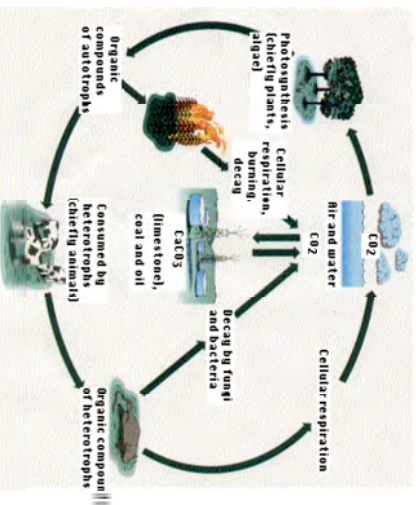
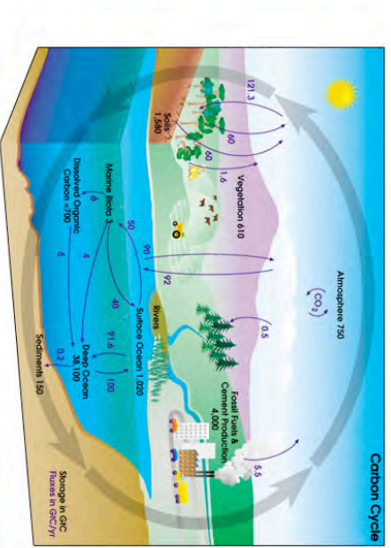


Carbon Cycling in the Deep!



Where Does CO2 Come From?



CO2 in the Ocean

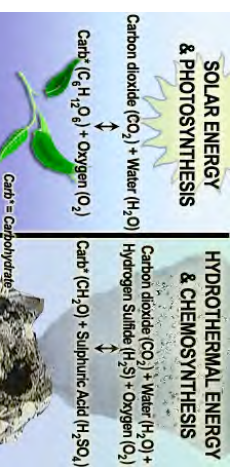
Major Sources

- Respiration
- Volcanoes
- Burning hydrocarbons
- Decomposition

Major Sinks

- Autotrophy:
- Photosynthesis
- Chemosynthesis
- Burial in sediments
- Subduction zones & volcanoes though!
- Incorporation into animal skeletons

Carbon Fixation



- Different metabolic pathways with different evolutionary histories → same end result
- Reduction of carbon, then fixation into a macromolecule (note the byproducts of each)

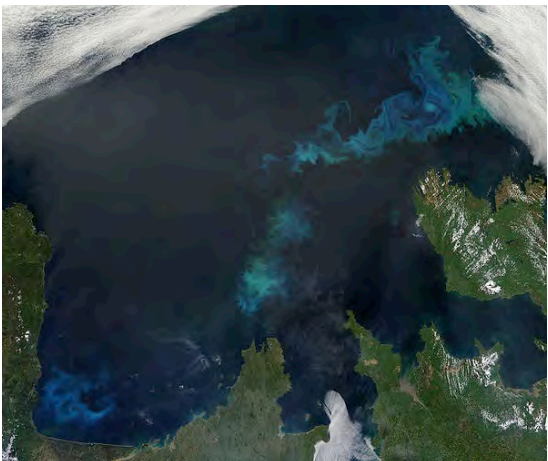
Huge Variety of REDOX Reactions

Table 1. Energetically favorable redox reactions available to chemolithotrophic microorganisms in the deep-sea hydrothermal vent environments.

Energy Metabolism	Electron Donor	Electron Acceptor	Fossil Reaction	Identified	Confirmed
Methanotrophy	CH ₄	O ₂	CH ₄ + 2O ₂ = CO ₂ + 2H ₂ O	Yes	Yes
Methanotrophy/aerobic reduction	CH ₄	SO ₄ ²⁻	CH ₄ + SO ₄ ²⁻ = HCO ₃ ⁻ + HS ⁻ + H ₂ O	Yes	Not Yet
Methanotrophy/denitrification	CH ₄	NO ₃ ⁻	CH ₄ + 2NO ₃ ⁻ = HCO ₃ ⁻ + 2OH ⁻ + N ₂	No	No
H ₂ oxidation/methanogenesis	H ₂	CO ₂	H ₂ + CO ₂ = CH ₄ + H ₂ O	Yes	No
H ₂ oxidation/aerobic reduction	H ₂	O ₂	H ₂ + 1/2O ₂ = H ₂ O	Yes	Yes
H ₂ oxidation/nitrate reduction	H ₂	NO ₃ ⁻	H ₂ + NO ₃ ⁻ = H ₂ O + NH ₄ ⁺	Yes	Yes
S oxidation	H ₂ S	O ₂	H ₂ S + O ₂ = SO ₄ ²⁻ + 2H ⁺	Yes	Yes
S oxidation	SO ₂	O ₂	SO ₂ + 1/2O ₂ = SO ₃ ²⁻ + 2H ⁺	Yes	Yes
S oxidation	SO ₂	O ₂	SO ₂ + H ₂ O + 1/2O ₂ = SO ₄ ²⁻ + 2H ⁺	Yes	Yes
S oxidation/denitrification	S ⁰	NO ₃ ⁻	SO ₂ + 8OH ⁻ + 4NO ₃ ⁻ + 4HS ⁻ = SO ₄ ²⁻ + 1/2S ₂ O ₃ ²⁻ + 2HS ₂ S + 2H ₂ O	Yes	Yes
S oxidation/denitrification	S ⁰	NO ₃ ⁻	H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃ ⁻	2H ₂ S + 8NO ₃ ⁻ + 8OH ⁻ = SO ₄ ²⁻ + 4N ₂ + 4H ₂ O + 4HS ⁻	Yes	Yes
S oxidation/denitrification	H ₂ S	NO ₃			

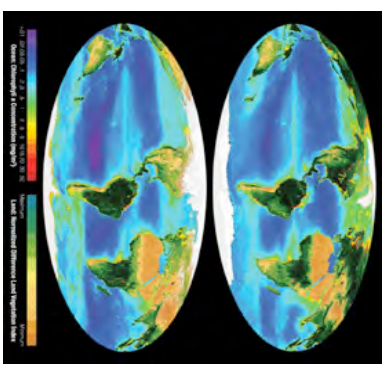
Phytoplankton Blooms

- **Optimal**
 - Light
 - Temperature
 - Nutrients
 - Few grazers
- **Consequences**
 - Rapidly decomposition consumes O₂



Phytoplankton Blooms

- Seasonal seas
- Track Chlorophyll-A, satellite (SeaWiFS)
- Productivity varies latitudinally
 - Highest in polar regions, equator

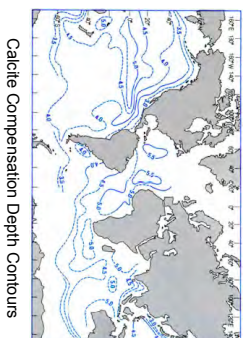


Seasonal Seas (Blue Planet)



<http://www.youtube.com/watch?v=h6XOgoXDWlc>

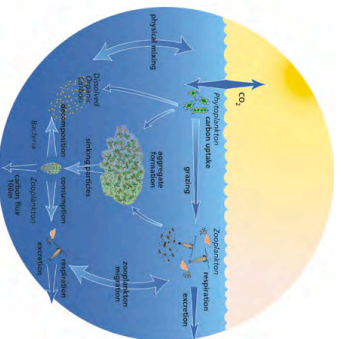
Carbonate Compensation Depth



- Carbonate Compensation Depth
- Rate of supply of CaCO₃=rate of dissolution
- Calcite vs Aragonite
 - Aragonite more stable mineral but dissolves shallower (~2000m)

Biological Pump

- Export of C to the deep via marine snow
- Conglomerate of of dead/dying organic material
- Carbon fixed by primary producers 2 ways: Photosynthesis and shell formation



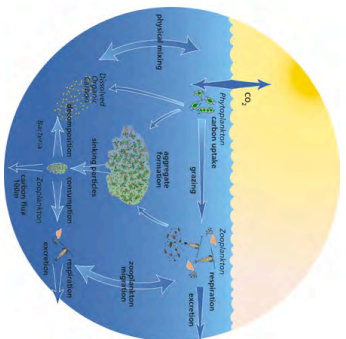
Deep Sea Food Bonanza!



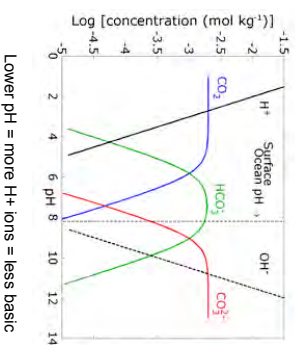
<http://www.youtube.com/watch?v=5qblwORXWg>

Biological Pump

- Without export to the deep, atmosphere would have higher [CO₂] → higher temperature
- Phytoplankton keep the pump downward

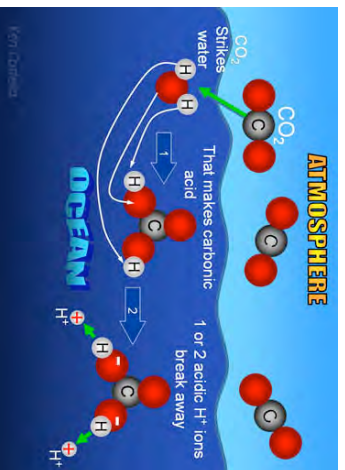


The Carbonate System

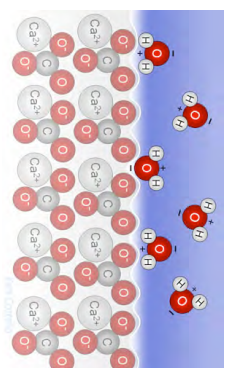


- PH is a log scale!
- 0.1 decrease in pH = 29% increase in [H⁺]
- Affects calcification and physiology in animals and plants

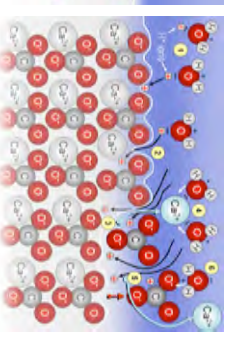
How Does CO2 Enter the Ocean?



Acidification



- Water is not strong enough enough to pull apart CaCO₃

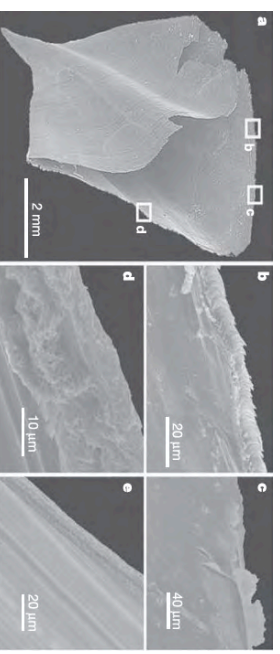


- [H⁺] ions disrupt bond between Ca²⁺ & CO₃²⁻ by water (dissolved)
- Ca²⁺ ions surrounded by water (dissolved)
- Bicarbonate formed

Pteropods



Acidification



Orr et al. 2005 (Nature 437:681) – held pteropods for 48 hrs in solution undersaturated with CaCO₃ and observed rapid decay of shell

Acidification

A positive feedback

- More CO₂ in solution shifts the balance of CO₂, HCO₃⁻ & CO₃²⁻
- Less CO₃²⁻ availability for calcifiers
- Less calcareous phytoplankton = less CO₂ pumped to the deep sea
- Reduces the oceans buffering capacity with the atmosphere
- More CO₂ in atmosphere

Canaries in the Acidification Coal Mine?

- Pteropods as early indicators of climate change?
 - High latitudes have cold waters which absorb CO₂ more readily → less carbonate ions in seawater
 - Pteropods have aragonitic shells and compose base of polar food chains
 - Shell repair takes energy away from metabolism and reproduction
 - Their range could be limited in as little as 50-100 generations