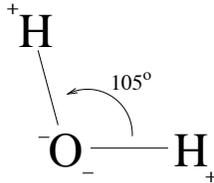


Lecture 6 - Determinants of Seawater Composition

Prof. Scott Doney

- What is seawater?
 - Water
 - Dissolved inorganic salts (major ions)
 - Trace species, organics, colloids, particles, life, . . .
- Water: H_2O
 - A very odd molecule



Sets up electric dipole because O is more electronegative and bond angle is asymmetric

Figure 1.

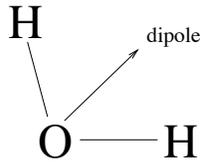


Figure 2.

Hydrogen bond - 4.5 kcal/mol, while covalent bond is ~ 100 kcal/mol.

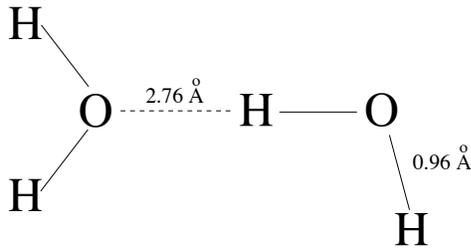
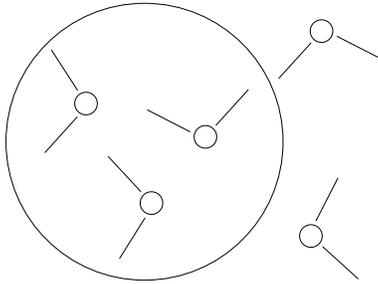


Figure 3.

Hydrogen bonding has a large impact on physical properties of water, ion-pairing solvent solubility; anomalous relative to similar H_2S , surface tension

– Flickering cluster model



Water does not like to be broken up (unless adding ionic species)
 This causes a high heat capacity, latent heat of evaporation, and latent heat of fusion

Figure 4.

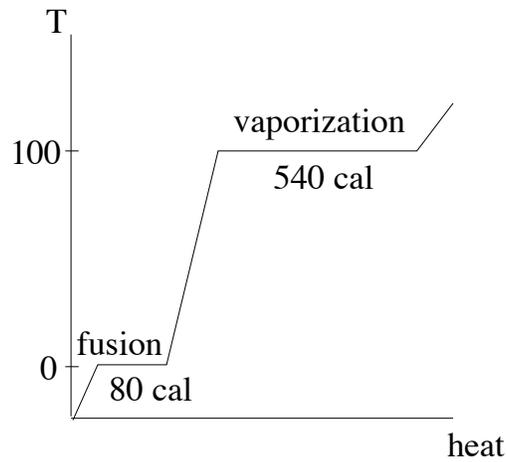


Figure 5.

$$1.2 \frac{\text{m}}{\text{y}} \cdot 1025 \frac{\text{kg}}{\text{m}^3} \cdot 590 \frac{\text{cal}}{\text{g}} \cdot 4.184 \frac{\text{J}}{\text{cal}} \cdot 1000 \frac{\text{g}}{\text{kg}} \cdot \frac{1 \text{ yr}}{3.15 \cdot 10^7 \text{ s}} \sim 96 \frac{\text{W}}{\text{m}^2}$$

compared to solar heating of $\sim 170 \frac{\text{W}}{\text{m}^2}$

- Water as a solvent
 - Very good at dissolving ionic species and polar compounds

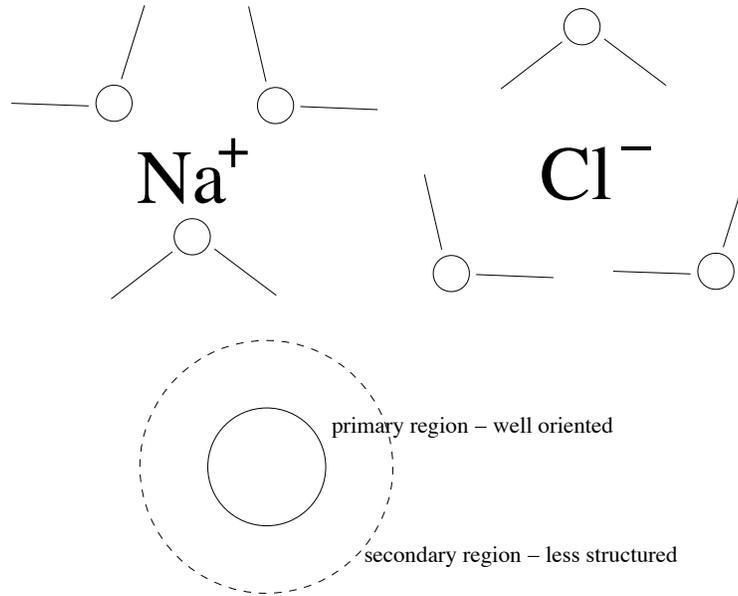


Figure 6.

- Water more dense than ice
 - Profound impacts for climate, life, etc.
- Seawater versus freshwater
 - Comparison

| increase with salinity | decrease with salinity |
|-------------------------|--------------------------------|
| density | freezing point |
| electrical conductivity | temperature of maximum density |
| osmotic pressure | |

- Salinity
 - Total mass of salt in water $\sim 35 \frac{g}{kg}$, that is, 35 parts per thousand (ppt), and there is a relatively constant composition for major ions
- Methods of salinity measurement
 - Simply drying and weighing (± 0.01 ppt)
 - Lose some species with heat (HCl)
 - Oxide formation
 - Reproducibility
 - Tedious

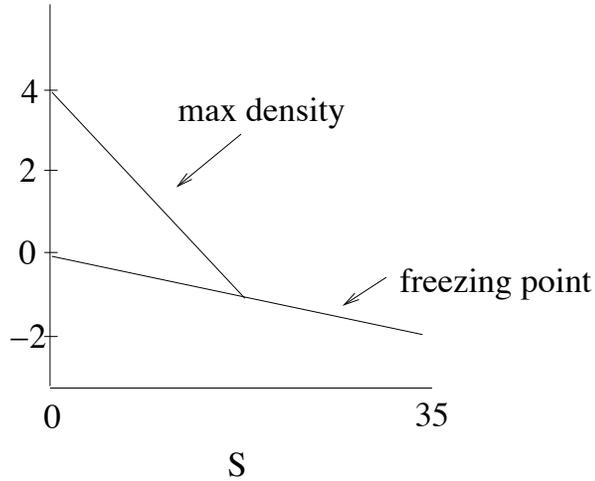


Figure 7.

- Titration of Cl^- (and Br^- ions with $AgNO_3$ (or electrochemical)

$$S = 1.806 \cdot Cl \text{ parts per thousand} \quad \text{Chlorinity in } \frac{\text{g}}{\text{kg}}, \pm 0.002$$

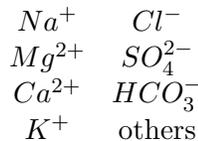
- Conductivity (± 0.001)
 - Compare against KCl standard at fixed pressure, 15°C

$$K_{15} = \frac{\text{sample}}{KCl \text{ solution}}$$

$$s = a_1 - a_2 K_{15}^{1/2} + a_3 K_{15} + a_4 K_{15}^{3/2} - a_5 K_{15}^2 + a_6 K_{15}^{5/2}$$

- in practice use “secondary standards” (Wormely water) Standard Sea Water UNESCO, 1978.
- Practical salinity scale (PSS)
- isotopes - empirically derived from lab work ($s = f(K_{15}), \rho$, etc)

– Major constituents in seawater, charge balance



- “law of constant proportions”
- Except for comments below, major ions act essentially conservatively in ocean - change due to net E-P input

| Ion | Residence time (in units of 10^6 y) |
|-------------|---------------------------------------|
| Na^+ | 70 |
| Mg^{2+} | 14 |
| Ca^{2+} | 0.7 |
| Cl^- | 100 |
| SO_4^{2-} | 10 |

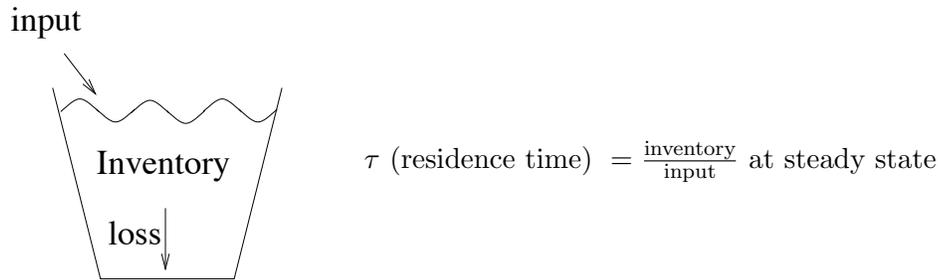
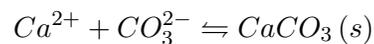


Figure 8.

Compare with mixing time of the ocean $\sim 10^3$ years

– Where does this fall apart?

- Estuaries
 - Average river composition differs
 - Much lower inventories - ~ 0.2 parts per thousand
 - Increased ratios of Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} , HCO_3^- to Cl^- , $s = f(K_{15})$ and ρ do not work as accurately
- Evaporative basins
 - As salinity increases, start to deposit salts
(Brine can also differ from seawater)
 - $CaCO_3$ (Mg)
 - $CaSO_4 \cdot 2H_2O$ (gypsum)
 - $NaCl$ halite
 - $MgSO_4$, KCl , $NaBr$, $MgCl_2$ bitterns (K , Mg salts)
 - Internal biological cycling of $CaCO_3$



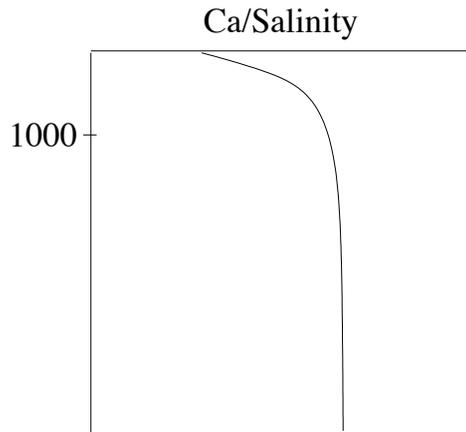


Figure 9.

Depletion of SO_4^{2-} in anoxic basins or sediments; microbes using SO_4^{2-} as an electron acceptor

- Geochemical cycles - what controls the major ion composition ?
 - Two models - “equilibrium” (Sillen), “kinetic”
 - Equilibrium model says that solution chemistry of seawater in thermodynamic equilibrium with atmosphere and minerals on ocean floor; has not held up well but deviations from thermodynamics equilibrium are quite interesting

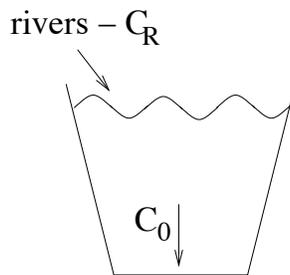


Figure 10.

$$\begin{aligned} \text{input} &= C_R F_R \\ \text{output} &= \frac{1}{k} C_0 V_0 \quad k = \text{residence time} \\ \frac{C_0}{C_R} &= \frac{F_R}{V_0 k} \end{aligned}$$

input > output $\rightarrow C_0$ increases

input < output $\rightarrow C_0$ decreases

Examine ratio of seawater concentration/river water concentration versus residence time.

- Major ion budgets
 - Rivers and terrestrial weathering are primary source for most major ions.
 - Loss mechanisms include:
 - Cl^-
 - Cyclical salts - salt spray transported to land; makes river Cl^- source look larger than what is really coming from weathering.
 - Pore water trapping - burial in interstitial waters

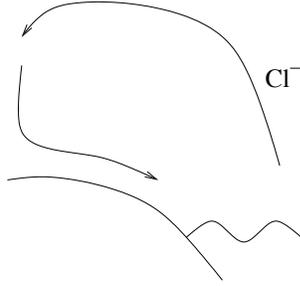


Figure 11.

- Evaporite production
 - Many of the land masses underlain by evaporite deposits
 - Not occurring to great extent right now
 - Lots of shallow seas - episodic in geological history

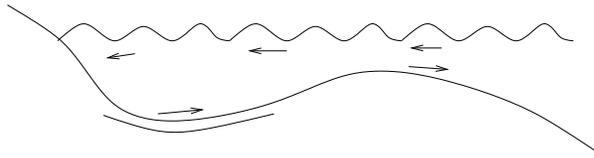
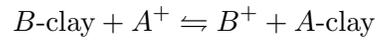


Figure 12.

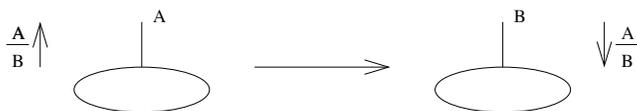
- On long time-scale evaporite formation must balance sources
- Na^+ - exchangeable cations on clays



$$\frac{X_{A\text{-clay}}}{X_{B\text{-clay}}} = K_{AB} \frac{[A^+]}{[B^+]}$$

X: mole fraction at exchange site

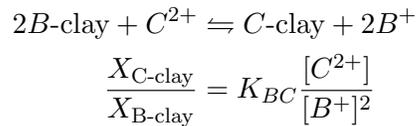
Concentration of Na^+ to other cations is higher as one goes from fresh water to salty water



Freshwater \rightarrow saltwater, act as removal mechanism for Na^+

Figure 13.

also



which shows how the charge balance for divalent ions and concentration affect the equilibrium: $10\times$ concentration $\rightarrow \frac{1}{1} \rightarrow \frac{10}{100}$

As total value of $[B^+]$ increases, it forces more B onto clay and release more C into solution.

- Was once thought that clays were heavily altered in interstitial waters/sediments forming source/sinks for ions (reverse weathering).

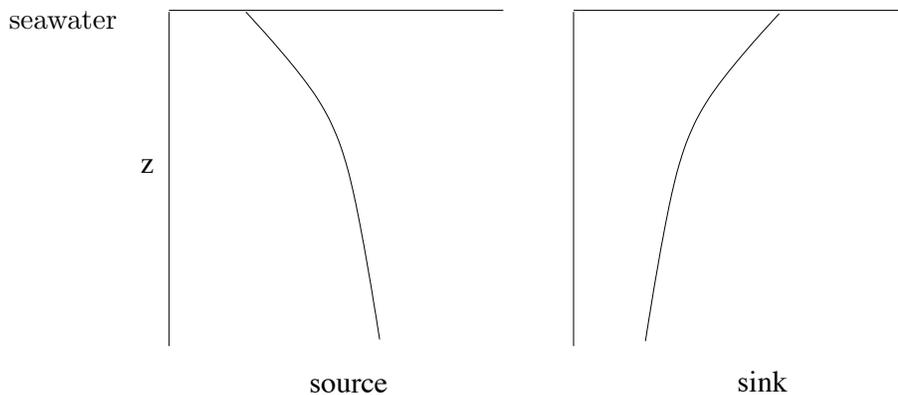
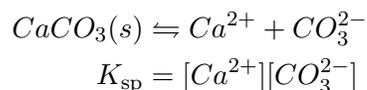


Figure 14.

Does not appear to be a major process for most elements

- Mid-ocean ridges

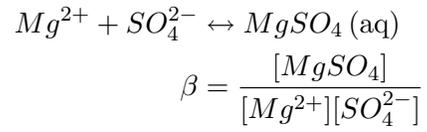
- hot 300-350°C reactions of rock with seawater - variability from vent to vent; some generalizations
- sinks for $MgSO_4$ (though sulfate may have source from low temperature hydrothermal off the ridge axis)
- Biogenic
 Ca^{2+} , $CaCO_3$ sediments
 $SO_4^{2-} \rightarrow H_2S$ some lost as elemental sulfur/pyrite DMS (?), cont. (?) margin sediments
- Complications in closing ocean budgets for major ions
 - River concentrations reflect natural levels plus pollution and human perturbations.
 - Long term imbalance because of episodic evaporites.
- Ion-ion pairing or chemical speciation



- Conditional or apparent solubility product

- Ionic strength; activities rather than concentrations
- Affected by presence of other ions in seawater mix

Similar equations



| | |
|----------------------|-----------------------------|
| Na^+, K^+, Cl^- | mostly/all in free ion form |
| Mg^{2+}, Ca^{2+} | 90% free |
| SO_4^{2-} | ~ 50% free |
| CO_3^{2-}, Ca^{2+} | ~ 10% free |