Chemical composition of seawater; Major constituents

OCN 623 – Chemical Oceanography
1/24/2013

Reading
Libes, Chapters 2 - 4
Can skim section 4.3 (Transport of Heat and Salt via Water Movement)
Outline

• Concentration units
• Salinity measurement
• Salinity variability
• Oceanic concentrations of elements
• Element speciation
• Vertical profiles of elements
• Conservative vs. non-conservative elements
• Conditions under which major elements may not be conservative
Concentration Units
Aqueous solutions, gases, and solids

Molar concentration units

1. **Molarity** = moles per liter of solution = $M$
   - Commonly used terms include:
     - mM = millimolar = millimoles per liter = $10^{-3}$ moles per liter
     - $\mu$M = micromolar = micromoles per liter = $10^{-6}$ moles per liter
     - nM = nanomolar = nannomoles per liter = $10^{-9}$ moles per liter
     - pM = picomolar = picomoles per liter = $10^{-12}$ moles per liter
     - fM = femtomolar = femtomoles per liter = $10^{-15}$ moles per liter

2. **Molality** = moles per kilogram of solvent = $m$
   - No longer in common use except in some computer programs that calculate distribution of chemical species
3. Moles per kilogram of solution
   • The preferred usage in geochemistry, if not in marine chemistry
   • Sometimes defined as "formality"; however, this latter term has been inconsistently defined in the past and is in disuse

4. *Normality* = moles of charge equivalents per liter of solution
   (analogous to molarity, except that it refers to charge)
   • Can also use equivalents per kg of solution (meq/kg)

5. g-atom/liter = mole/liter (a gram-atom is a mole)

6. *Mole fraction* (used for mixtures of gases and for solid solutions)
Mass concentration units

1. wt.% = “weight percent” (actually, mass percent)
   = g per 100 g
   • Used for solids

2. ‰ = parts per thousand (ppt)
   = g/kg for liquids and solids
   = mL/L for gas mixtures

3. Per mil = parts per thousand
   • Term is analogous to "per cent"
   • Is used extensively for isotopic analyses – specifies the deviation from an isotopic standard reference material (SRM)
4. ppm = parts per million
   = \( \mu g/g \) or mg/kg for liquids and solids
   = \( \mu L/L \) for mixtures of gases = ppmv
   • "ppm" is commonly used for solids, whereas "mg/kg" is generally preferred for liquids

5. ppb = parts per billion
   = ng/g or \( \mu g/kg \)

6. mg/L = milligrams per liter
   • commonly used for solutions
Thus, there is a need for a measurement of the overall salt content of seawater
Salinity Measurement – The Past

• Salinity is roughly the number of grams of dissolved matter per kilogram of seawater

• Salinity is difficult to measure gravimetrically because many of the salts are hydrophilic, and some decompose on heating to dryness

• From about 1900 to the 1960's, salinity was calculated from chlorinity $Cl$, as determined by titration with silver ion

\[ \text{Salinity} = 1.80655 \times Cl \]

• As of 1978, it became standard to calculate “practical salinity” $S$ from measured conductivity (PSS-78)

• Note: practical salinity is unit-less, and is not a SI quantity!

Standard Mean Ocean Water (SMOW): $S \approx 35$, $Cl \approx 19\%$
A salinity measure (g/kg) that:

• Is more accurate than conductivity-based Practical Salinity

• Handles the spatial variations in the composition of seawater which upset the relationship between
  • Practical Salinity $S_P$ (which is a function of conductivity, temperature and pressure), and
  • Absolute Salinity $S_A$ (defined as the mass of dissolved material (“salt”) per mass of seawater solution….a true “mass fraction”)
• Absolute Salinity:
  • Ends the debate in the oceanographic literature about which “salinity” is proper
  • Makes research papers more readable to the outside scientific community
  • Is consistent with SI

• A Reference Composition, consisting of the major components of Atlantic surface seawater, was determined

• A new Reference-Composition Salinity $S_R$ is defined to provide the best available estimate of Absolute Salinity

• The value of $S_R$ can be related to Practical Salinity $S_P$ by
  
  \[ S_R = \left( \frac{35.16504}{35} \right) \text{ g kg}^{-1} \times S_P \]

• A correction factor ($\delta S_A$) accounts for the variation of seawater composition from the standard composition – using either measured parameters (e.g., pH/DIC/alkalinity/fCO$_2$, silicate and nitrate) or simply the spatial location (longitude, latitude and pressure)
Spatial distribution of Absolute Salinity Anomaly ($\delta S_A$)
Salinity Variability

- Variations in salinity depend almost entirely on:
  - Balance between evaporation and precipitation
  - Extent of mixing between surface and deeper waters

- The salinity of surface sea water:
  - **High** (up to 37.5 g/kg) in mid-latitudes due to net evaporation
  - **Low** at high latitudes (to ~33 g/kg above 40°N and S) and at the equator (~35 g/kg) due to net precipitation
Radiometer-derived sea-surface salinity
- Aquarius spacecraft

• Set of three radiometers -- sensitive to salinity (1.413 GHz; L-band)
• Scatterometer -- corrects for the surface roughness (1.2 GHz; L-band)
There typically is a halocline from the base of the mixed surface layer to about 1000 m depth

- At high latitudes: salinity increases with depth

- At mid and low latitudes: salinity decreases with depth

- Below 1000 m, salinities are generally between 34 and 35 at all latitudes
The presence of dissolved salts alters the properties of water:

- The **freezing point** is lowered from 0° to −1.8°C

- The **temperature of maximum density** is lowered from +4° to −1.8°C. (Freshwater is less dense at 0°C than at +4°C!)

- This drives the global **thermohaline circulation** because it causes the coldest (and saltiest) water to sink
  - Temperature and salinity determine the density of seawater
The “density anomaly” of seawater in “mass per volume in excess of 1 kg/m$^3$, multiplied by 1000”, is designated by the symbol “$\sigma$” (sigma).

In this notation, a specific gravity of 1.025 kg/m$^3$ is expressed as $\sigma = 25$. 

Sarmiento & Gruber, 2006
Residence time ($y$): $\tau \equiv M/Q$

$M =$ mass of element in ocean (mol)

$Q =$ input from rivers (mol $y^{-1}$) = $c \cdot f$

$c =$ conc of element in average river water (mol kg$^{-1}$)

$f =$ annual flux of river water (kg $y^{-1}$)

$\log \tau \geq 6.5$

($\tau \geq 3.2 \times 10^6$ y)

Conservative elements

### TABLE 9.6 MAJOR COMPOSITION OF SEAWATER

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Seawater at $S = 35%$</th>
<th>(g kg$^{-1}$) Chlorinity$^a$</th>
<th>(mol kg$^{-1}$) Chlorinity</th>
<th>Residence Time in Oceans, $\log \tau$ (years)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>10.77</td>
<td>0.556</td>
<td>0.0242</td>
<td>7.7</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1.29</td>
<td>0.068</td>
<td>0.0027</td>
<td>7.0</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.4121</td>
<td>0.02125</td>
<td>0.000530</td>
<td>5.9</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.399</td>
<td>0.0206</td>
<td>0.000527</td>
<td>6.7</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>0.0079</td>
<td>0.00041</td>
<td>0.0000047</td>
<td>6.6</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>19.354</td>
<td>0.9989</td>
<td>0.0282</td>
<td>7.9</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>2.712</td>
<td>0.1400</td>
<td>0.0146</td>
<td>6.9</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>0.1424</td>
<td>0.00735</td>
<td>0.00012</td>
<td>4.9</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.0673</td>
<td>0.00348</td>
<td>0.000044</td>
<td>8.0</td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.0013</td>
<td>0.000067</td>
<td>0.0000035</td>
<td>5.7</td>
</tr>
<tr>
<td>B</td>
<td>0.0045</td>
<td>0.000232</td>
<td>0.0000213</td>
<td>7.0</td>
</tr>
<tr>
<td>$\sum$</td>
<td>35</td>
<td>$\sum = 1.82$</td>
<td>$\sum = 0.058$</td>
<td></td>
</tr>
</tbody>
</table>

$\sum = 35$

$\sum = 1.82$

$\sum = 0.058$

### TABLE 9.7 MINOR ELEMENTS IN SEAWATER

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration ($-\log M$)</th>
<th>Residence time, $[\log \tau$ (years)]</th>
<th>Element</th>
<th>Concentration ($-\log M$)</th>
<th>Residence time, $[\log \tau$ (years)]</th>
<th>Element</th>
<th>Concentration ($-\log M$)</th>
<th>Residence time, $[\log \tau$ (years)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>8.8</td>
<td>—</td>
<td>V</td>
<td>7.3</td>
<td>5</td>
<td>Rb</td>
<td>5.85</td>
<td>—</td>
</tr>
<tr>
<td>Li</td>
<td>4.6</td>
<td>6.3</td>
<td>Cr</td>
<td>8.2</td>
<td>—</td>
<td>Mo</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>3.39</td>
<td>7.0</td>
<td>Mn</td>
<td>8.4</td>
<td>4</td>
<td>Ag</td>
<td>9.4</td>
<td>5</td>
</tr>
<tr>
<td>N</td>
<td>1.97</td>
<td>6.3</td>
<td>Fe</td>
<td>7.5</td>
<td>2</td>
<td>Cd</td>
<td>9</td>
<td>4.7</td>
</tr>
<tr>
<td>F</td>
<td>4.17</td>
<td>5.7</td>
<td>Co</td>
<td>9.1</td>
<td>4.5</td>
<td>Sn</td>
<td>10</td>
<td>—</td>
</tr>
<tr>
<td>Ne</td>
<td>8.2</td>
<td>—</td>
<td>Ni</td>
<td>7.6</td>
<td>4</td>
<td>Sb</td>
<td>8.7</td>
<td>4</td>
</tr>
<tr>
<td>Al</td>
<td>7.1</td>
<td>2</td>
<td>Cu</td>
<td>8.1</td>
<td>4</td>
<td>T</td>
<td>6.3</td>
<td>6</td>
</tr>
<tr>
<td>Si</td>
<td>4.1</td>
<td>3.8</td>
<td>Zn</td>
<td>4.9</td>
<td>4</td>
<td>Xe</td>
<td>9.4</td>
<td>—</td>
</tr>
<tr>
<td>P</td>
<td>5.7</td>
<td>4</td>
<td>As</td>
<td>7.3</td>
<td>5</td>
<td>Cs</td>
<td>8.5</td>
<td>5.8</td>
</tr>
<tr>
<td>Ar</td>
<td>6.96</td>
<td>—</td>
<td>Kr</td>
<td>8.6</td>
<td>—</td>
<td>Ba</td>
<td>6.8</td>
<td>4.5</td>
</tr>
<tr>
<td>W</td>
<td>—</td>
<td>—</td>
<td>Au</td>
<td>10.7</td>
<td>5</td>
<td>Hg</td>
<td>9.8</td>
<td>5</td>
</tr>
<tr>
<td>Pb</td>
<td>9.7</td>
<td>—</td>
<td>Th</td>
<td>10.4</td>
<td>—</td>
<td>U</td>
<td>7.9</td>
<td>3.3</td>
</tr>
</tbody>
</table>


Stumm & Morgan (1981)
Mean Oceanic Concentrations of Elements

Figure 1.1.1: A graphical illustration of the dissolved concentrations of elements and some compounds expressed as log to the base 10 [Johnson and Jannasch, 1994]. The higher concentration elements are given on the right-hand side and the lower concentration elements are given on the left-hand side. The bars represent the range of concentrations in the ocean. The full range of concentrations covers almost 12 orders of magnitude.
Figure 1.1 Some of the more important elements in natural waters, their form of occurrence, and their concentration. Elements whose distribution is significantly affected by biota are shaded. P, N, and Si (fully shaded) are often depleted in surface waters. (1) Species in parentheses are major ion pairs in seawater. (2) Concentrations \( M = \text{mol liter}^{-1} \) valid for seawater from P. G. Brewer, in Chemical Oceanography, Vol. 1, J. P. Riley and G. Skirrow, Eds., Academic, New York, 1975. (3) From A. D. Livingstone, Chemical Components of Rivers and Lakes, U.S. Geological Survey Paper No. 440G, 1963.

Stumm & Morgan (1981)
Vertical Profiles of Elements in the Pacific Ocean

Sarmiento & Gruber 2006

Figure 1.2.1: Vertical profiles of elements from the Pacific Ocean arranged as in the periodic table of elements (Nizatski, 1997). The biounlimited elements have nearly uniform concentrations. Most other elements have lower concentrations at the surface than at depth due to biological removal. Biolimiting elements are nearly depleted to 0 mmol m\(^{-3}\) at the surface, whereas biointermediate elements show only partial depletion. Oxygen and the noble gases on the right side of the figure are influenced in part by their higher solubility in colder
waters deep in the ocean (see chapter 3) and, in the case of oxygen, by biological production as part of photosynthesis and consumption by respiration. A few elements such as Pb have higher concentrations at the surface due to delivery by dust transport, and lower concentrations at depth due to rapid scavenging from the water column to the sediments.
Distribution patterns are classified into the following four categories: **conservative, nutrient-type, scavenged, and redox-controlled**.
Conservative vs. Nonconservative Elements

• **Conservative**
  
  • Non-reactive
  
  • Thus, remain in ocean for long periods (long residence time)
  
  • Examples: Na, K, S, Cl, Br, Sr, B ("conservative major elements")

• **Nonconservative**
  
  • Biologically and/or chemically reactive
  
  • Examples: C, P, Fe
Conditions Under Which Major Elements May Not be Conservative

• Estuaries and Land-locked Seas
  • Examples: Black Sea, Baltic Sea, Chesapeake Bay
  • These element rations are much larger in river water than in seawater:

\[
\begin{align*}
\text{SO}_4^{2-} & \quad \text{HCO}_3^- & \quad K^+ & \quad \text{Mg}^{2+} & \quad \text{Ca}^{2+} \\
\text{Cl}^- & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Na}^+ & \quad \text{Mg}^{2+} \\
\end{align*}
\]

• Runoff can be a major effect for these ions

• Anoxic Basins
  • Sulfate reduction:

\[
\text{SO}_4^{2-} + \text{CH}_2\text{O} + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HS}^- + \text{HCO}_3^- + 2\text{H}_2\text{O}
\]
• Freezing
  • Fractionates major ions
  • Example: Sea ice contains proportionally more \( \text{SO}_4^{2-} \) than \( \text{Cl}^- \)

<table>
<thead>
<tr>
<th>Cl (‰)</th>
<th>0°C</th>
<th>5°C</th>
<th>10°C</th>
<th>15°C</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.999868</td>
<td>0.999992</td>
<td>0.999728</td>
<td>0.999129</td>
<td>0.998234</td>
<td>0.997075</td>
<td>0.995678</td>
<td>0.994063</td>
<td>0.992247</td>
</tr>
<tr>
<td>3.42</td>
<td>1.004944</td>
<td>1.004959</td>
<td>1.004599</td>
<td>1.003921</td>
<td>1.002962</td>
<td>1.001744</td>
<td>1.000295</td>
<td>0.998643</td>
<td>0.996783</td>
</tr>
<tr>
<td>6.05</td>
<td>1.008665</td>
<td>1.008705</td>
<td>1.008292</td>
<td>1.007566</td>
<td>1.006575</td>
<td>1.005335</td>
<td>1.003868</td>
<td>1.002190</td>
<td>1.000307</td>
</tr>
<tr>
<td>8.17</td>
<td>1.011851</td>
<td>1.011731</td>
<td>1.011265</td>
<td>1.010502</td>
<td>1.009472</td>
<td>1.008201</td>
<td>1.006707</td>
<td>1.005013</td>
<td>1.003113</td>
</tr>
<tr>
<td>11.69</td>
<td>1.016982</td>
<td>1.016758</td>
<td>1.016208</td>
<td>1.015368</td>
<td>1.014275</td>
<td>1.012949</td>
<td>1.011407</td>
<td>1.009669</td>
<td>1.007745</td>
</tr>
<tr>
<td>13.67</td>
<td>1.019835</td>
<td>1.019564</td>
<td>1.018970</td>
<td>1.018102</td>
<td>1.016986</td>
<td>1.015641</td>
<td>1.014087</td>
<td>1.012346</td>
<td>1.010406</td>
</tr>
<tr>
<td>16.33</td>
<td>1.023703</td>
<td>1.023352</td>
<td>1.022695</td>
<td>1.021772</td>
<td>1.020611</td>
<td>1.019229</td>
<td>1.017642</td>
<td>1.015866</td>
<td>1.013920</td>
</tr>
<tr>
<td>19.05</td>
<td>1.027648</td>
<td>1.027227</td>
<td>1.026511</td>
<td>1.025538</td>
<td>1.024335</td>
<td>1.022921</td>
<td>1.021311</td>
<td>1.019528</td>
<td>1.017564</td>
</tr>
<tr>
<td>21.53</td>
<td>1.031240</td>
<td>1.030774</td>
<td>1.029989</td>
<td>1.028941</td>
<td>1.027731</td>
<td>1.026307</td>
<td>1.024658</td>
<td>1.022890</td>
<td>1.020925</td>
</tr>
</tbody>
</table>

*These densities are relative to those tabulated by Kell (1967) for pure water assuming the density of pure water is 1.000000 g ml\(^{-1}\) at 3.98°C.*

• Note: The “freezing point” of seawater is the initial freezing point (i.e., the temperature at which an infinitely small amount of ice is in equilibrium with the solution)

• As soon as any ice has formed, the concentration of dissolved material in the remaining brine increases

• Hence, the formation of additional ice can only take place at lower temperature
• **Submarine Volcanism**
  
  • Hydrothermal fluids have major- and minor-element ratios different from those of seawater (e.g., higher Si; lower $\text{SO}_4^{2-}$ and $\text{Mg}^{2+}$)

• **Evaporation of Seawater in Isolated Basins**

  ![Table 4.7](image)

<table>
<thead>
<tr>
<th>Stage No.</th>
<th>Density of brine</th>
<th>Weight % of liquid remaining</th>
<th>Principal solid phases deposited</th>
<th>% of total dissolved solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.026</td>
<td>100</td>
<td>Calcium carbonate + dolomite</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>1.140</td>
<td>50</td>
<td>Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)</td>
<td>3</td>
</tr>
<tr>
<td>III</td>
<td>1.214</td>
<td>10</td>
<td>Halite ($\text{NaCl}$)</td>
<td>70</td>
</tr>
<tr>
<td>IV</td>
<td>1.236</td>
<td>3.9</td>
<td>Sodium-magnesium-potassium sulphates and chlorides</td>
<td>26</td>
</tr>
</tbody>
</table>

• In nature: organic matter oxidation consumes oxygen due to stagnant conditions, then sulfate reduction occurs

• Thus, sulfate minerals are rarely found in natural marine evaporite deposits