Introduction to Oceanography

Geological Controls on Ocean Chemistry

Salinity:
- The dissolved salt content of seawater is called *salinity*.
- Average salinity of seawater is 3.5% or 35‰ (%‰ = parts per thousand).

Dissociation of water & pH

\[ H_2O = H^+ + OH^- \]

**H^+** and **OH^-** concentrations will adjust themselves so that:

\[ [H^+] \times [OH^-] = 10^{-14} \]

- In pure water
  \[ [H^+] = [OH^-] = 10^{-7} \]
- In other words, the concentration of **H^+** and **OH^-** will both be 10^{-7}.
- pH is defined as negative logarithm of the hydrogen ion concentration.
  \[ pH = -\log [H^+] \]
- In pure water, pH = -log [10^{-7}] = 7.

If pH is less than 7, there is an excess of **H^+** over **OH^-** and water is said to be *acidic*; if pH is greater than 7, there is an excess of **OH^-** over **H^+** and water is said to be *alkaline*.
- Seawater has a pH of 7.6 to 8.2; Seawater is mildly *alkaline*.

Weathering

Igneous Rock + Water = Sediments + Seawater

\[ 2NaAlSi_3O_8 + 3H_2O = Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2Na^+ + 2OH^- \]

- albite + water = kaolinite + quartz + solution
- Weathering of rock on continents generates both solids (such as clays and quartz) and an *alkaline solution*.
- This is why the sea is salty and why it is alkaline.

The River Water Paradox
- Seawater is approximately a *sodium chloride* solution; river water is approximately a *calcium bicarbonate* solution. Why?

Another Paradox
- At present rates, it would take rivers about 90 million years to deliver all the salt now in the oceans. Yet, the oceans are over 4 billion years old?
  Furthermore, the oceans are not getting saltier with time.
- Why?
- **Seawater composition is controlled by both the rate at which elements are added and the rate at which they are removed.**

The Steady-State Ocean
- If the oceans are not getting saltier, and if their composition is not changing, we may say they are in *steady-state*.
- Therefore, *salts must be removed from seawater in the same proportion and at the same rate at which they are being delivered*.

Residence Time is the average time an atom of an element will spend in seawater.
The Cyclic Salts
- Some elements, most notably anions such as Cl\(^-\) and SO\(_4\)^{2-}, are not released from rock by weathering, but are added to the oceans by volcanic eruptions.
- They nevertheless cycle through the hydrologic system (oceans \(\rightarrow\) atmosphere \(\rightarrow\) rivers \(\rightarrow\) oceans).

Sources and Sinks
- **Sources**: mechanisms by which elements are added to seawater
  - Rivers (and glaciers)
  - Atmosphere
    - gases
    - Dust (delivered by wind)
  - Reaction with oceanic crust
  - Dissolution of sediments
- **Sinks**: mechanisms by which elements are removed from seawater.
  - Biological precipitation
  - Direct precipitation
  - Reaction with oceanic crust
  - Adsorption on particle surfaces
  - Atmosphere (gases and cyclic salts).

Evaporites
- Evaporites form when seawater in a closed basin evaporates until salt precipitates
- Ancient (Paleozoic) evaporites underlay Ithaca.

The Messinian Salinity Crisis
- 5.9 million years ago (late Miocene), the convergence of the African and Eurasian plates closed the Strait of Gibraltar.
- Consequently, much of the Mediterranean Sea dried up.
  - Mediterranean sea level dropped 3000 m.
  - Evaporites, gypsum and halite deposited widely on Mediterranean Sea floor.

Distribution of Elements in the Ocean
- **Conservative**: constant concentration with depth
  - Always present in constant proportions
  - Na\(^+\) (sodium), Ca\(^{2+}\) (calcium), Mg\(^{2+}\) (magnesium), K\(^+\) (potassium), Cl\(^-\) (chlorine), SO\(_4\)^{2-} (sulfate), but not bicarbonate.
  - Concentrated by freezing, evaporation, diluted by rain and river water
- **Biologically Controlled**: depleted in surface water
  - Elements and ions taken up by phytoplankton in surface waters.
  - Released back into water by decomposition at depth.
Surface Reaction Controlled: depleted in deep water
  - Elements with low solubilities that are quickly adsorbed onto particle surfaces and removed from solution.

The Carbonate System

Key Reactions
\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightarrow \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightarrow \text{H}^+ + \text{CO}_3^{2-} \\
\text{Ca}^{2+} + \text{CO}_3^{2-} & \rightarrow \text{CaCO}_3
\end{align*}
\]

Importance of carbonate system reactions
- Buffers the pH of seawater to around 8.
- Buffers atmospheric CO$_2$

Biological Reactions
- Photosynthesis: CO$_2$ + H$_2$O $\rightarrow$ CH$_2$O + O$_2$
  - decreases dissolved CO$_2$ and increased dissolved O$_2$ in surface water.
- Respiration: CH$_2$O + O$_2$ $\rightarrow$ CO$_2$ + H$_2$O
  - increases dissolved CO$_2$ and decreased dissolved O$_2$ in deep water.
  - One consequence is decreasing pH in deep water.

Calcium Carbonate Dissolution
- Calcite (calcium carbonate) solubility increases with depth because of decreasing pH and increasing pressure
- Lysocline: Depth where calcite dissolution increases rapidly
- Carbonate Compensation Depth (CDD): Depth where rate of dissolution just compensates the rate of deposition. Thus the CDD is sometimes called the marine snowline
- CCD controls distribution of carbonate oozes: they occur only where depths are less than 4500 m.

Dissolution of silica shells
- SiO$_2$ tests of diatoms and radiolaria are most soluble in surface water (where dissolved silicate is lowest).
- Diatom and radiolarian oozes found only beneath high productivity areas where dissolved silicate and production rate of tests is highest: equatorial and southern ocean high productivity belts.

Some Study Questions

Name two major cations and two major anions in seawater
If water has an H$^+$ ion concentration of $10^{-9.2}$, what is its pH? Is it alkaline or acid? What is the corresponding OH$^-$ concentration?
What did Lavosier mean when he said that the oceans were the “rinsings of the Earth”?
Explain why the principal ions in seawater are sodium and chloride even though the principal ions in river water are calcium and bicarbonate.

Why are ions like chloride and sulfate called “cyclic salts”?

Sketch a graph of the concentration of a biologically utilized element vs. depth in the ocean.

Give one examples of a biologically utilized element.

Explain why pH decreases with depth in the ocean.

Explain the analogy between the “CCD” in the ocean and the “snowline” in mountains.