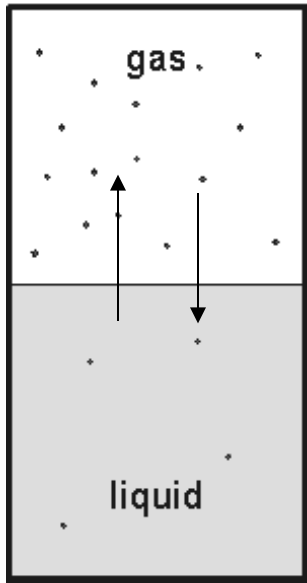


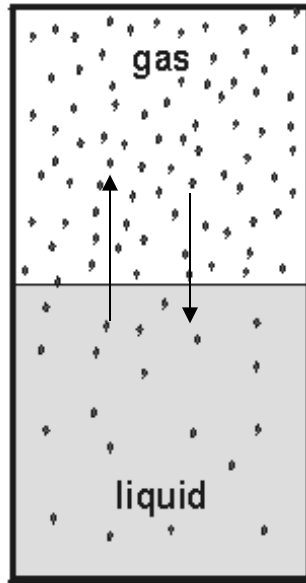
# Carbon cycle theme

- The Earth's carbon cycle has a stabilizing mechanism against sudden addition of CO<sub>2</sub> to the atmosphere
  - About 50% of carbon emission is absorbed into land and ocean surfaces
  - Climate warming would be twice as severe if there were no such carbon sink
  - Ocean carbon uptake is helpful but it comes with certain consequences: ocean acidification

# Henry's Law



Low Gas Pressure



High Gas Pressure

At equilibrium:

$$[\text{CO}_2]_{\text{ocean}} = K_0 \times p\text{CO}_2^{\text{atm}}$$

Where  $K_0$  the solubility constant for  $\text{CO}_2$  and increases with decreasing temperature and salinity

Define:

$$p\text{CO}_2^{\text{oce}} = [\text{CO}_2]_{\text{ocean}} / K_0$$

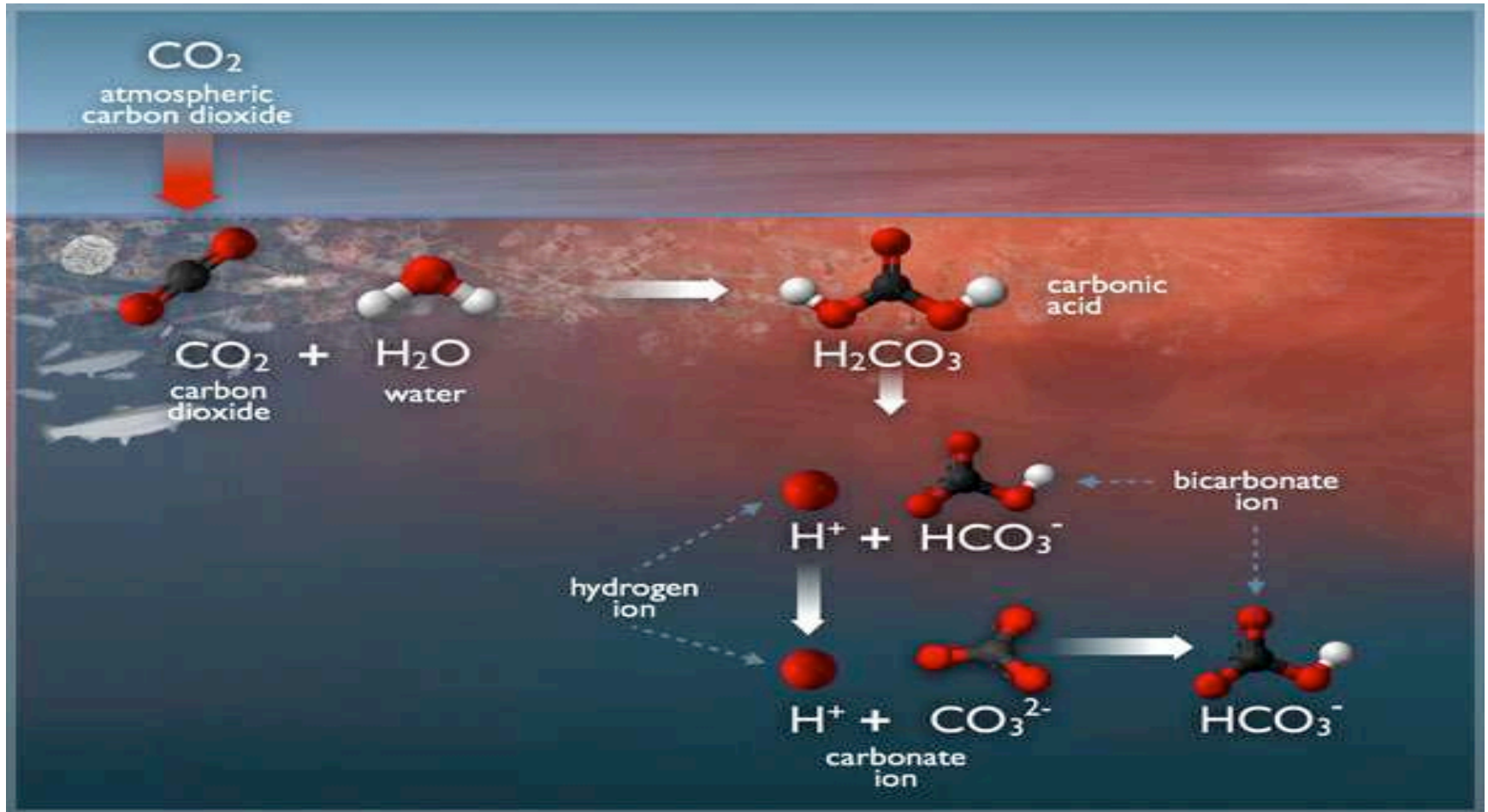
At equilibrium:

$$p\text{CO}_2^{\text{oce}} = p\text{CO}_2^{\text{atm}}$$

If  $p\text{CO}_2^{\text{oce}} < p\text{CO}_2^{\text{atm}}$ , net transfer of  $\text{CO}_2$  into ocean

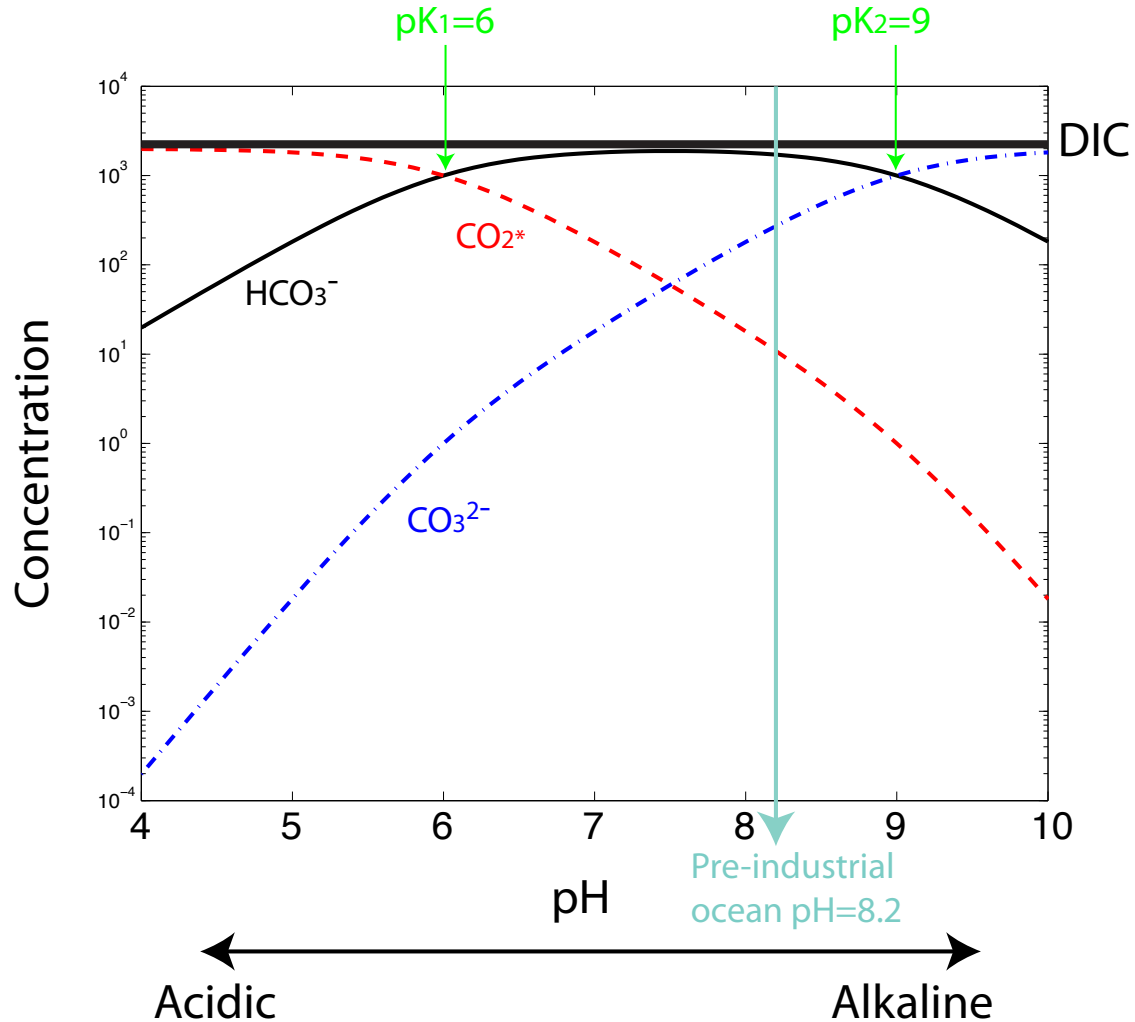
If  $p\text{CO}_2^{\text{oce}} > p\text{CO}_2^{\text{atm}}$ , net transfer of  $\text{CO}_2$  out of ocean<sup>2</sup>

# Ocean carbon cycle (2)



# Carbonate chemistry

- $\text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$



# What is pH?

- $\text{pH} = -\log_{10}[\text{H}^+]$ 
  - Lower pH value indicate increasing acidity
- Notation:  $\text{pX} = -\log_{10}X$ 
  - Potential of X
  - Logarithmic scale: If pH decreases by 1, it's a factor of ten increase in acidity

**pH**

**H+**

(moles per liter)

**change  
in acidity**

7.2

$6.3 \times 10^{-8}$

+900%

7.3

$5.0 \times 10^{-8}$

+694%

7.4

$4.0 \times 10^{-8}$

+531%

7.5

$3.2 \times 10^{-8}$

+401%

7.6

$2.5 \times 10^{-8}$

+298%

7.7

$2.0 \times 10^{-8}$

+216%

7.8

$1.6 \times 10^{-8}$

+151%

7.9

$1.3 \times 10^{-8}$

+100%

8.0

$1.0 \times 10^{-8}$

+58%

8.1

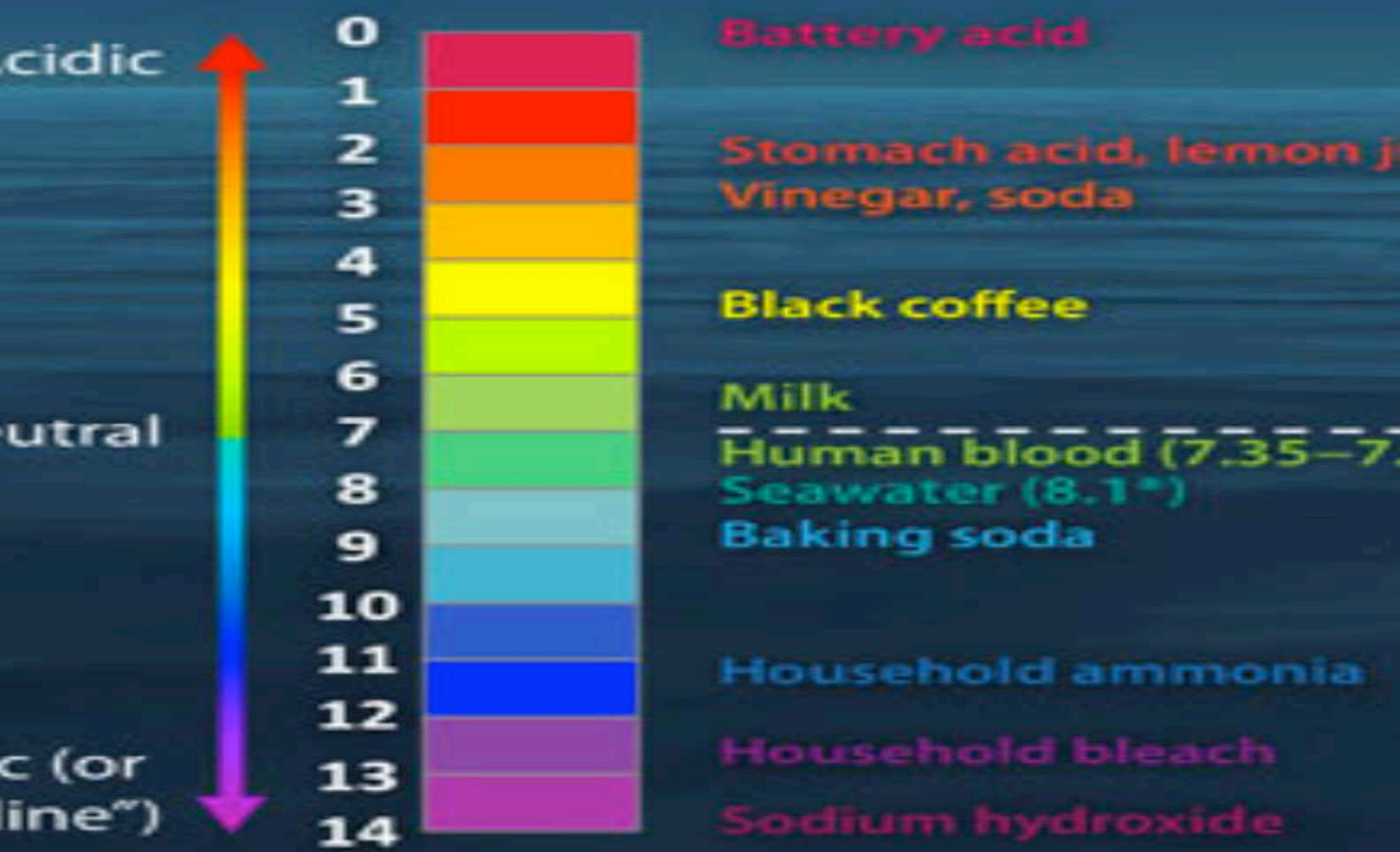
$7.9 \times 10^{-9}$

+26%

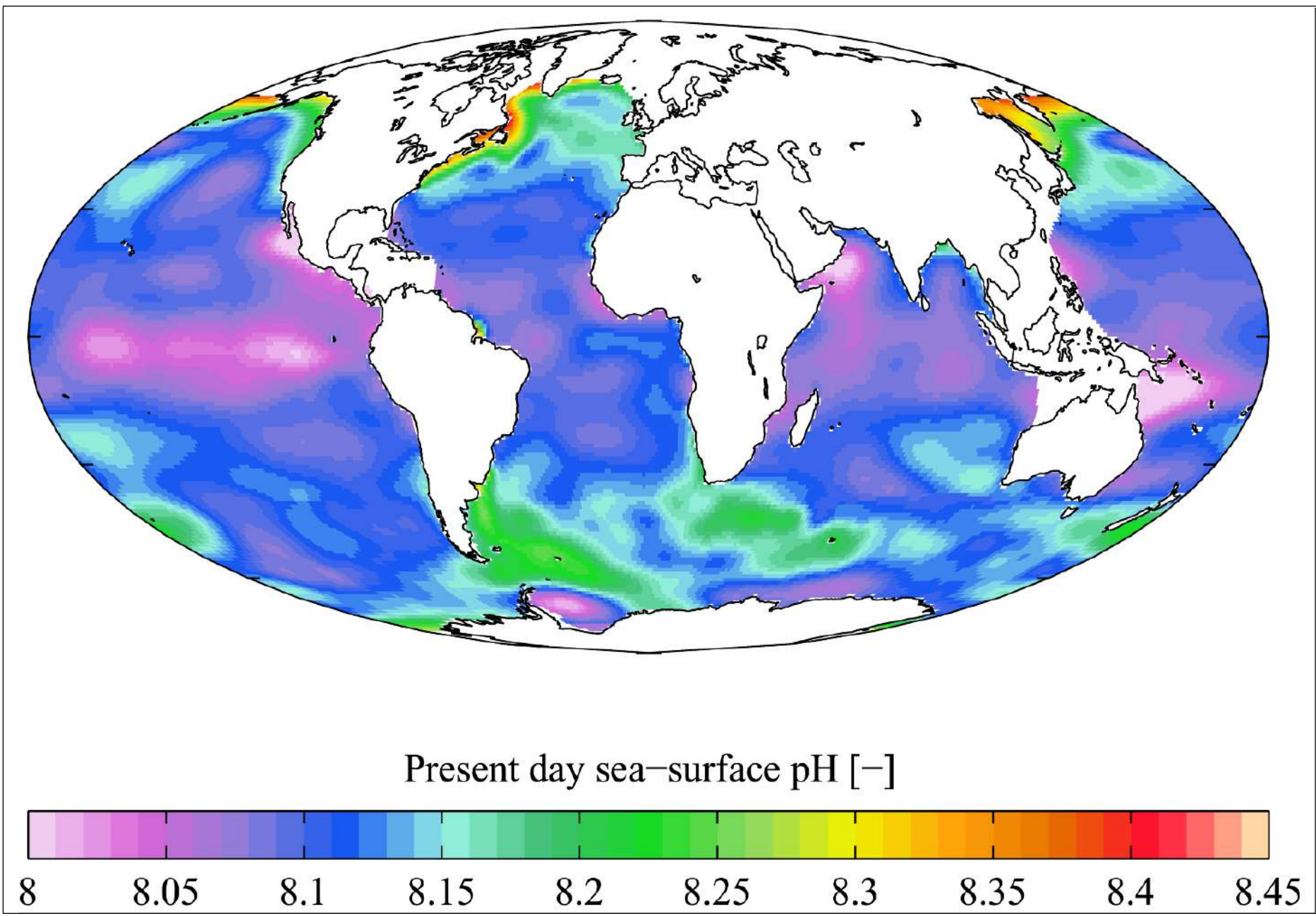
8.2

$6.3 \times 10^{-9}$





\* Average global surface ocean





# What controls the pH of seawater?

- Ions in the seawater
  - Cations and anions
  - $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{B}(\text{OH})_4^-$ , etc...
- **Charge balance**
  - The charge-weighted sum of positively and negatively charged ions must be zero.
- Alkalinity
  - The net positive charge from strong ions

## ***Definition of Alkalinity***

**Alkalinity: is the net molar concentration, in charge-equivalents, of the cations of strong bases in excess of the anions of strong acids**

$$A = \left\{ \begin{array}{l} \text{Strong base cations} \\ [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] \end{array} \right\} -$$

**(less) strong acid anions**

$$\left\{ [Cl^-] + 2[SO_4^{2-}] + [Br^-] \right\}$$
$$\approx \left\{ [HCO_3^-] + 2[CO_3^{2-}] \right\}$$

**Weak acid anions**

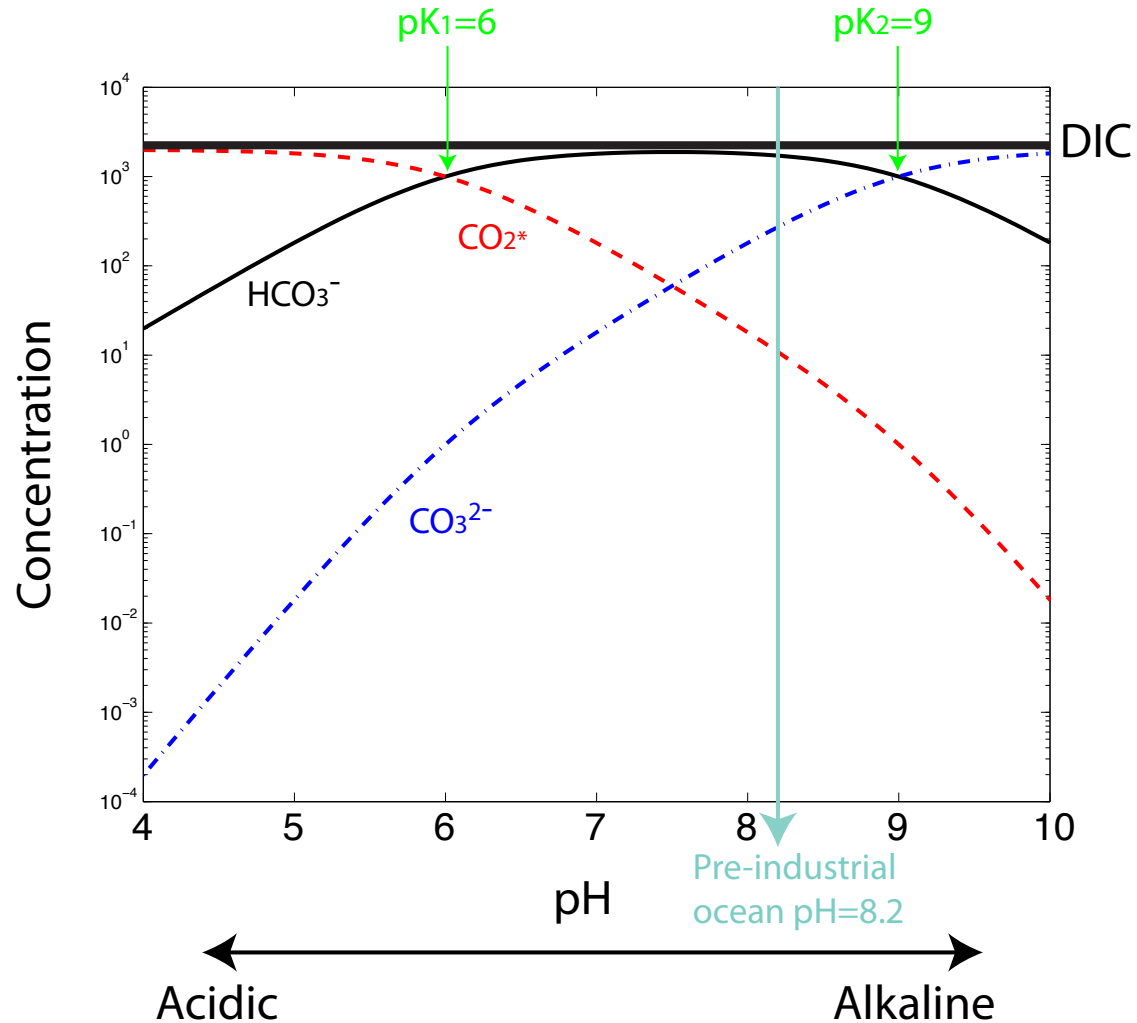
## ***Approximate relation***

$$Alk \approx \{ [HCO_3^-] + 2[CO_3^{2-}] \}$$

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

$$[CO_3^{2-}] \approx Alk - DIC$$

- $\text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$
- $\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$



# FAQs about Ocean Acidification

The screenshot shows the top navigation bar of the Woods Hole Oceanographic Institution website. The logo is on the left, and navigation links for 'PRESS ROOM', 'SHOP WHOI', and 'DIRECTORY' are on the right. Below the logo are buttons for 'WHO WE ARE', 'WHAT WE DO', 'KNOW YOUR OCEAN', 'JOIN US', and 'DONATE'. The main content area has a sidebar on the left with a 'KNOW YOUR OCEAN' section containing a list of topics like 'Climate & Ocean', 'Ocean Chemistry', and 'Ocean Circulation'. The main text area is titled 'FAQs about Ocean Acidification' and includes a 'SHARE THIS:' section, an 'Introduction' section with a paragraph about the field of research, and a paragraph about the OCB program's FAQ compilation process.

**Woods Hole Oceanographic INSTITUTION**

PRESS ROOM SHOP WHOI DIRECTORY

WHO WE ARE WHAT WE DO KNOW YOUR OCEAN JOIN US DONATE

**KNOW YOUR OCEAN** **FAQs about Ocean Acidification**

▼ **Ocean Topics**

- › Climate & Ocean
- › Coastal Science
- › Hazards
- ▼ **Ocean Chemistry**
  - Biogeochemistry
  - Carbon Cycle
  - **Ocean Acidification**
- › Ocean Circulation
- › Ocean Life
- › Ocean Resources
- › Polar Research
- › Pollution
- › Seafloor & Below
- › Tools & Technology
- › Underwater Archaeology

› **Blogs & Expeditions**

Visual WHOI  
Image of the Day

SHARE THIS:

### Introduction

Ocean acidification is a new field of research in which most studies have been published in the past 10 years. Hence, there are some certainties, but many questions remain. Ocean acidification is also a multi-disciplinary research area that encompasses topics such as chemistry, paleontology, biology, ecology, biogeochemistry, modeling, and social sciences. Furthermore, some aspects of ocean acidification research, for example the carbonate chemistry, are intricate and counterintuitive. For these reasons, the media and the general public find some scientific issues or results confusing.

The U.S. Ocean Carbon and Biogeochemistry (OCB) program, supported by the European Project on Ocean Acidification (EPOCA) and the UK Ocean Acidification Research Programme, has compiled a list of frequently asked questions (FAQs). These questions were widely distributed to the research community with the request to draft concise replies summarizing current knowledge, yet avoiding jargon. The replies were then subject to an open peer-review and revision process to ensure readability without any loss of scientific accuracy. The response of the community was

<https://www.whoi.edu/page.do?pid=83380&tid=3622&cid=131410>

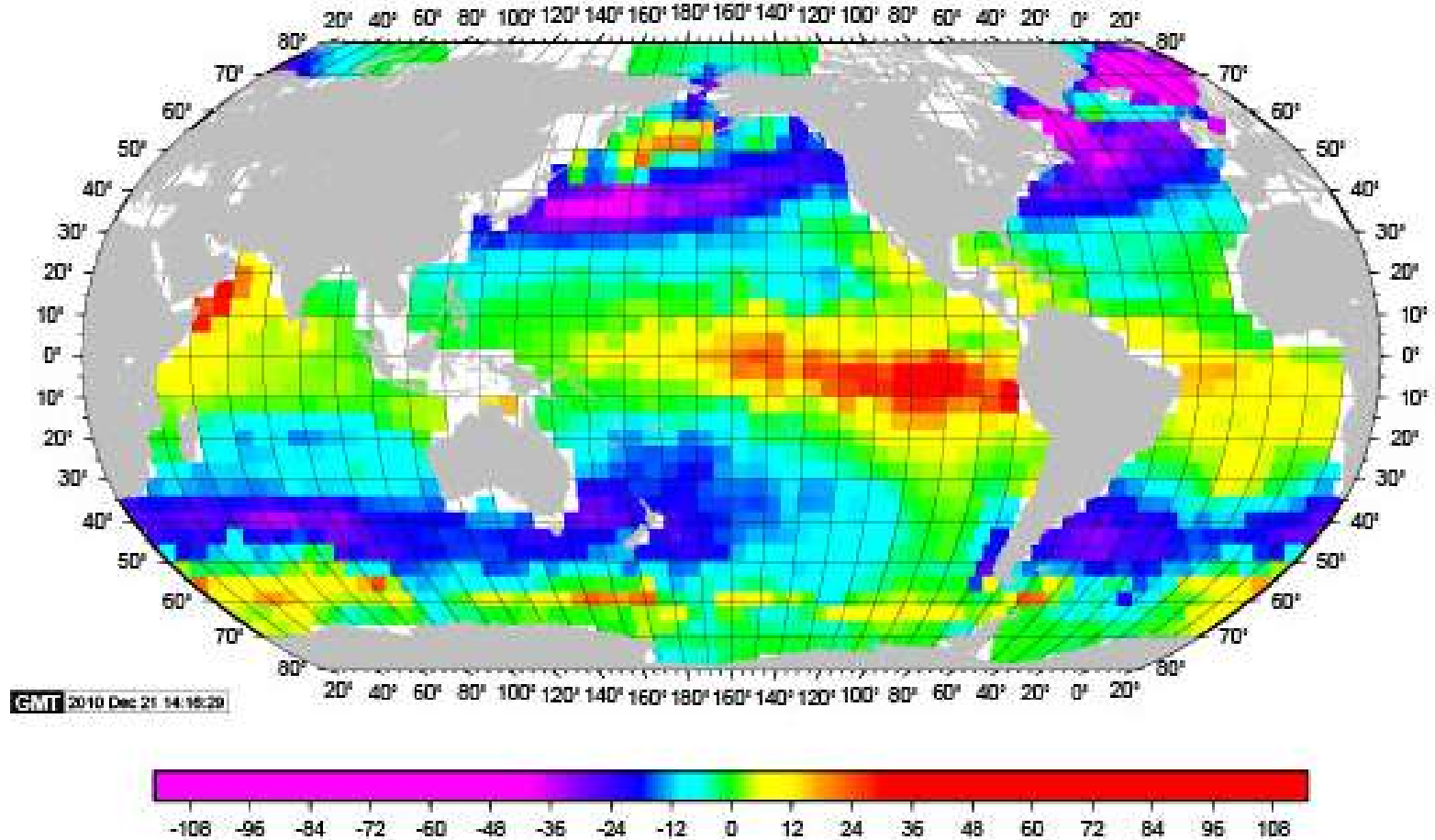
# Carbon Pumps

- Solubility pump
  - Soft-tissue pump
  - Carbonate pump
- ) Biological Pump

# Air-sea carbon exchange

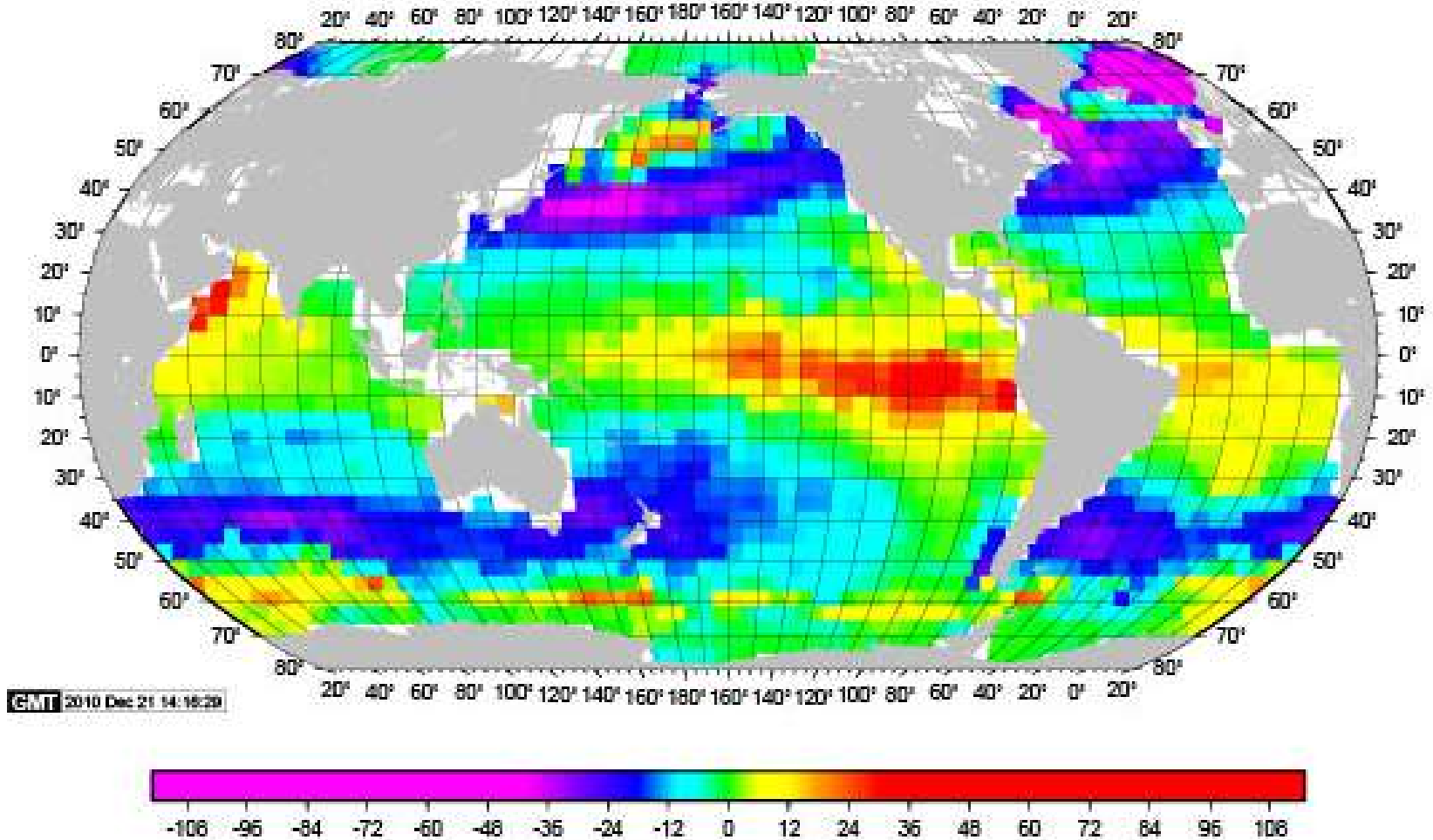
Note: positive upward

Takahashi et al., (2009)



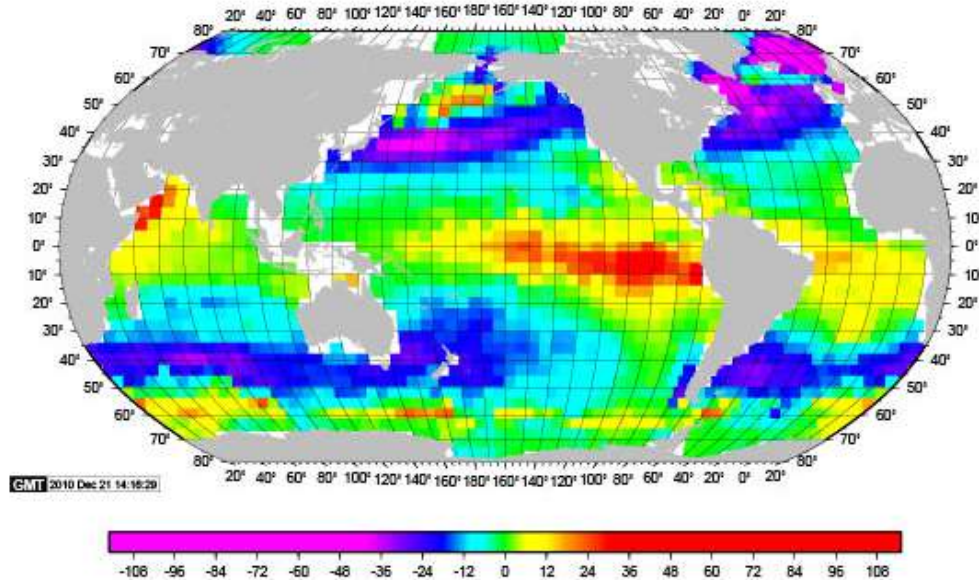
Into the ocean

Out of the ocean



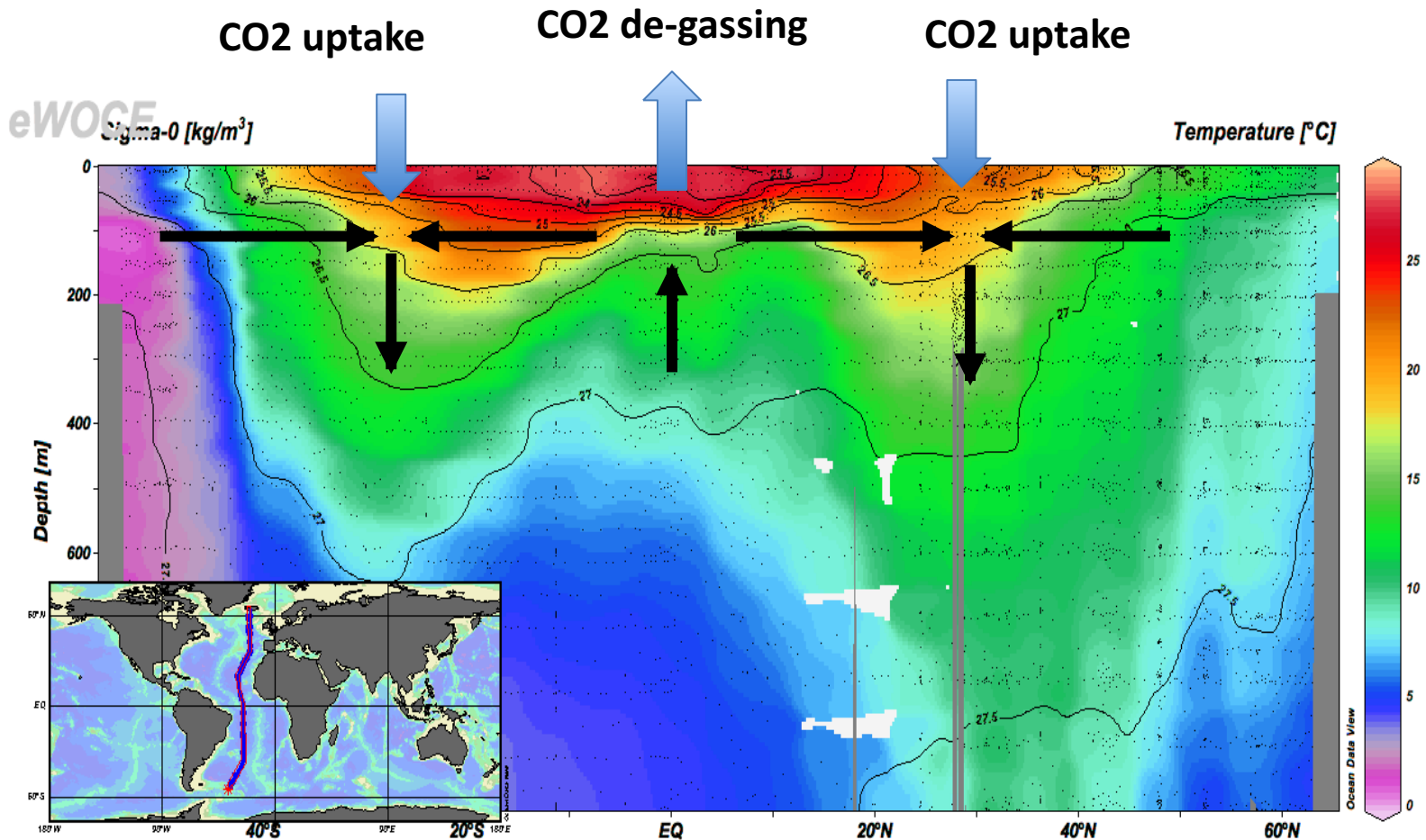
$\Delta p\text{CO}_2 = p\text{CO}_2^{\text{ocean}} - p\text{CO}_2^{\text{atm}}$  When  $> 0$  outgassing of CO<sub>2</sub>  
 from the Ocean, when  $< 0$   
 invasion of CO<sub>2</sub> into the ocean





- Timescale for CO<sub>2</sub> equilibration is about 10X longer for ordinary gas and surface ocean is not in equilibrium with atmosphere.
- pCO<sub>2</sub><sup>ocean</sup> is high where cold waters are warmed, and where carbon rich deep waters are exposed to the surface
- pCO<sub>2</sub><sup>ocean</sup> is low where warm waters are cooled
- At steady state, for entire ocean pCO<sub>2</sub><sup>ocean</sup> = pCO<sub>2</sub><sup>atm</sup>

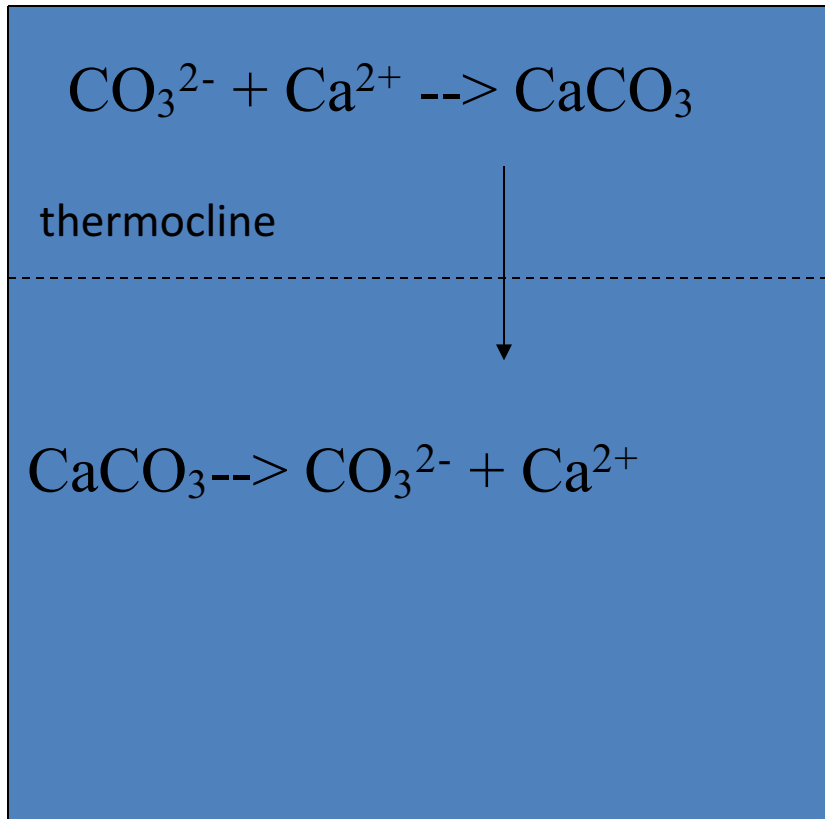
# Air sea heat and carbon flux



# Carbon Pumps

- Solubility pump
  - Soft-tissue pump
  - Carbonate pump
- ) Biological Pump

# Carbonate pump

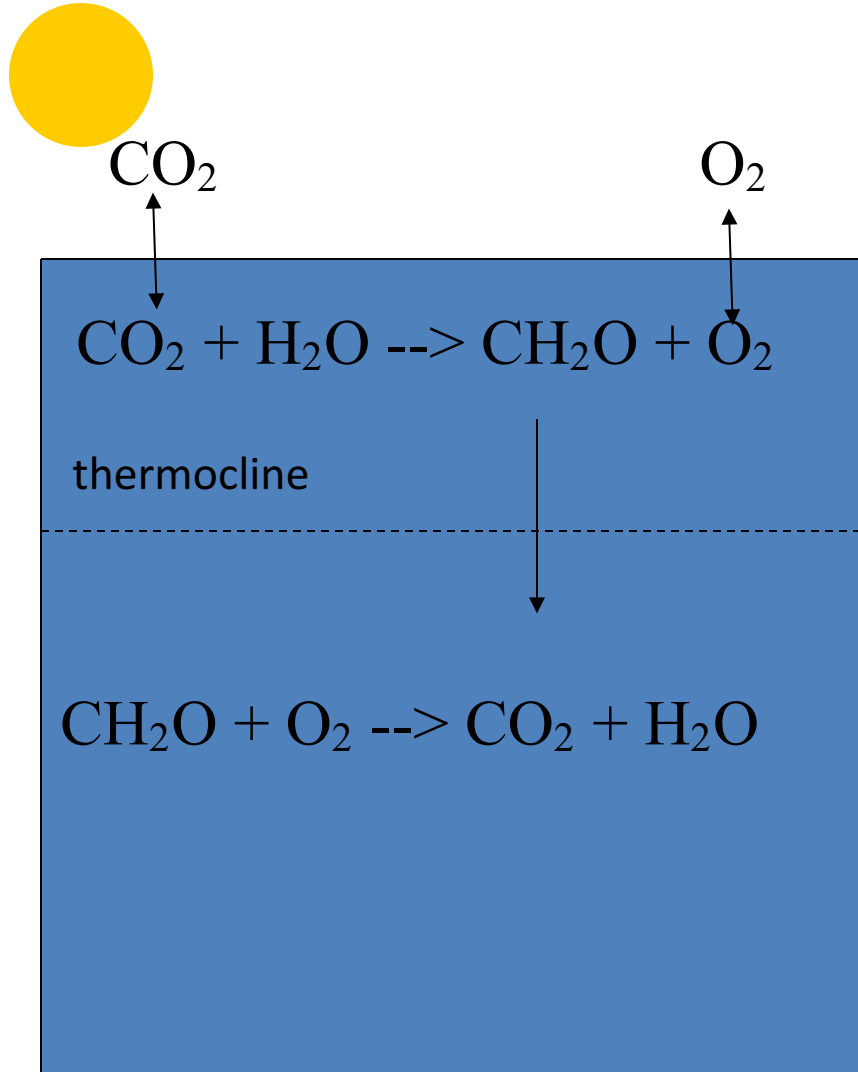


- Carbon is taken up to form  $\text{CaCO}_3$  shells in surface ocean
- The  $\text{CaCO}_3$  dissolves in the deep ocean

# Carbon Pumps

- Solubility pump
  - Soft-tissue pump
  - Carbonate pump
- ) Biological Pump

# Biological (soft-tissue) pump



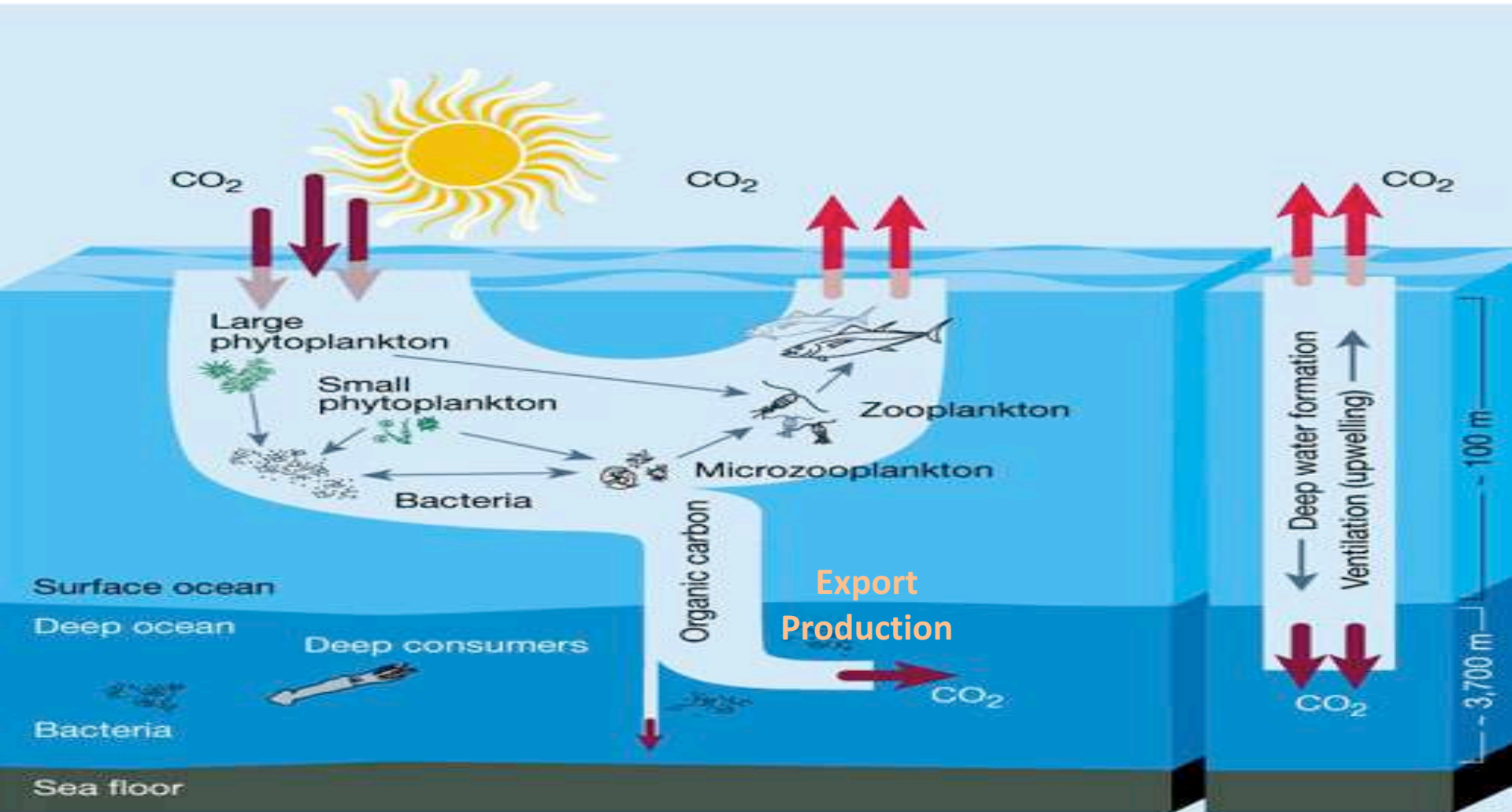
- Organisms take up carbon during photosynthesis in the surface ocean
- When they die they sink into the deep ocean
- The carbon is returned to seawater when the organic material is broken down by bacteria

# Primary production

- Photosynthesis measured by the amount of carbon molecule in the newly generated organic matter

(Solar radiation) + Nutrient + CO<sub>2</sub> + Water  
→ Organic matter + O<sub>2</sub>

# Vertical transfer of carbon





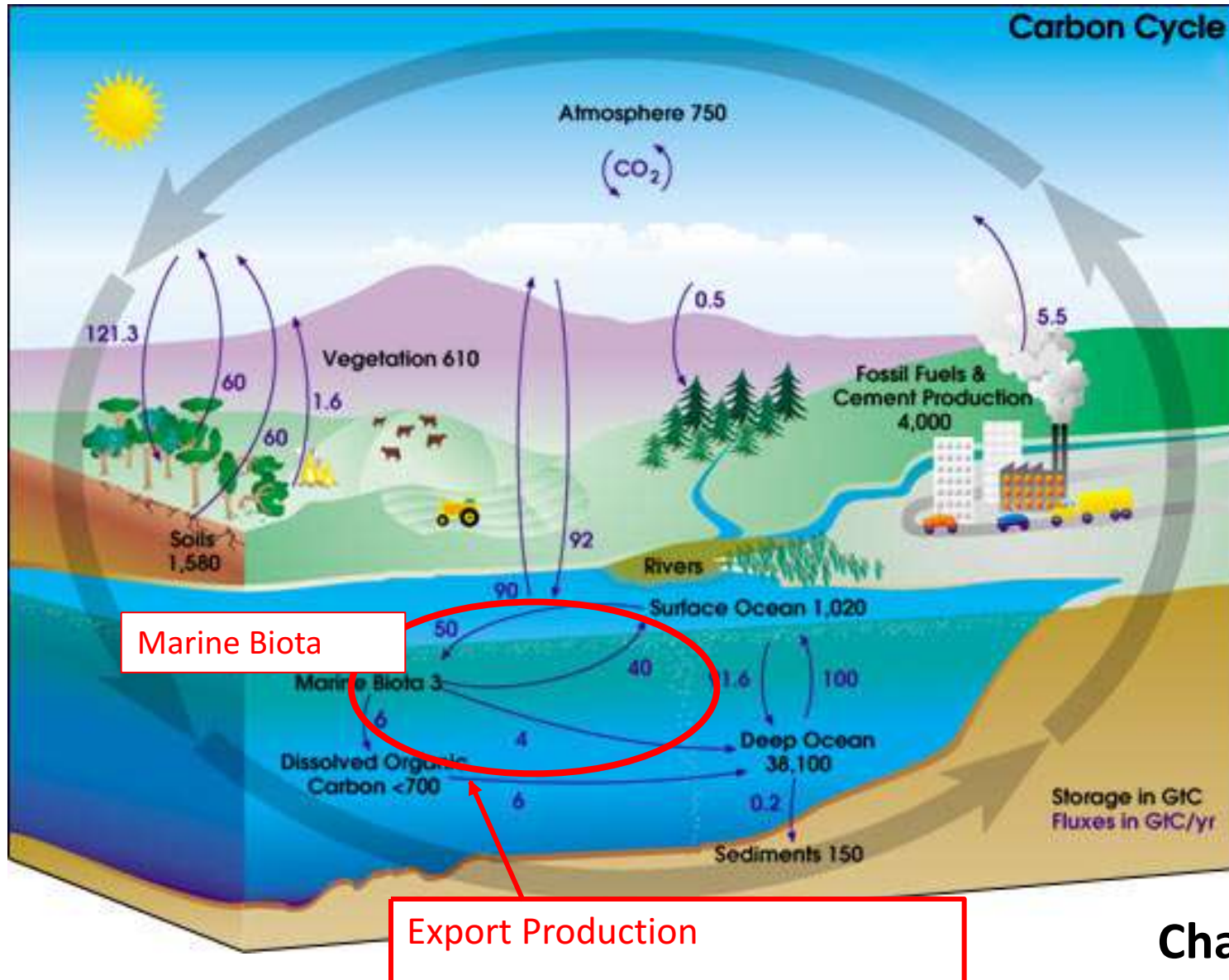
# Export production

- Sinking organic matter
- Sinking speed depends on particle sizes and density
  - Particle sizes depends on ecosystem structure

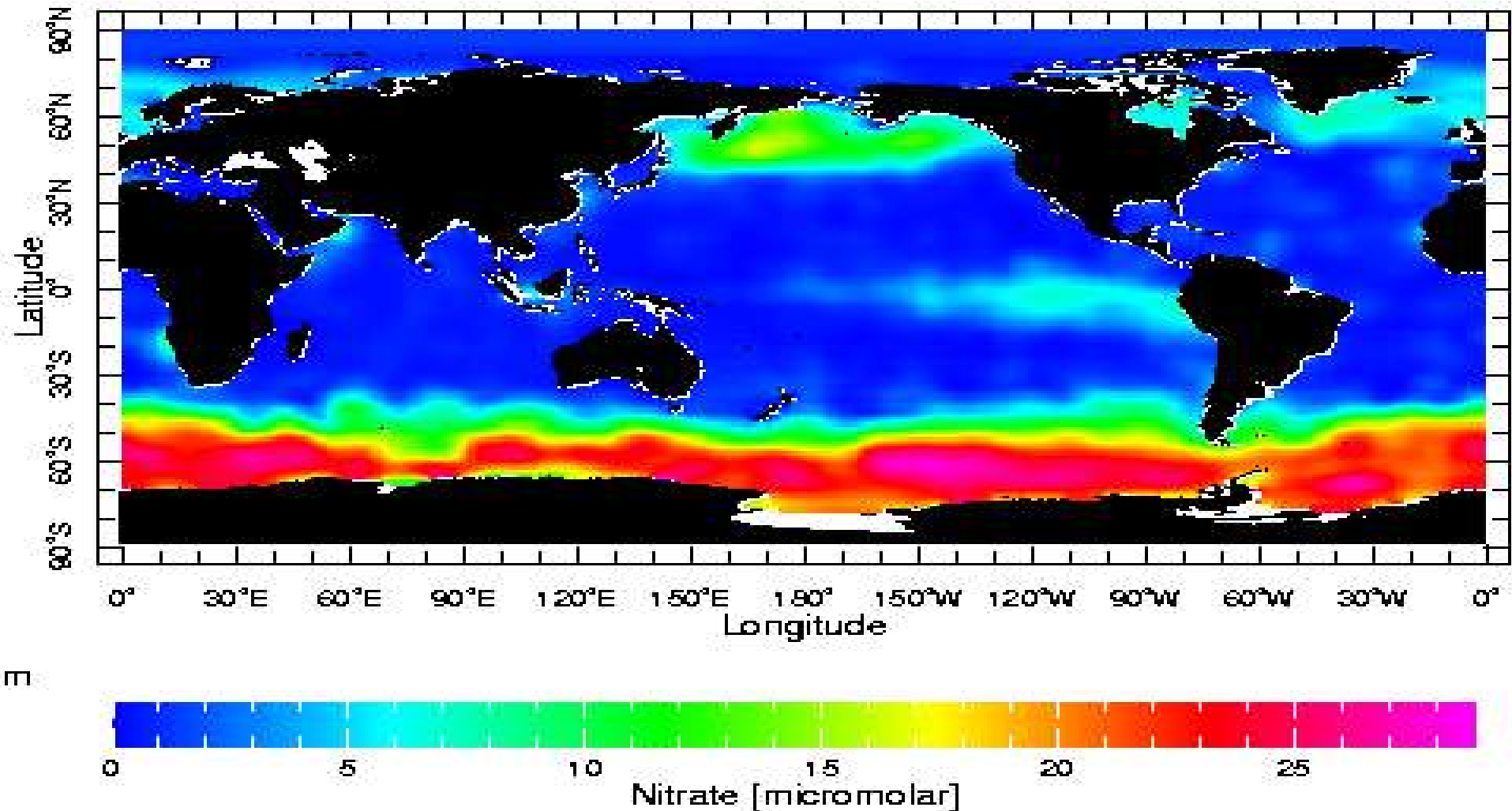


About 10% of primary production gets exported to the deep ocean

# Biological pump



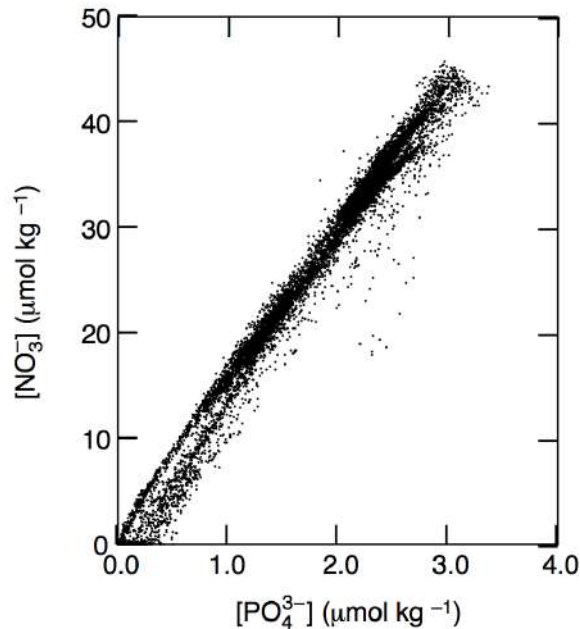
# What regulates the strength of biological carbon pump?



# Redfield ratio

- Average composition of organic matter in typical marine snow

$$P : N : -O_2 : C_{\text{org}} = 1 : 16 : 170 : 106$$



N:P ratio of seawater

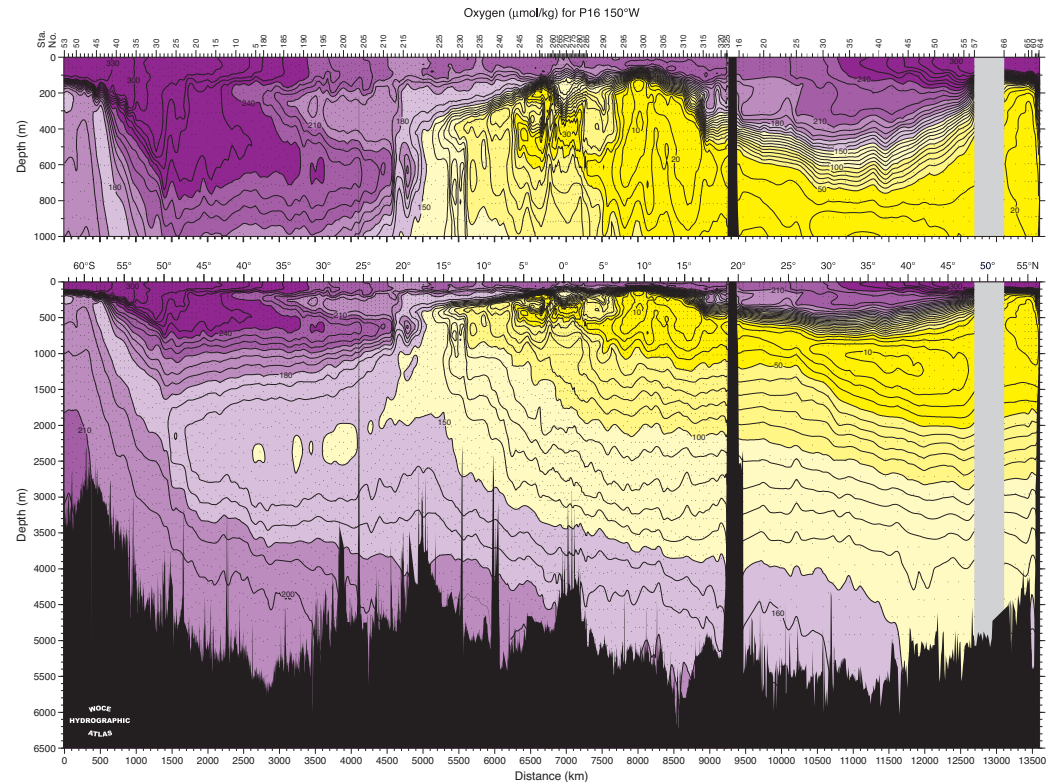
Tyrell (1999)

# Controls on biological pump

- *Bottom up control*: availability of nutrients (PO<sub>4</sub>, NO<sub>3</sub>)
  - Ocean nutrient inventory
  - Supply of nutrients to the surface ocean by ocean upwelling and mixing
- *Top-down control*
  - Predators can limit prey population
  - Ecosystem processes

# Remineralization

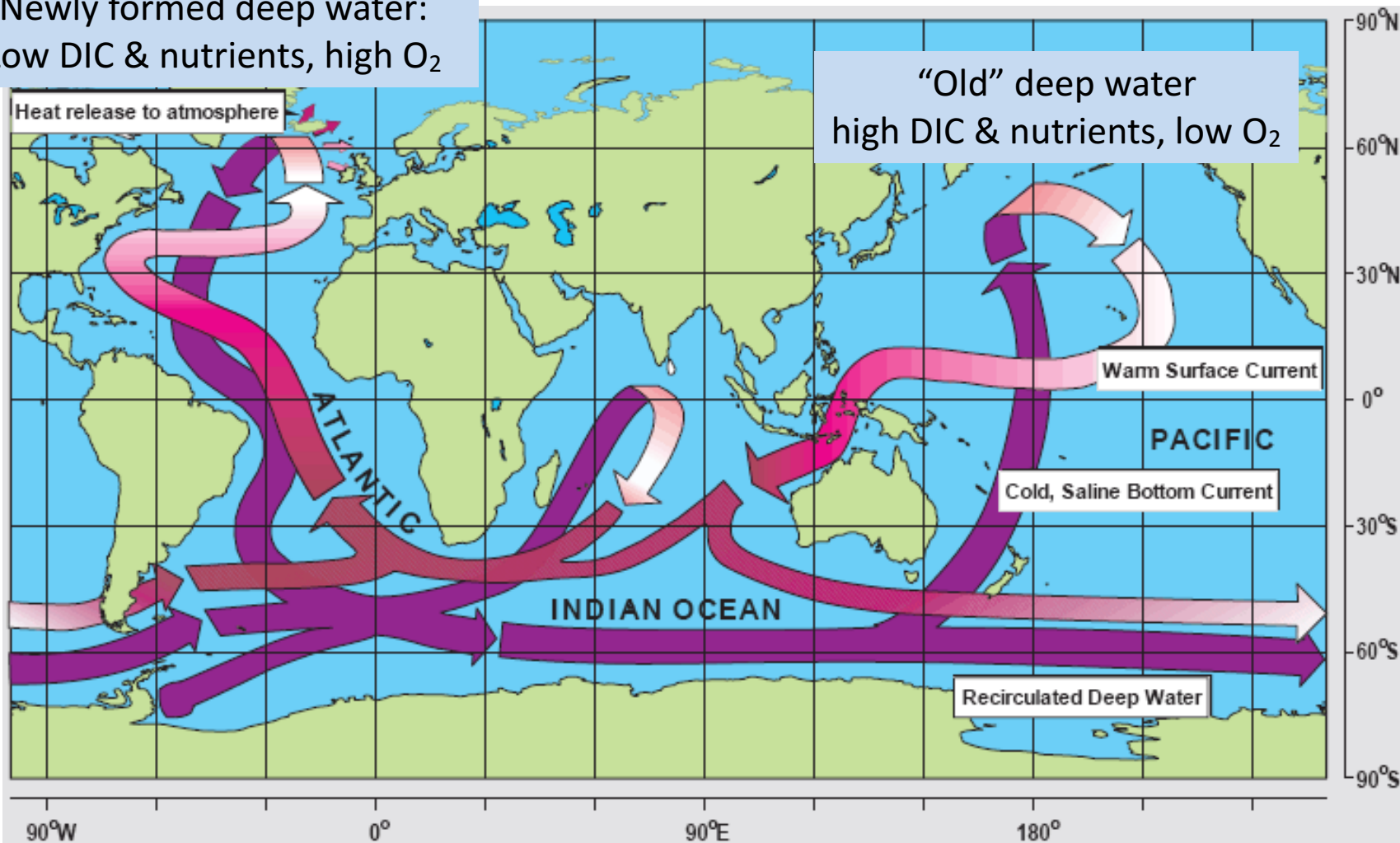
- Sinking organic matter is consumed by bacteria
  - Regeneration of nutrients, DIC
  - Consumption of oxygen



# A model of the vertical overturning circulation

Newly formed deep water:  
Low DIC & nutrients, high O<sub>2</sub>

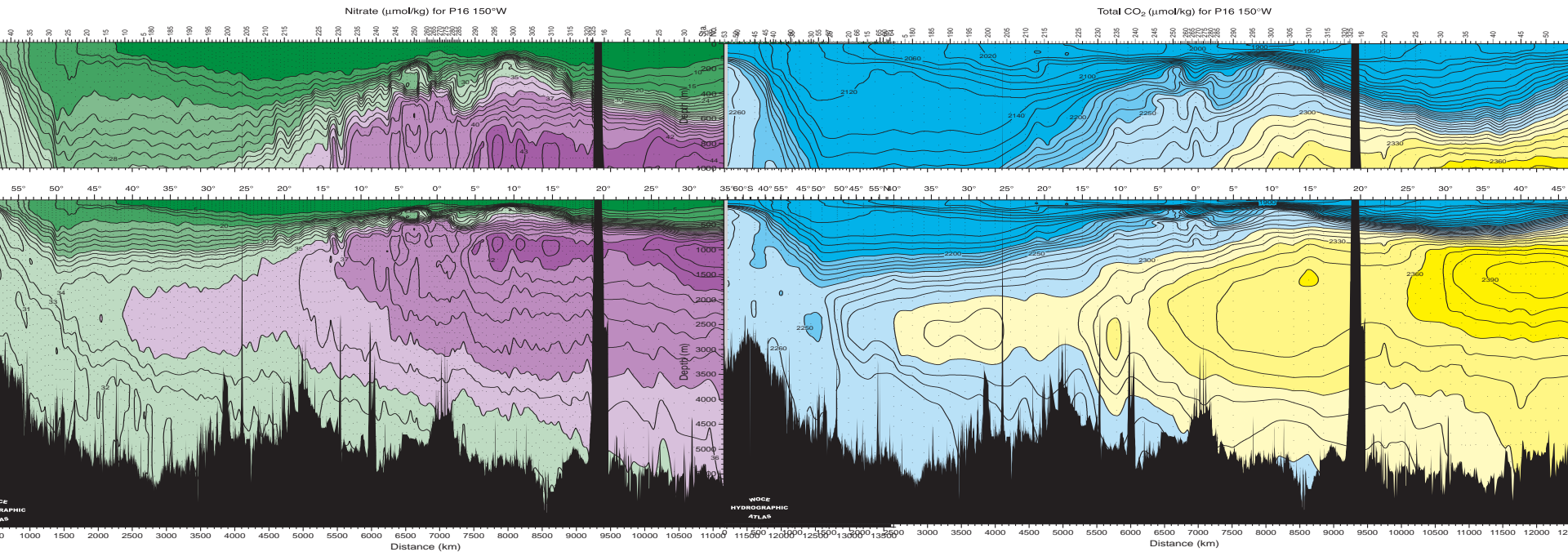
“Old” deep water  
high DIC & nutrients, low O<sub>2</sub>



# Distribution of nutrients vs DIC

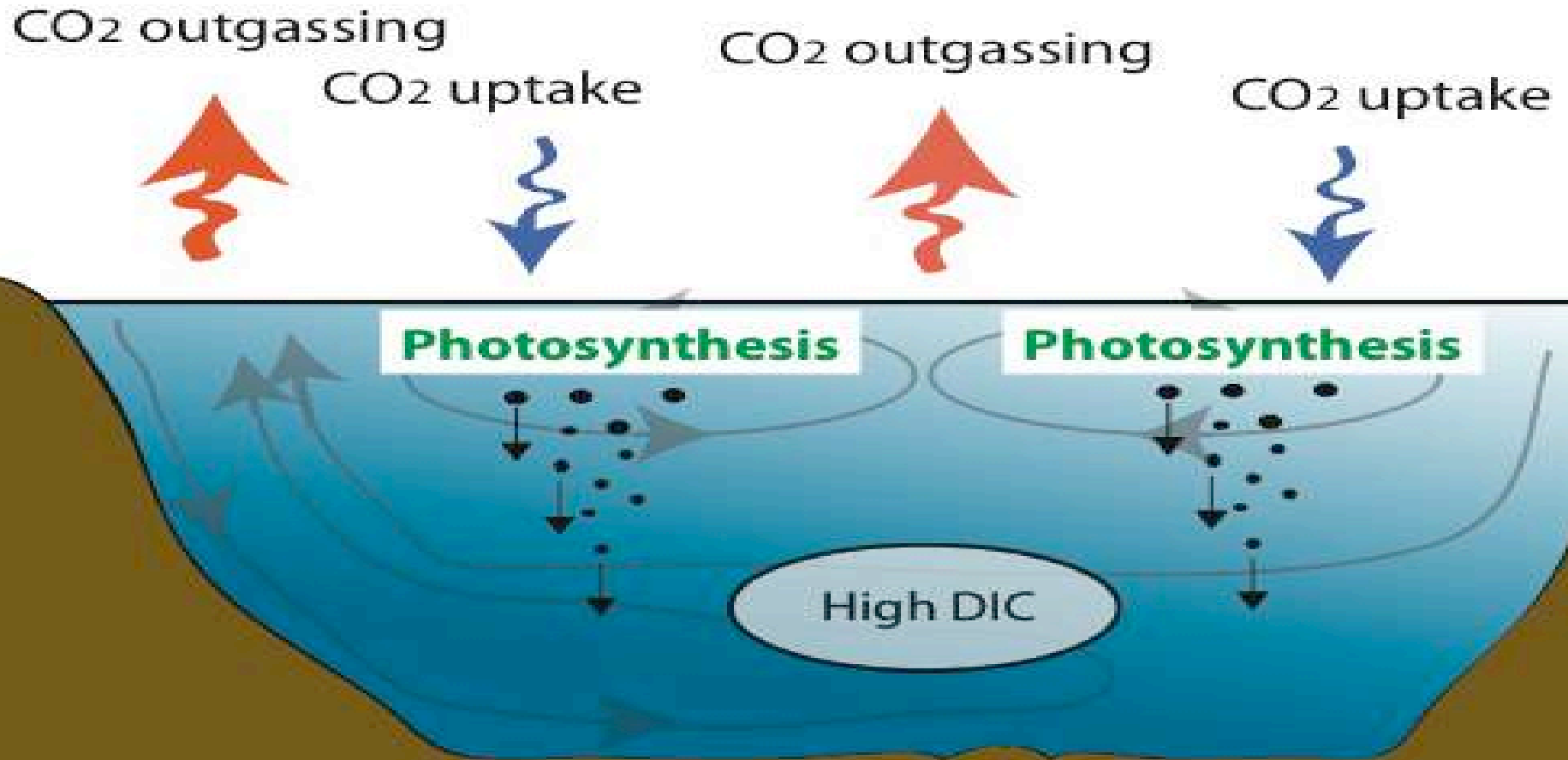
Nitrate:  $\text{NO}_3$

DIC





# Air-sea CO<sub>2</sub> flux driven by the biological pump



Eq

