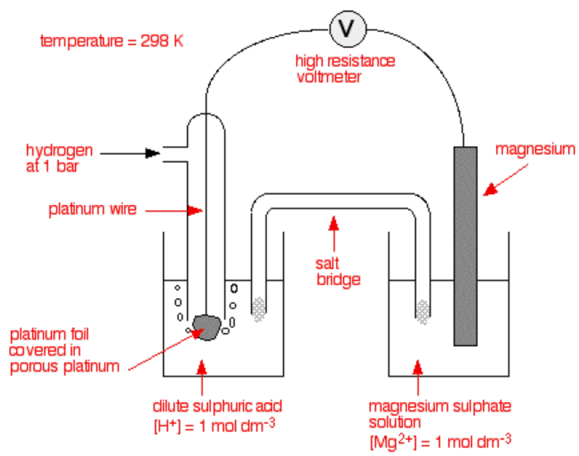
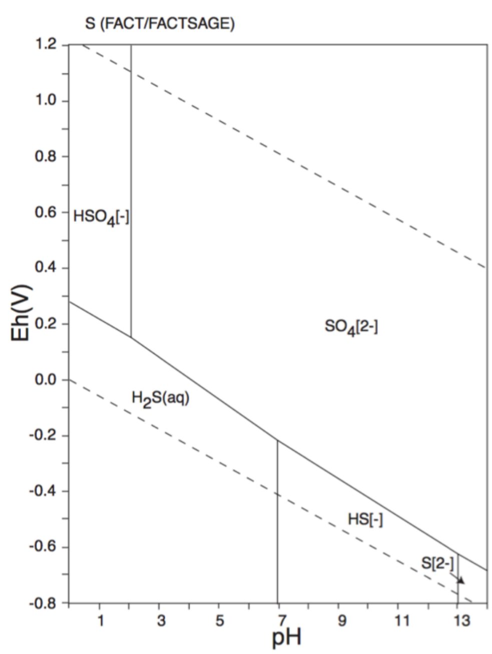
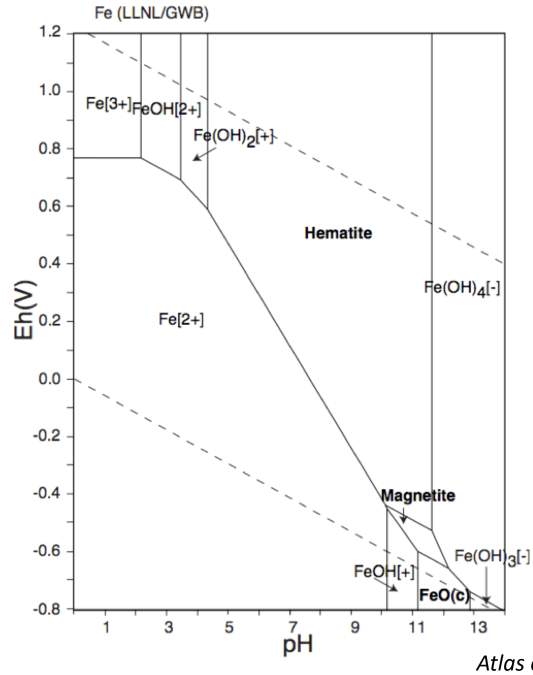
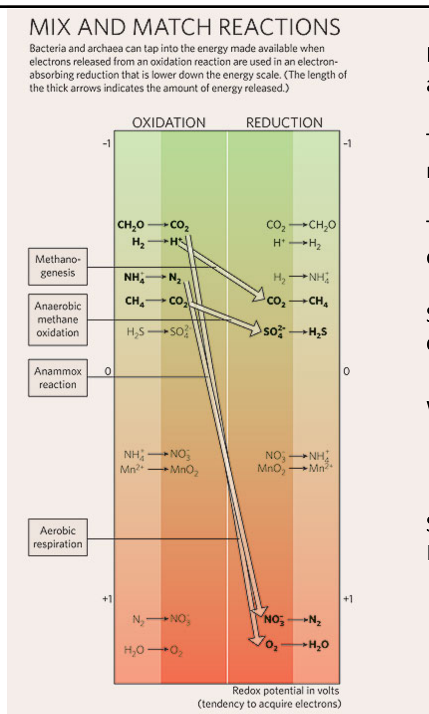
Electrochemistry and the long-term preservation of organic carbon







Atlas of Eh-pH Diagrams, Takeno (2005)



Energy is liberated when an oxidizer (electron acceptor) and reducer (electron donor) react.

This is the most common source of energy for metabolism.

The greater the oxidative contrast, the more energy is liberated.

Separation of oxidizers from reducers is the most common for of biological energy storage.

Which is a more energy rich red-ox system?

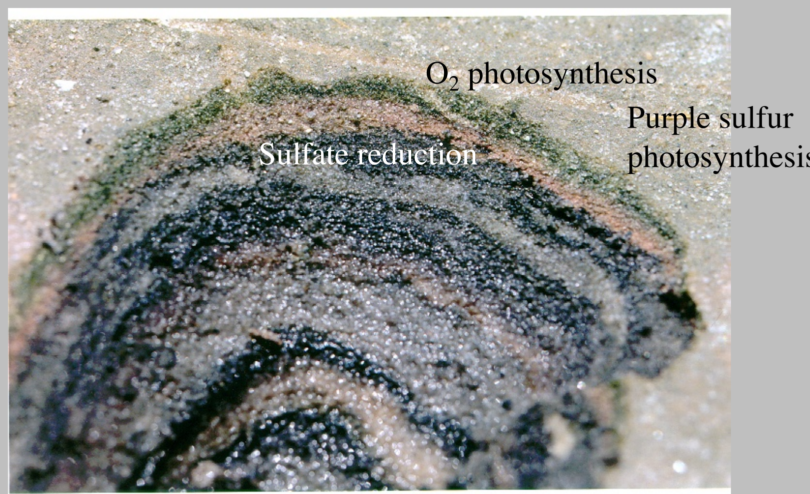
Methanogenesis 2: H_2 + CO_2 ➔ CH_4

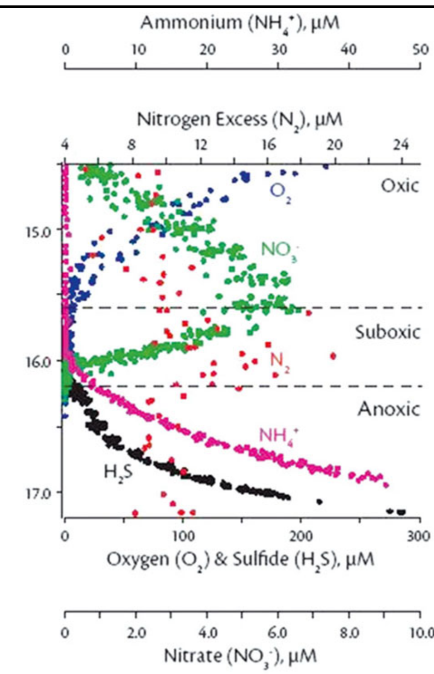
Sulfate reduction: 2 CH_2O + SO_4^{2-} ➔ 2 CO_2 + 2 H_2S

Which is the ***most*** energy rich red-ox system?

Graphic by Nick Lane (2006) Nature, 441, 274-277

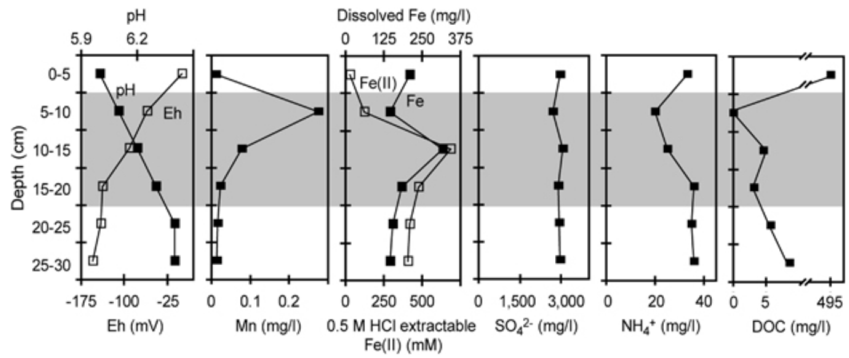
Layered microbial communities
Saline lagoon, Baja California del Norte, Mexico





Black Sea
depth section

Iron-rich marine hydrothermal sediment, Greece



Handley, 2010

Cross-section of peat accumulation
Mt. Battock, Scotland

Cross-section of peat accumulation
Cramalt Craig, Scotland

https://commons.wikimedia.org/wiki/File:Cross_section_in_a_peat_hag,_Cramalt_Craig_-_geograph.org.uk_-_1542214.jpg

Biogeochemistry in Salt Marshes

- High net primary production (NPP)
  - Root growth contributes considerable fraction of NPP
- Effective filters & transformers of nutrients
  - NO_3 (rivers) -> Organic N (oceans)
  - Anaerobic conditions allow for denitrification (NO_3 --> N_2)
- Contribution of new inputs and nutrient recycling is equal
  - In uplands new inputs account for ~10% of available nutrients
  - Nitrogen is still limiting nutrient for salt marsh vegetation
    - Dominant form of available nitrogen is NH_4

Sulfate Reduction

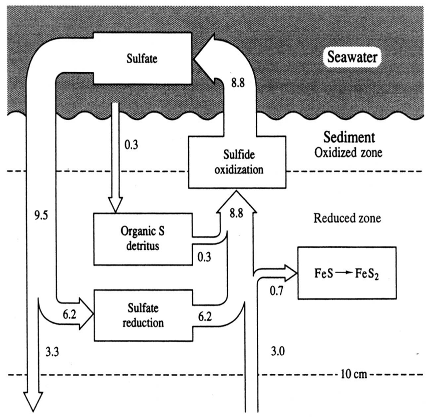


Figure 8.10 Transformations of sulfur in a coastal marine sediment. Note that of 6.2 g S m^{2-} yr^{-1} undergoing sulfate reduction, only 0.7 g S m^{-2} yr^{-1} is permanently stored in the sediment as pyrite or other reduced minerals. From Jørgensen (1977).

'S Transformations in Estuaries'

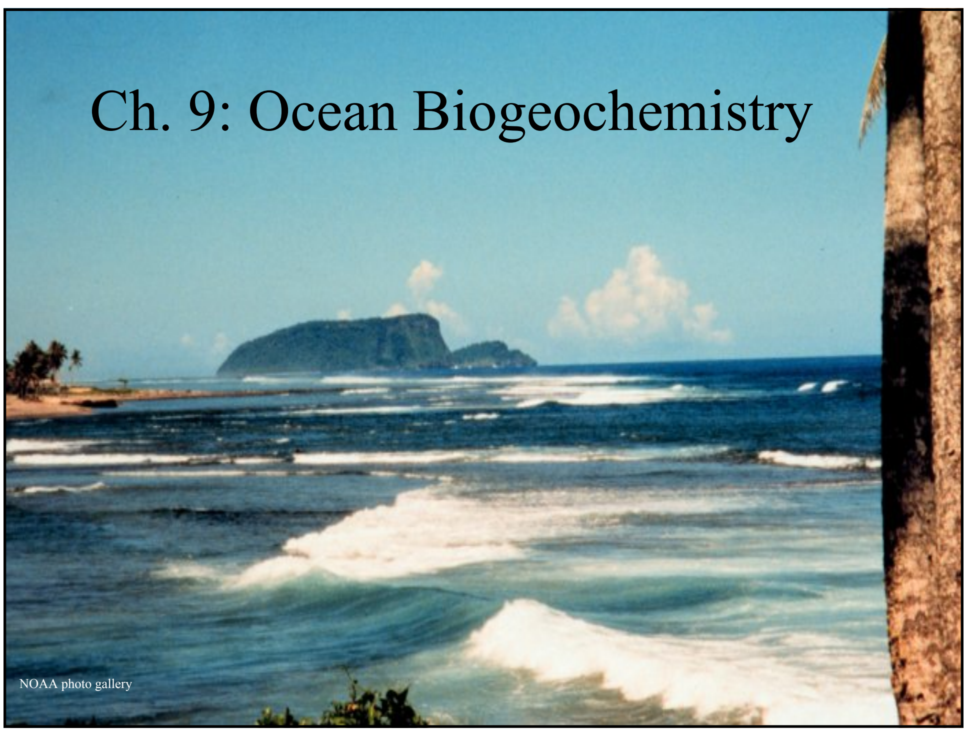
- Reoxidation of pyrite & sulfides
  - Small accumulation of reduced S
    - (.7 versus 6.2 gmS/m^2year)
    - ~15% permanently buried (pyrite)
    - Retention of metallic pollutants
- Produces thiosulfate (percolates ⇓)
- S diffuses ⇑ (oxidized to SO_4)

Nitrification & Denitrification

- Bacterial oxidation of NH_4 occurs rapidly in estuaries (nitrification)
  - NH_4 converted to NO_3
  - Occurs in upper layers of sediment
  - Process influenced by availability of NH_4 (fertilizer/sewage/manure)
- Denitrification in lower layers supported by NO_3 diffusing down
  - NO_3 converted to gaseous N_2
  - From upper layers of sediment or water column
  - Narragansett Bay (Seitzinger, 1980)
    - Denitrification removes:
      - 50% of available NO_3 from incoming riverflow
      - 35% of available NO_3 from mineralization within estuary
      - N_2 = major product of denitrication

Net Primary Production

- Direct relation to nitrogen inputs
- Estuaries show excessive levels of productivity
  - High levels of available N & P
    - Sewage/agricultural runoff/acid rain
  - ⥣ Occurrence of anoxic conditions in bottom waters & sediments
- Estuaries show peak in NPP at intermediate salinities
  - Reflects zone of ⥣ nutrient availability/phytoplankton occurrence
    - Fuels high fish/shellfish productivity
- Dependent of local conditions & human activities
  - Direct pollution/global sea level rise



Surface Currents

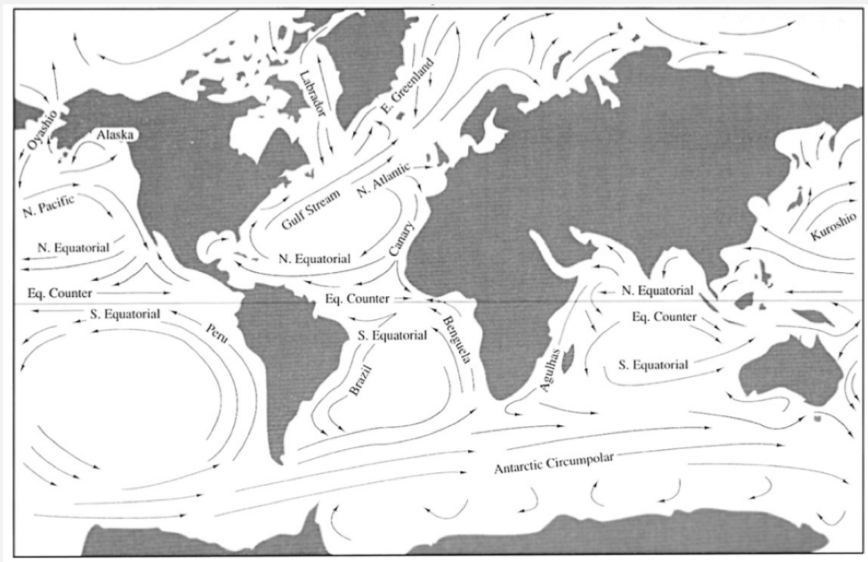


FIGURE 9.1 Major currents in the surface waters of the world's oceans. *Source: From Knauss (1978). Used with permission of Dr. John Knauss.*

Deep Ocean Circulation

- Deep and Surface Oceans separated by density gradient caused by differences in Temperature and Salinity
- This drives thermohaline deep circulation:

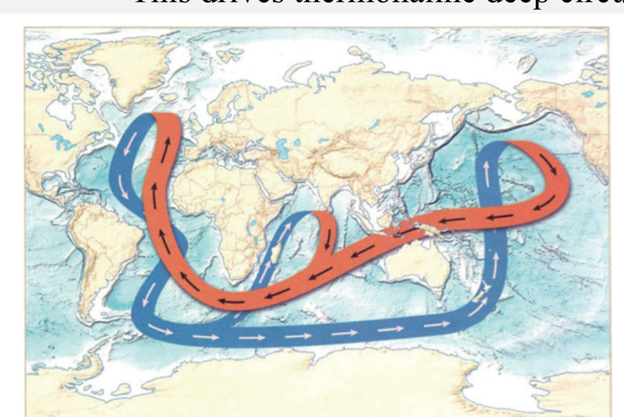


FIGURE 9.3 The global ocean thermohaline circulation forms a conveyor that moves water among the various ocean basins in surface (*red*) and deep-water (*blue*) currents. *Source: From Lozier (2010). Used with permission of the American Association for the Advancement of Science.*

* Ice forms in the N. Atlantic and Southern Ocean, leaving behind cold, saline water which sinks
* Oldest water is in N. Pacific
* Distribution of dissolved gases and nutrients: N, P, CO_2

Major Ions in Seawater

TABLE 9.1 Major Ion Composition of Seawater, Showing Relationships to Total Chloride and Mean Residence Times for the Elements with Respect to Riverwater Inputs

Constituent	Concentration in seawater[a] (g kg^{-1})	Chlorinity ratio[a] (g kg^{-1})	Concentration in river water[b] (mg/kg)	Mean residence time[b] (10^6 yr)
Sodium	10.78145	0.556492	5.15	75
Magnesium	1.28372	0.066260	3.35	14
Calcium	0.41208	0.021270	13.4	1.1
Potassium	0.39910	0.020600	1.3	11
Strontium	0.00795	0.000410	0.03	12
Chloride	19.35271	0.998904	5.75	120
Sulfate	2.71235	0.140000	8.25	12
Bicarbonate	0.10481	0.005410	52	0.10
Bromide	0.06728	0.003473	0.02	100
Boron	0.02739	0.001413	0.01	10
Fluoride	0.00130	0.000067	0.10	0.05
Water	964.83496	49.800646		0.034

[a] *Source: Millero et al. (2008).*
[b] *Source: Meybeck (1979) and Holland (1978).*

Residence time vs. chemistry

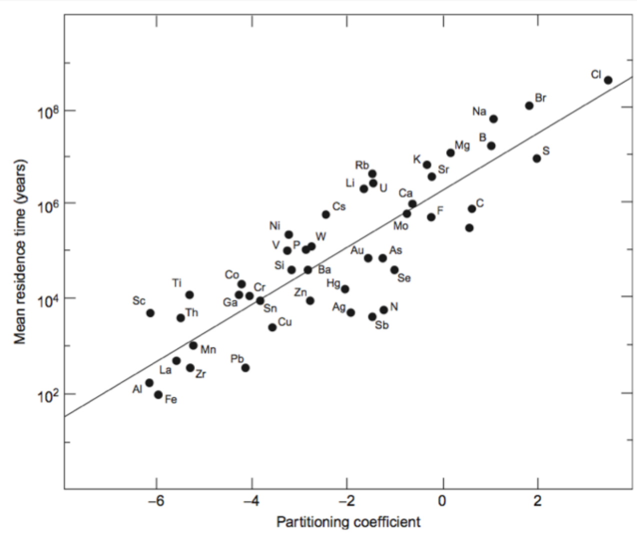


FIGURE 9.6 Mean residence time of elements in seawater as a function of their concentration in seawater divided by their mean concentration in the Earth's crust—with high values of the index indicating elements that are very soluble. *Source: From Whitfield and Turner (1979). Reprinted with permission from* Nature, *copyright 1979 Macmillan Magazines Limited.*

Marine Primary Production

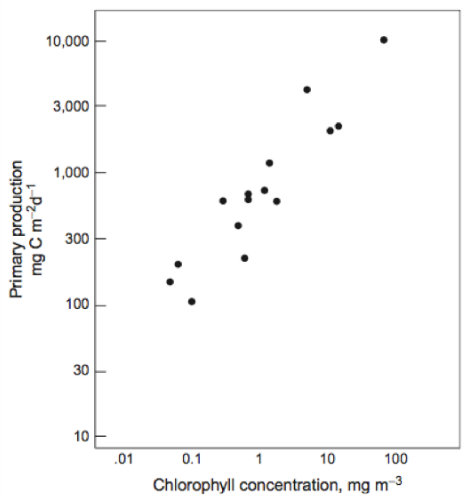
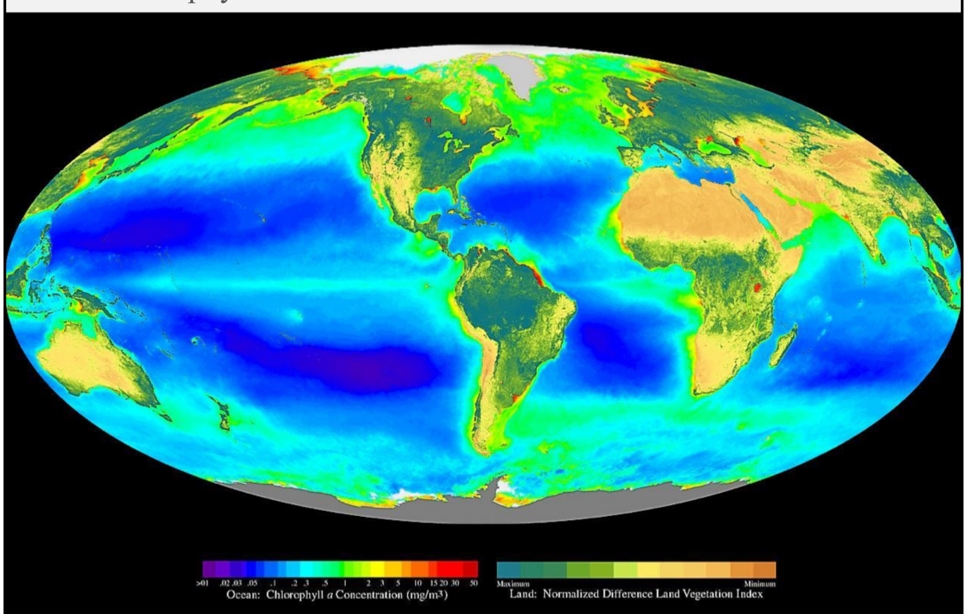


FIGURE 9.7 Net primary productivity as a function of surface chlorophyll in waters of coastal California. *Source: From Eppley et al. (1985),* Journal of Plankton Research. *Reprinted by permission of Oxford University Press.*

Chlorophyll-a abundance in the ocean 1997-2000. SeaWiFS



http://oceancolor.gsfc.nasa.gov/SeaWiFS/BACKGROUND/Gallery/index.html and from en:Image:Seawifs global biosphere.jpg

Marine Primary Production

TABLE 9.2 Estimates of Total Marine Primary Productivity and the Proportion That Is New Production

Province	% of ocean	Area ($10^{12}m^2$)	Mean production (g C $m^{-2}yr^{-1}$)	Total global production (10^{15}g C yr^{-1})	New production[a] (g C $m^{-2}yr^{-1}$)	Global new production (10^{15}g C yr^{-1})
Open ocean	90	326	130	42	18	5.9
Coastal zone	9.9	36	250	9.0	42	1.5
Upwelling area	0.1	0.36	420	0.15	85	0.03
Total		**362**		**51**		**7.4**

[a] *New productivity defined as C flux at 100 m.*
Source: From Knauer (1993). Used with permission of Springer-Verlag.

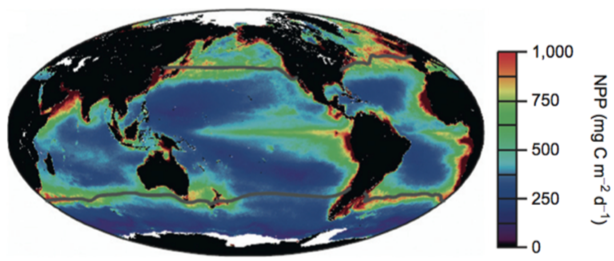


FIGURE 9.8 Global map of marine NPP. *Source: From Behrenfeld et al. (2006).*

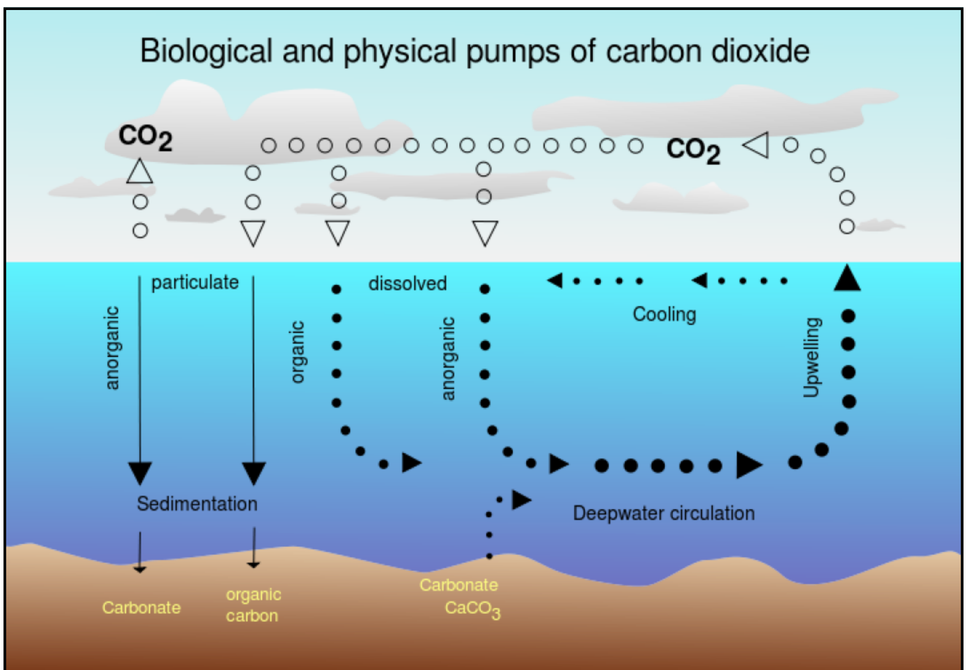
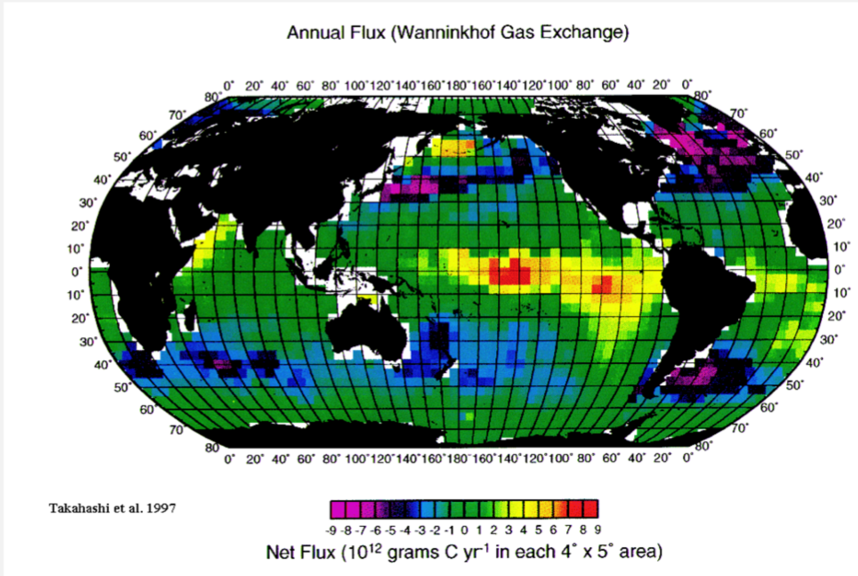


Image adapted by McSush from one by Hannes Grohe.
https://commons.wikimedia.org/wiki/File:CO2_pump_hg.svg



SeaWiFS website: NFS/NASA