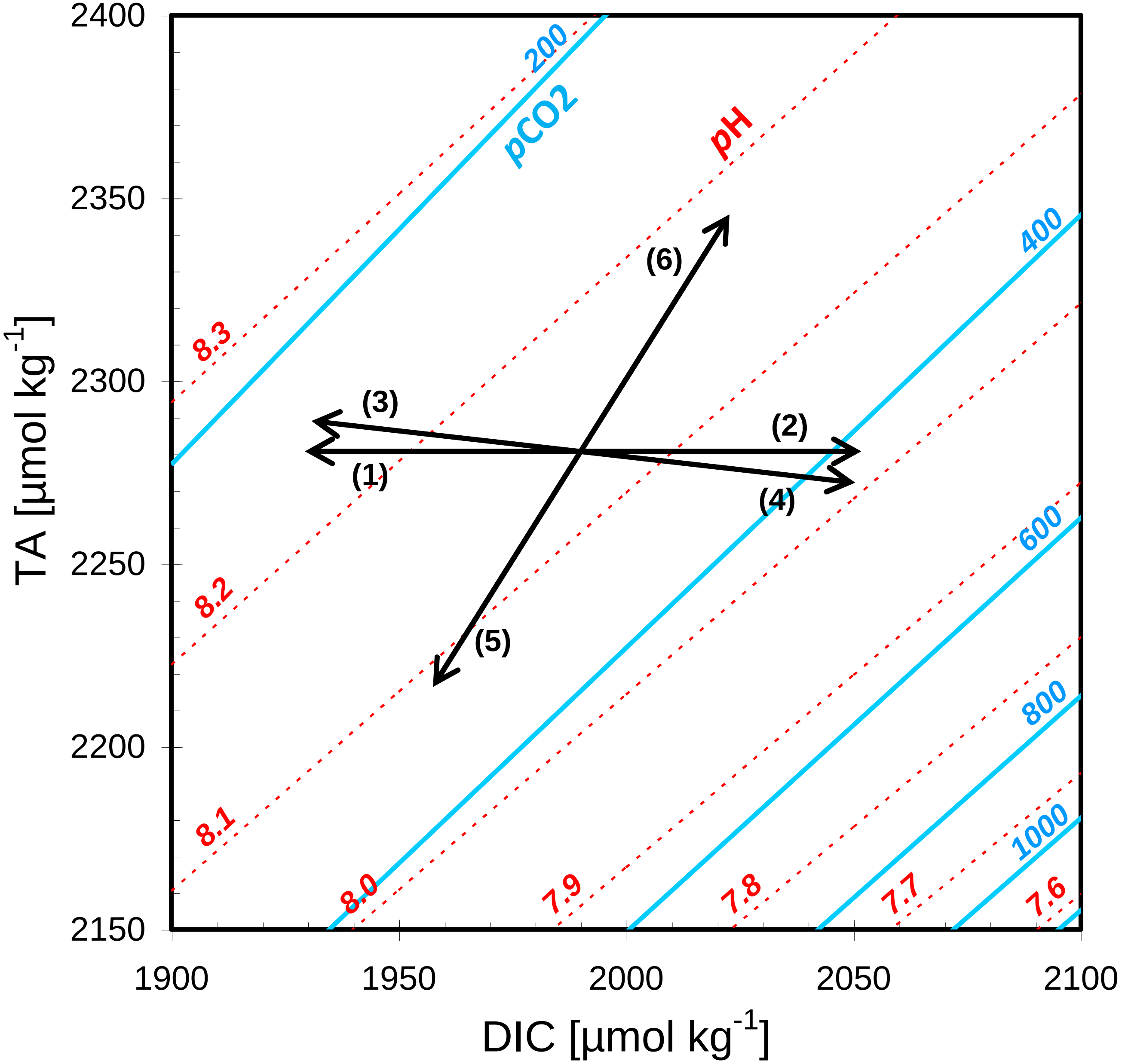
$\Delta A_T = -2\ \Delta C_T = -1$ $\quad$ pH ↓ $\quad$ pCO$_2$ ↑

Dissolution of particulate calcium carbonate

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

$\Delta A_T = +2 \Delta C_T = +1$ $\quad$ pH ↑ $\quad$ pCO$_2$ ↓

Biogeochemical processes in the parameter space of the marine CO_2 system



?

CO_2 release to atmosphere

CO_2 uptake from atmosphere

Primary production

Respiration

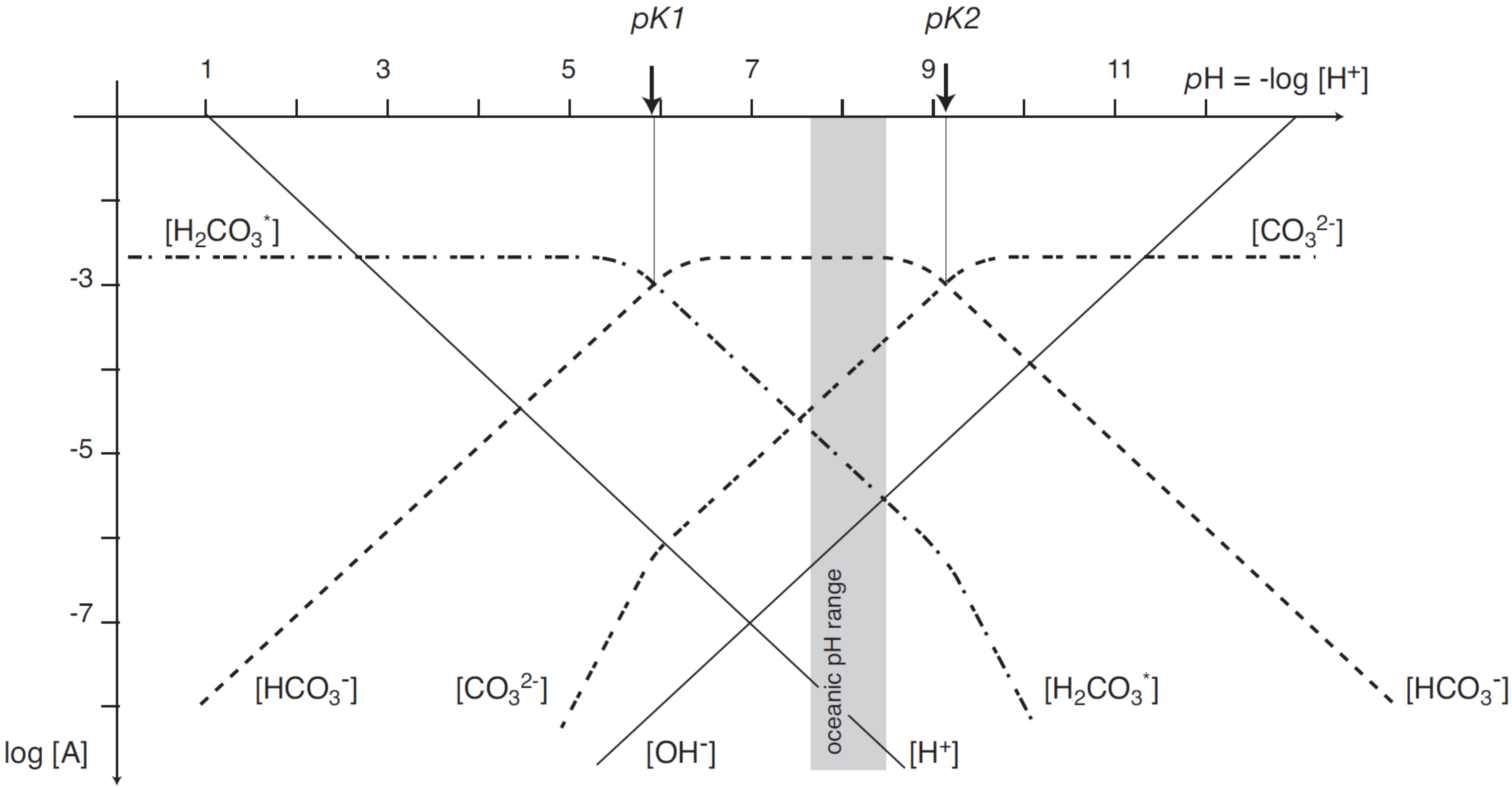
Calcification

Carbonate dissolution

Zeebe and Wolf-Gladrow (2001): CO_2 in Seawater: Equilibrium, Kinetics, Isotopes

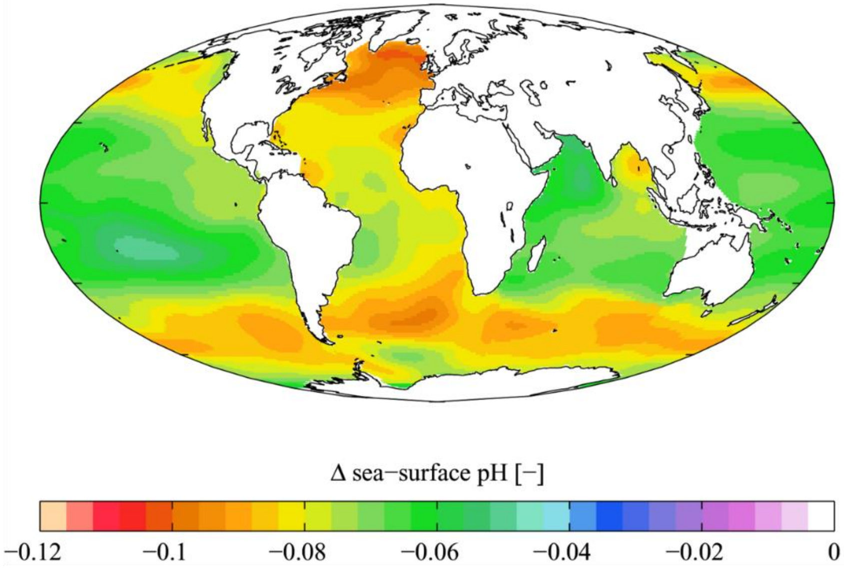
Marine CO_2 system: the ocean‘s major buffer system

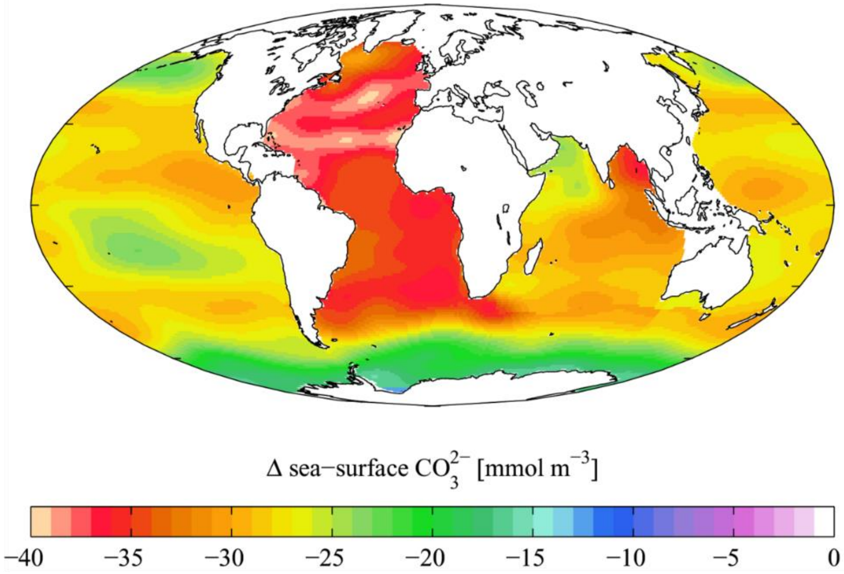
Bjerrum plot of carbonic acid species in seawater



Sarmiento & Gruber, *Ocean Biogeochemical Dynamics*, Princeton University Press, 2006.

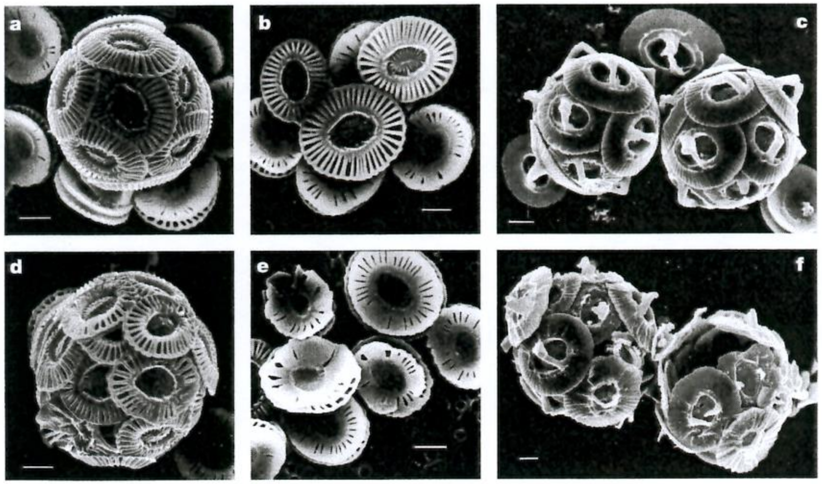
Ocean Acidification: Impact on Biota





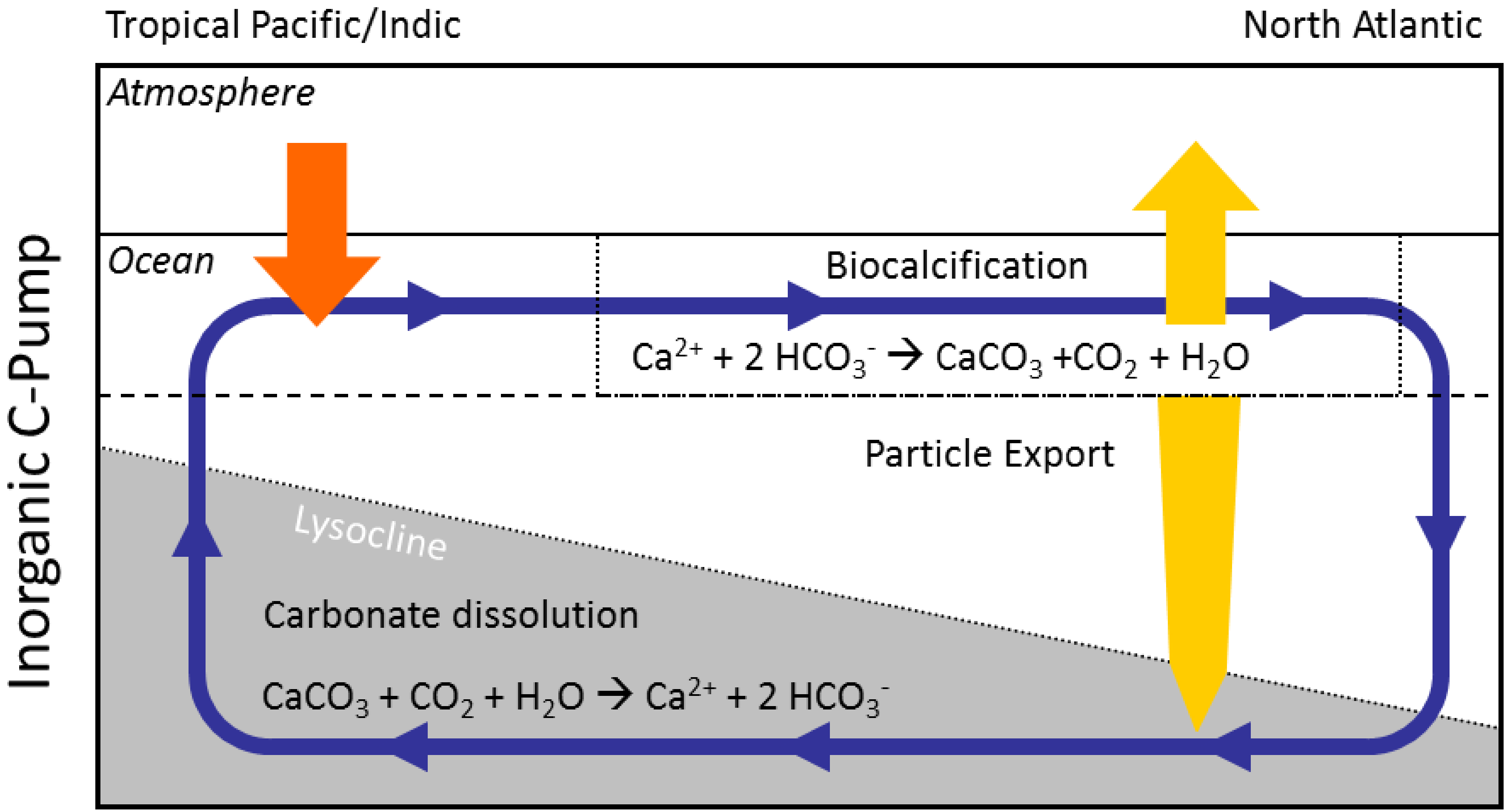
Estimated change in annual mean sea surface pH and carbonate ion (CO_3^{2-}) concentration between the pre-industrial period (1700s) and the present day (1990s).

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

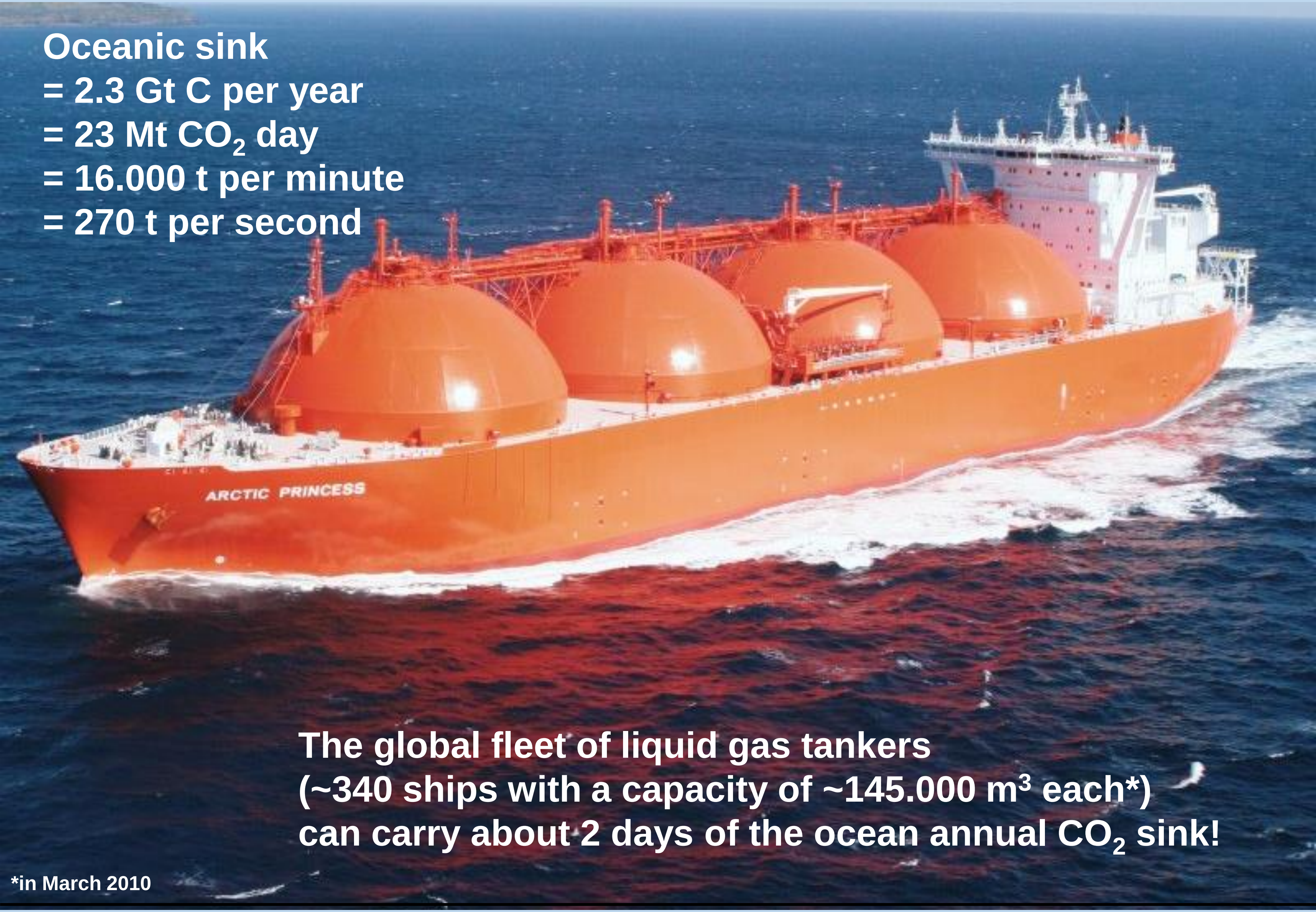


Riebsesell et al. (2000)

Inorganic Carbon Pump (aka: Hard Tissue Pump)



We are not talking peanuts here...



Oceanic sink
= 2.3 Gt C per year
= 23 Mt CO_2 day
= 16.000 t per minute
= 270 t per second

The global fleet of liquid gas tankers (~340 ships with a capacity of ~145.000 m^3 each*) can carry about 2 days of the ocean annual CO_2 sink!

***in March 2010**

Take home messages

- Henry’s law describes solubility of gases
- Air sea gas exchange controlled by partial pressure difference, wind speed and temperature
- Surface ocean O_2 distribution and deep ventilation
- Global conveyor belt
- Physical, organic and inorganic carbon pump
- 2 out of 4 measurable parameters determine state of CO_2 system
- Alkalinity causes high CO_2-uptake capacity