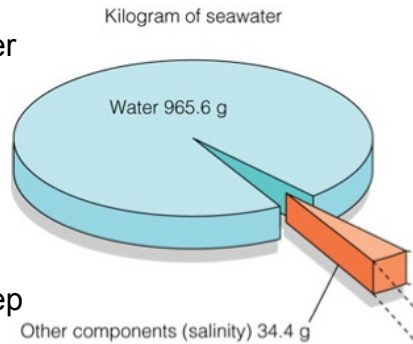


# What is Sea Salt?

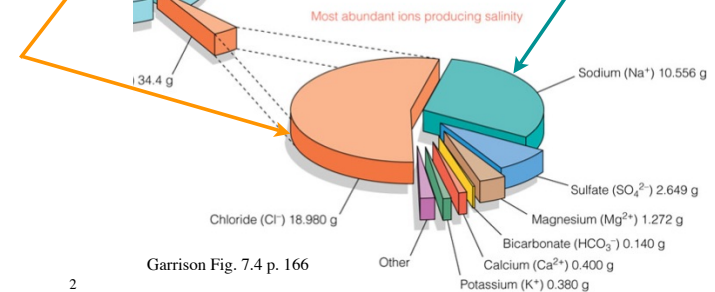
- Water
- Salts
  - Salinity = grams salts per kilogram sea water
  - Average = 35 g/kg = 3.5%
- World ocean has  $5 \times 10^{15}$  (quadrillion) kg salts
  - Cover Earth 45 m deep



Garrison Fig. 7.4 p. 166

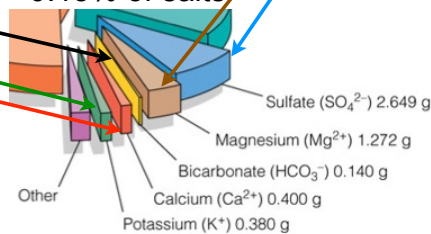
# What are Sea Salts?

- Mostly what you already know
  - Sodium ( $\text{Na}^+$ ) ~ 31% of salts
  - Chloride ( $\text{Cl}^-$ ) ~ 55% of salts
  - Together NaCl ~86% of salts



# What are Sea Salts?

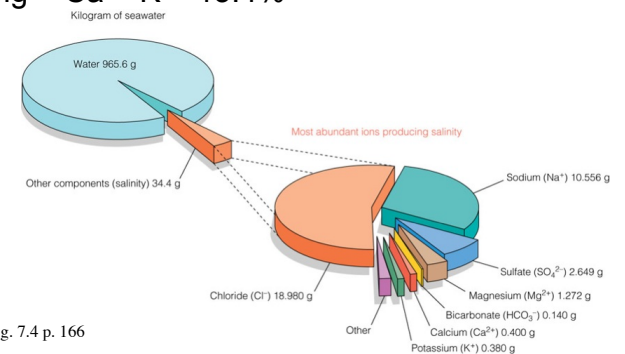
- Some other familiar dissolved chemicals
  - Sulfate ( $\text{SO}_4^{2+}$ ) ~ 3% of salts
  - Magnesium ( $\text{Mg}^{2+}$ ) ~ 1% of salts
  - Calcium ( $\text{Ca}^{2+}$ ) ~0.4% of salts
  - Potassium ( $\text{K}^+$ ) ~0.4% of salts
  - Bicarbonate ( $\text{HCO}_3^-$ ) ~0.15% of salts



Garrison Fig. 7.4 p. 166

# What are Sea Salts?

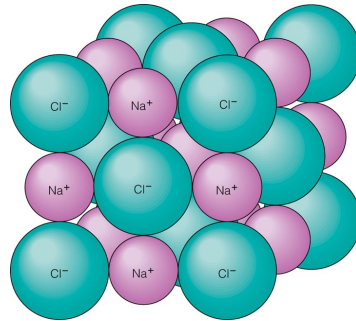
- Big 6 account for 99.4% of all sea salts
  - Na + Cl = 86%
  - $\text{SO}_4 + \text{Mg} + \text{Ca} + \text{K} = 13.4\%$



## Chemical Nature of Sea Salts



- Salts are molecules that break apart easily in water solution
  - Atoms separate from each other
  - Form ions
    - Electrically charged atoms
    - Gain or lose one or more electrons while in solution
  - NaCl ionizes to form:
    - Na<sup>+</sup> (loses the electron)
    - Cl<sup>-</sup> (gains the electron)
  - Only occurs with certain combinations of atoms



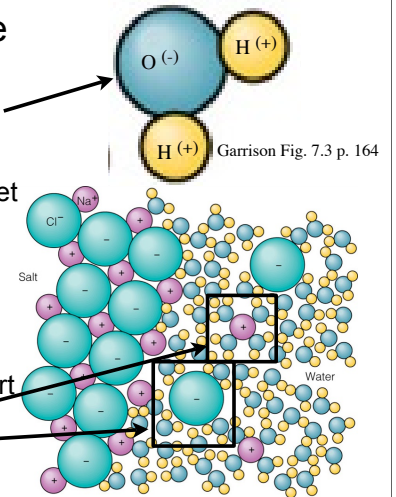
Garrison Fig. 7.2 p. 164

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## Chemical Nature of Sea Salts



- Ionic molecules dissolve easily in water
  - Water molecule H<sub>2</sub>O has electrical polarity
    - Like a v-shaped bar magnet
    - Oxygen more negative
    - Hydrogen more positive
  - Water molecules attract salt ions
    - Help pull Na & Cl ions apart
      - O<sup>-</sup> attracted to Na<sup>+</sup>
      - H<sup>+</sup> attracted to Cl<sup>-</sup>



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## Salts in the Sea



- Solubility affects fate of chemicals when they enter the ocean
  - High solubility
    - Accumulates at high concentrations in sea water
    - Remains in the ocean a long time
  - Low solubility
    - Low concentrations in sea water
    - Leaves the ocean relatively sooner
  - NaCl a very soluble salt
    - But only a salt when it is solid
    - Dissolves to yield two most abundant ions
    - Remains in the oceans for millions of years

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## Why the Sea is Salt



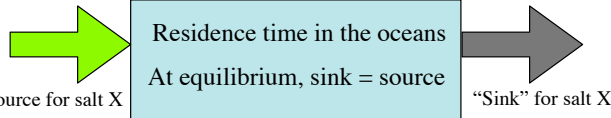
- The real question:
  - Why isn't the sea much saltier than it is?
- Total mass of dissolved solids entering the oceans each year
  - 0.000005 of one percent ( $5 \times 10^{-8}$ ) of the total mass of dissolved solids already in the oceans
- How long until the oceans would reach their present salinity?
  - “Only” 20 million years
- But sediments indicate constant ocean salinity
  - Last 1.5 billion years

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# Why the Sea is Salt



- The real question:
  - Why isn't the sea much saltier than it is?
- Something is removing salts from the oceans
  - Ocean chemistry is at equilibrium
  - Inputs are equaled by outputs
  - Sources = Sinks
    - Sink= a removal location or process
  - Residence time = how long salt stays in ocean

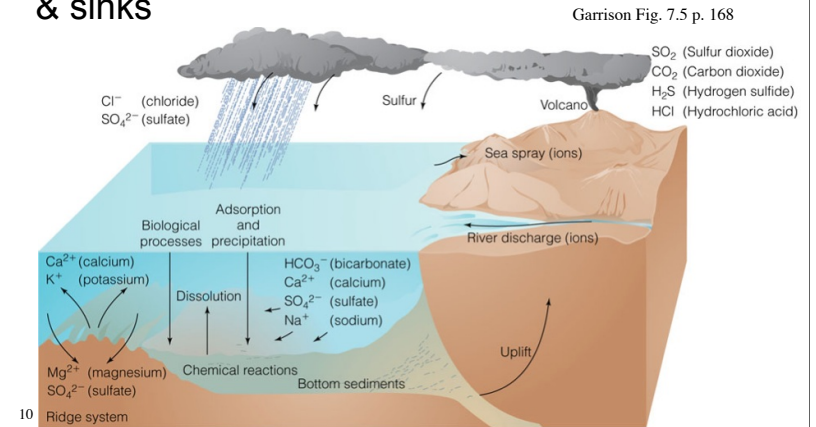


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# Sources & Sinks



- Each type of ion has a different set of sources & sinks

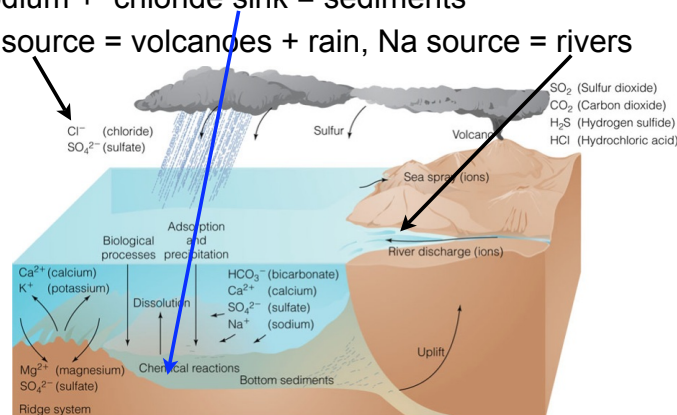


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# Sources & Sinks



- Example: Na & Cl
  - Sodium + chloride sink = sediments
  - Cl source = volcanoes + rain, Na source = rivers

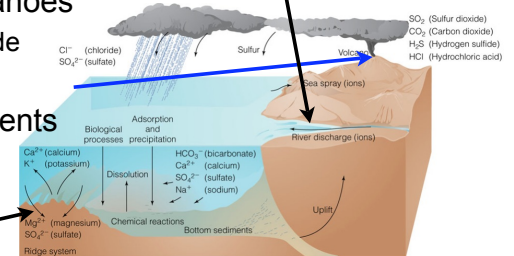


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# Sources



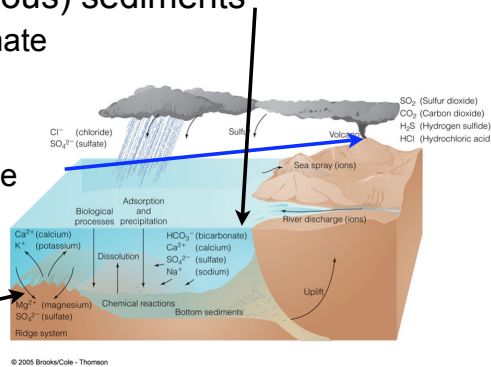
- Erosion of land, transport by rivers
  - Sodium, Calcium, Sulfate, Bicarbonate
- "Excess volatiles"
  - Ions delivered as gases rather than dissolved solids
  - Terrestrial volcanoes
    - Sulfate, Chloride
    - Carbon
  - Hydrothermal vents at rift valleys
    - Calcium
    - Potassium



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# Sinks

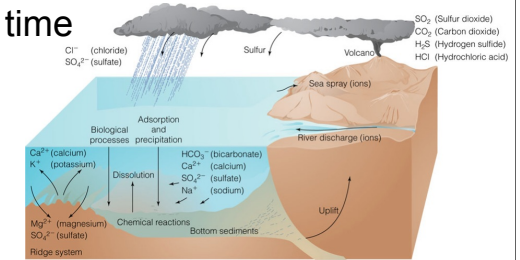
- Inorganic (non-biogenous) sediments
  - Sodium, Calcium, Sulfate, Bicarbonate
- Organic (biogenous) sediments
  - Calcium, carbonate
  - Silicon
- Evaporation
  - Sodium, Chloride
- Hydrothermal vents
  - Magnesium
  - 1.3 - Sulfate



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# Residence Time

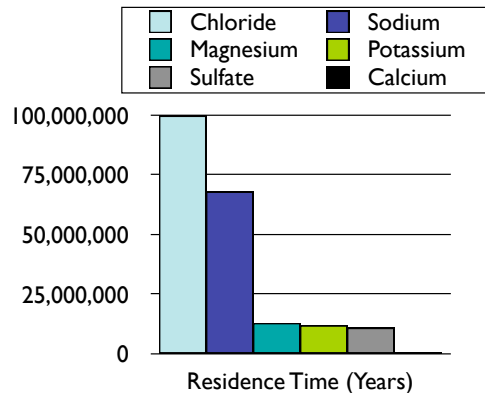
- Residence time (years) =
  - Amount in ocean ÷ amount entering/leaving per year
- Long residence time
  - Large amount in ocean
  - Very soluble
- Short residence time
  - Small amount in ocean
  - Poorly soluble



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# Residence Time

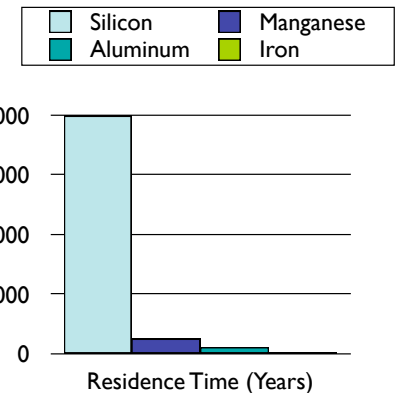
- Residence time (years) =
  - Amount in ocean ÷ amount entering/leaving per year
- Long residence
  - Large amount in ocean
  - Very soluble
  - The Big 6 ions



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# Residence Time

- Short residence
  - Small amount in ocean
  - Poorly soluble
- Sources
  - Erosion & rivers
- Sinks: sediments
  - Silicon part of diatom skeletons
  - Manganese in Mn nodules
  - Aluminum in clay

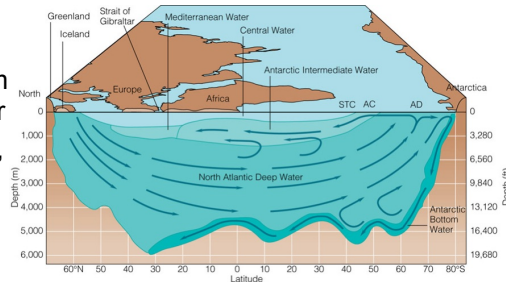


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## Dissolved Gases



- Also have sources & sinks
  - Both inorganic (non-living) & organic (living)
  - Inorganic:
    - Gases from atmosphere dissolve in sea water
    - Main effect is on surface waters
    - Global density circulation transports them into deep water
    - Sinking of cold, salty water at polar latitudes



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## Important Gases in the Ocean



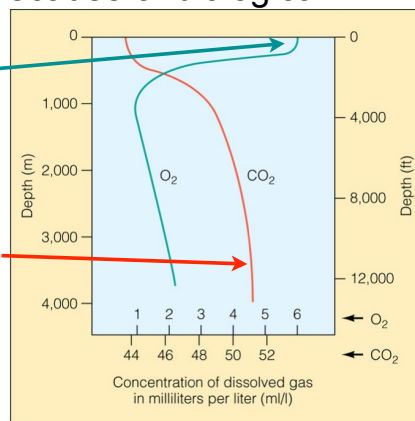
- Nitrogen ( $N_2$ )
  - “Fixed” nitrogen ( $NO_3$ ,  $NO_2$ ,  $NH_4$ ) an essential nutrient for photosynthesis
  - “Nitrogen fixing” bacteria convert  $N_2$  gas to fixed N
    - Make it available for biological production
- Oxygen ( $O_2$ )
  - Generated by photosynthesis
  - Consumed by respiration & decay
- Carbon dioxide ( $CO_2$ )
  - Generated by respiration & decay
  - Consumed by photosynthesis

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## Oxygen & Carbon Dioxide



- Change with depth because of biological activity
  - $O_2$  maximum at surface
    - Light available for photosynthesis
    - Consumes  $CO_2$
  - $CO_2$  maximum deep in water
    - Decomposition of sinking dead material
    - Consumes  $O_2$



Garrison Fig. 7.8 p. 172

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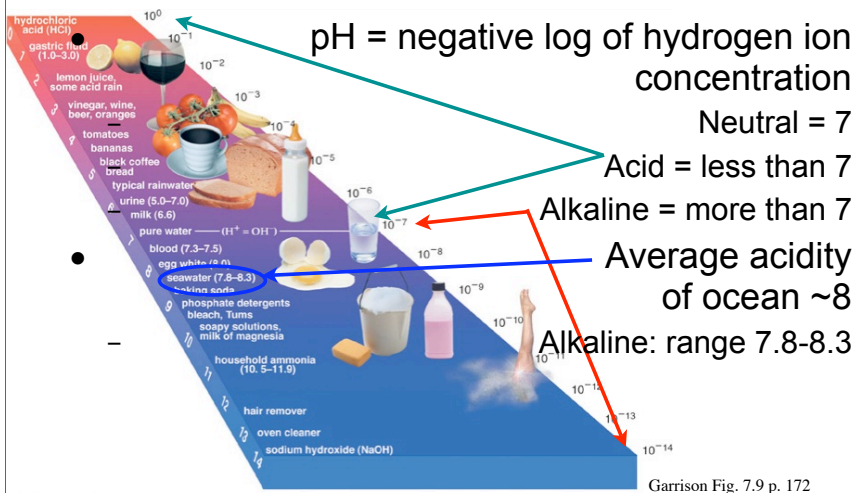
## Carbon Dioxide & Acidity



- $CO_2$  part of the complex dissolved carbonate system
- Key functions
  - Controls acidity & alkalinity of sea water
    - Affects many other chemical & biological reactions
  - Source of skeletal material for numerous organisms
    - Calcium carbonate  $CaCO_3$
    - Calcareous plankton
    - Bottom-living shellfish: clams, crabs, etc.
    - Coral reefs
  - Multiple interchangeable forms of combined carbon

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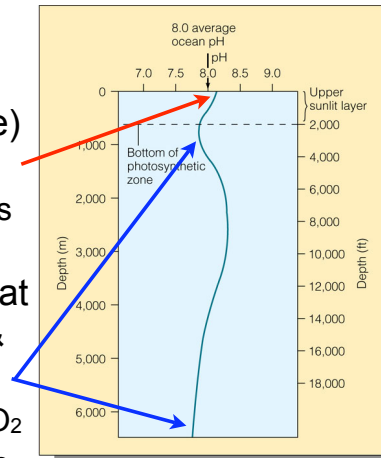
# Carbon Dioxide & Acidity



# Carbon Dioxide & Acidity



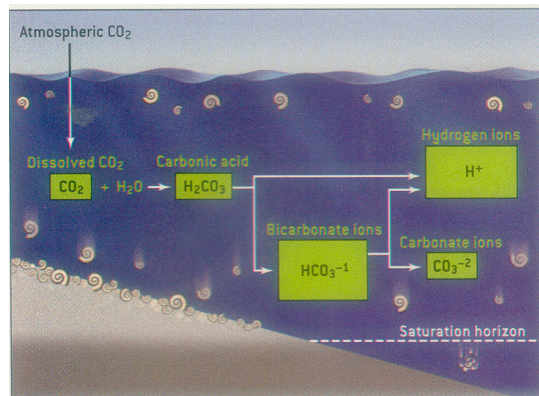
- pH always slightly alkaline (>7)
- pH higher (more alkaline) at surface
  - Photosynthesis consumes CO<sub>2</sub>
- pH lower (less alkaline) at bottom of lighted zone & in deep sea
  - Respiration generates CO<sub>2</sub>
  - CaCO<sub>3</sub> skeletons dissolve



# Carbon Dioxide in Sea Water



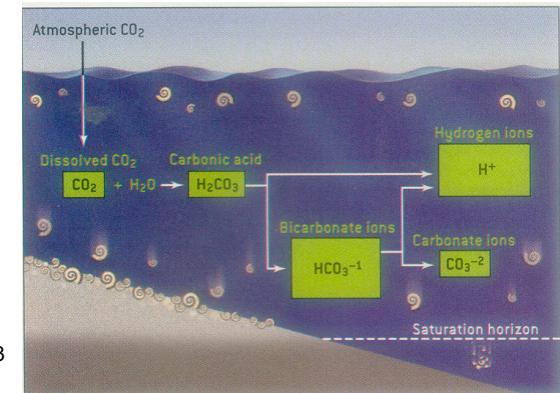
- CO<sub>2</sub> + water H<sub>2</sub>O gives carbonic acid H<sub>2</sub>CO<sub>3</sub>
  - H<sub>2</sub>CO<sub>3</sub> splits
    - HCO<sub>3</sub><sup>-</sup> & H<sup>+</sup>
  - HCO<sub>3</sub><sup>-</sup> splits
    - CO<sub>3</sub><sup>-2</sup> & H<sup>+</sup>
- 5 C species in equilibrium
  - Buffering
  - Proportions shift to keep pH constant



# Carbon Dioxide Buffering



- Proportions of CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>-2</sup>, H<sup>+</sup> shift to maintain constant pH
  - Reactions proceed in either direction
- Add CO<sub>2</sub>
  - CO<sub>3</sub><sup>-2</sup> & H<sup>+</sup> recombine
- Add CO<sub>3</sub><sup>-2</sup>
  - More H<sub>2</sub>CO<sub>3</sub> splits



## Carbon Dioxide Buffering



- Why does buffering of pH matter?
  - Some biochemical reactions sensitive to pH
  - Major example: formation of calcium carbonate  $\text{CaCO}_3$  skeletons
    - Calcareous plankton
    - Bottom-living shellfish: clams, crabs, etc.
    - Coral reef
- Ocean pH currently decreasing
  - Increasing atmospheric  $\text{CO}_2$
  - Mostly decreasing at surface
  - More difficult to form  $\text{CaCO}_3$  skeletons

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## Conservative Constituents



- Some dissolved constituents of sea water are biologically active & others are not
  - Conservative constituents not biologically active
    - Maintain a constant ratio to total salinity
    - Na, Cl, Mg, K,  $\text{SO}_4$
  - Nonconservative constituents are biologically active
    - Ratio to total salinity varies depending on biological use
    - Ca,  $\text{CO}_2$  system members,  $\text{O}_2$ , nutrients
- “Principle of Constant Proportions”
  - Can calculate concentration of one conservative ion from any other
    - Measure salinity from  $\text{Cl}^-$  alone (“Chlorinity”)

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## Nutrients



- Primary production = conversion of non-living to living material
  - Photosynthesis conducted by plants, algae, bacteria
  - Chemosynthesis conducted by bacteria, archaea
- Marine photosynthesizers require same nutrients as land plants
  - Fertilizers: Nitrogen N, phosphorus P, potassium K
    - Plenty of K in sea water (1 of the Big 6)
      - $\sim 0.4$  g/kg
    - N & P are present in very small amounts
      - $\sim 0.00001$  g/kg ( $\sim 100$ - $500$  micrograms/kg, parts/billion)

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## Marine Nutrients



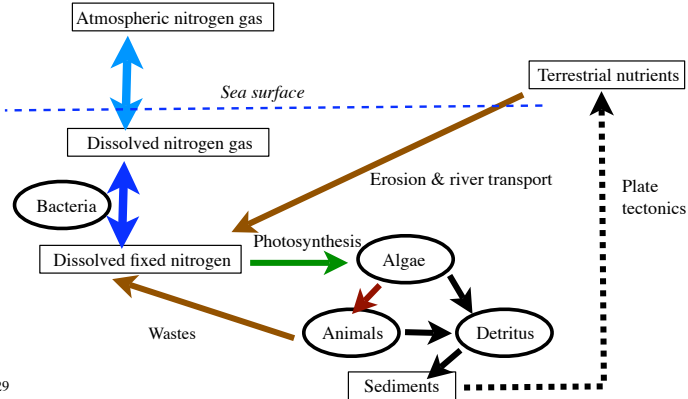
- Marine photosynthesizers require same nutrients as land plants
  - Also silicon for diatom skeletons
    - $\sim 0.003$  g/kg ( $\sim 3000$  micrograms/kg)
  - N, P, Si the “macronutrients”
  - Also “micronutrients”
    - Order of magnitude less abundant ( $\sim 10$  micrograms/kg)
    - Iron, other trace metals, vitamins
- Supply of these nutrients limits primary production under some conditions
  - Often depleted for photosynthesis at the surface

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# Nutrient Cycles



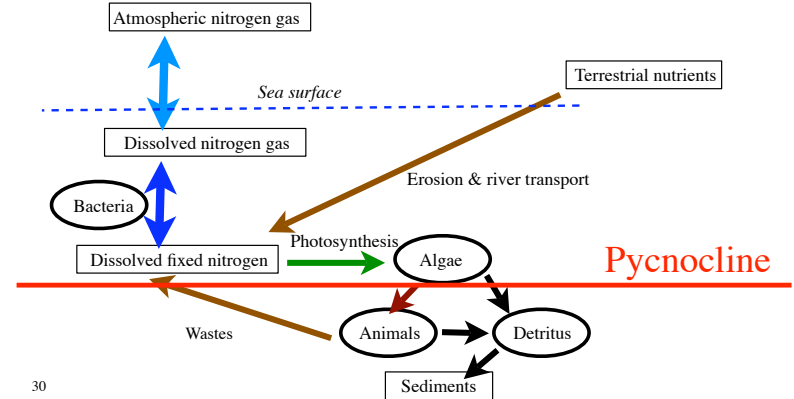
- Garrison has very complex diagrams
  - Nitrogen as an example



# Nutrient Depletion



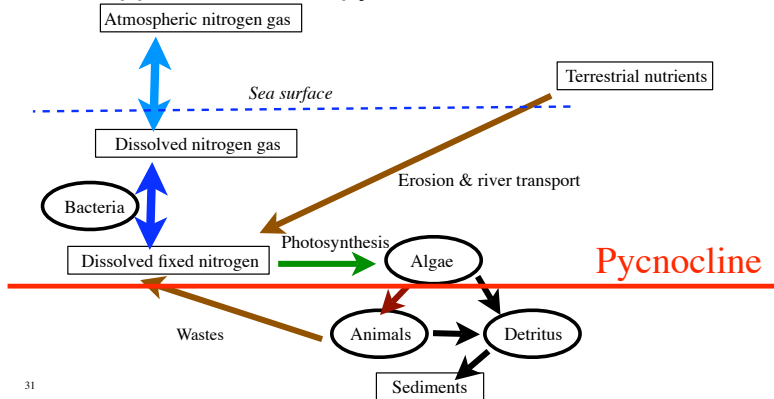
- 1 more critical factor for biological production
  - The oceans are layered



# Nutrient Depletion



- Organic matter sinks to deep water & bottom
  - Trapped below the pycnocline



# Nutrient Depletion



- What processes return nutrients to surface?
  - Not pictured here: Upwelling & vertical mixing

