Chemical composition of seawater: Salinity and the major constituents

OCN 623 – Chemical Oceanography
Salt dissolved in ocean water alters the properties of water

Freezing point of seawater is ~ -1.8°C

Density continually increases to freezing point

(see Libes, Fig 2.10)
Drives the circulation mode of the oceans - completely different from freshwater in lakes.
Outline

• SI units
• Residence time
• Elements in seawater
• Measuring salinity
  • Marcet’s Principle
• Salinity variability
Concentration units for aqueous solutions, gases, and solids

Molar units

1. \textit{Molarity} = moles per litre of solution = \( M \)
   - Commonly used terms include:
     - \( \text{mM} = \text{millimolar} = \text{millimoles per litre} = 10^{-3} \text{ moles per litre} \)
     - \( \mu \text{M} = \text{micromolar} = \text{micromoles per litre} = 10^{-6} \text{ moles per litre} \)
     - \( \text{nM} = \text{nanomolar} = \text{nannomoles per litre} = 10^{-9} \text{ moles per litre} \)
     - \( \text{pM} = \text{picomolar} = \text{picomoles per litre} = 10^{-12} \text{ moles per litre} \)
     - \( \text{fM} = \text{femtomolar} = \text{femtmoles per litre} = 10^{-15} \text{ moles per litre} \)
     - \( \text{aM} = \text{attomolar} = \text{attomoles per litre} = 10^{-18} \text{ moles per litre} \)

2. \textit{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, about 1.024 smaller than M
   - 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 litre of solution**
   (analogous to molarity, except that it refers to charge)
   - Comes from acidity, i.e. moles H\(^+\) per litre
   - Can also use equivalents per kg of solution (meq/kg)

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

6. **Mole fraction** (used for mixtures of gases and for solid solutions) = \(n_1/(n_1+n_2+n_3\ldots)\)
Mass concentration units

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

2. **‰** = parts per thousand
   
   = 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**
   
   \[ \mu g/g \text{ or } mg/kg \text{ for liquids and solids} \]
   
   \[ \mu L/L \text{ for mixtures of gases} = \text{ppmv} \]
   
   - "ppm" is commonly used for solids, whereas "mg/kg" is generally preferred for liquids

5. **ppb = parts per billion**
   
   \[ ng/g \text{ or } \mu g/kg \]

6. **mg/L = milligrams per litre**
   
   - commonly used for solutions
Residence Time

• Defined by the amount of the ion in seawater \((C \cdot V)\) and the sum of the inputs \((\sum I)\) in steady state:

\[
\tau_i = \frac{C_i \cdot V}{\sum I_i}
\]

• Units: \(I = [\text{mol/yr}], C = [\text{mol/L}], V = [\text{L}],\) so \(\tau = [\text{yr}]\)
Residence Time

• Example: Mg\(^{2+}\)
  • Inputs:

• Ocean inventory:
Conservative vs. Nonconservative Elements

- **Conservative**
  - Non-reactive
  - Thus, remain in ocean for long periods (long residence time)
- **Major ions**
  - Concentration > 10 µm
  - Examples: Na⁺, K⁺, Mg²⁺, Sr²⁺, Cl⁻, Br⁻ ("conservative major elements")
Conservative vs. Nonconservative Elements

- **Nonconservative**
  - Biologically reactive
    - Conc. usually depleted at surface, higher at depths
    - Examples: P, NO$_3^-$
  - Chemically reactive (adsorbed)
    - Conc. usually highest at surface, lower at depths
    - Examples: Mn, Al
  - Gases
    - May be chemically inert or bioactive
    - Examples: O$_2$, CO$_2$, CFCs, noble gases
Chemical composition of seawater

Major ions in seawater of salinity 35

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>% total (wt)</th>
<th>mmol/kg seawater</th>
<th>g/kg seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>Chloride</td>
<td>55.29%</td>
<td>545.87</td>
<td>19.353</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium</td>
<td>30.81%</td>
<td>469.07</td>
<td>10.784</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Sulphate</td>
<td>7.75%</td>
<td>28.24</td>
<td>2.712</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Magnesium</td>
<td>3.67%</td>
<td>52.82</td>
<td>1.284</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Calcium</td>
<td>1.18%</td>
<td>10.28</td>
<td>0.412</td>
</tr>
<tr>
<td>K⁺</td>
<td>Potassium</td>
<td>1.14%</td>
<td>10.21</td>
<td>0.399</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>99.84%</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(from Libes, Table 3.7)
CONSTANCY OF MAJOR ELEMENT RATIOS

1776 - Lavoisier - Analyzed English Channel deep seawater
    - First seawater analysis

1819 - Marcet - "Specimens of seawater contain the same ingredients all over the world.....these (ingredients) bear nearly the same proportion to each other.....(the samples) differ only as to the total amount of their saline content."

1884 - Dittmar - Analysed 77 samples from the HMS Challenger (1872-76)
    - Confirmed Marcet's finding, except Ca/Cl was lower in surface seawater as compared to deep seawater (i.e., nonconservative)
Salinity

- Salinity is the *amount* of dissolved solids in seawater
- Used for determining the *density* of seawater
- Affects the *freezing point* of seawater
- Affects the temperature of *maximum* density of seawater
- Changes in salinity drive *thermohaline circulation*
- Temperature and salinity characteristics allow determination of origin of water masses
- Accuracy of determination needed is a function of the problem being addressed, e.g. estuaries vs. deep ocean
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.
- Early oceanographers: Gravimetric Salinity.
- 1902 – 1960s: Chlorinity, measured by Knudsen titration (AgNO₃).
  \[
  \text{Salinity} = 1.80655 \text{ Cl}
  \]
  - NB: Chlorinity = [Cl⁻] + [Br⁻] + [I⁻]
- 1978: Practical Salinity Scale adopted internationally; "practical salinity" based on conductivity (PSS-78).
  - NB: practical salinity is unit-less, and is not a SI quantity!

| Standard Mean Ocean Water (SMOW): | S ≈ 35, Cl ≈ 19‰ |
**Salinity Measurement – The Future**

- Need for a salinity measure that is more accurate than conductivity-based Practical Salinity (g-salt/kg seawater)
- Spatial variations in the composition of seawater upsets the relationship between
  - Practical Salinity \( S \) (which is a function of conductivity, temperature and pressure) and
  - Absolute Salinity \( S_A \) (defined as the mass of dissolved material per mass of seawater solution)

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**TEOS-10**

*Thermodynamic Equation Of Seawater - 2010*

The Intergovernmental Oceanographic Commission (IOC), with the endorsement of the Scientific Committee on Oceanic Research (SCOR) and the International Association of the Physical Sciences of the Oceans (IAPSO) has adopted the Thermodynamic Equation Of Seawater - 2010 (TEOS-10) as the official description of seawater and ice properties in marine science. All oceanographers are now urged to use the new TEOS-10 algorithms and variables to report their work. We anticipate that within two years (2012) oceanographers will have completely migrated from EOS-80 to TEOS-10.

The TEOS-10 properties of seawater are all derived from a Gibbs function (by mathematical processes such as differentiation) and so are totally consistent with each other and are reversible (in contrast to the now obsolete EOS-80 approach where separate polynomials were provided for each thermodynamic variable and they were not mutually consistent).

Two notable differences of TEOS-10 compared with EOS-80 are:
1. the use of Absolute Salinity \( S_A \) to describe the salinity of seawater; Absolute Salinity takes into account the spatially varying composition of seawater, and
2. the use of Conservative Temperature \( \Theta \) to replace potential temperature \( \Theta \). Both of these temperatures are calculated quantities that result from an artificial thought experiment (namely, adiabatic and isoline change in pressure to the sea surface). Conservative Temperature has the advantage that it better represents the “heat content” of seawater by two orders of magnitude, and there seems no reason to continue the use of potential temperature in oceanography.

To enable oceanographers to implement TEOS-10, two software packages are available, (i) the Gibbs SeaWater (GSW) Oceanographic Toolbox (MATLAB) and, (ii) the Sea-Ice-Air (SIA) (FORTRAN and Visual Basic). Both are freely available from www.TEOS-10.org.

The GSW Oceanographic Toolbox will be of particular interest to the oceanographic community because the input variables are expressed in standard oceanographic (as opposed to SI) units, and because the algorithms are computationally efficient. This toolbox contains the functions to compute Absolute Salinity \( S_A \) and Conservative Temperature \( \Theta \) as well as a comprehensive collection of ocean properties based on \( S_A \) and \( \Theta \), e.g. density, dynamic height, various geostrophic streamfunctions, conversion between depth and pressure, buoyancy (Brunt-Vaisala) frequency, enthalpy, entropy and sound speed.

Quick introductions to TEOS-10 are available on the TEOS-10 web site (www.TEOS-10.org)
- **TEOS-10 Primer**
  - What every oceanographer needs to know about TEOS-10.
- **Getting started with the GSW Oceanographic Toolbox**
  - This lists the functions in the GSW toolbox and also illustrates the differences associated with using Absolute Salinity and Conservative Temperature compared with Practical Salinity and potential temperature.

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[www.TEOS-10.org](http://www.TEOS-10.org) The home of the Thermodynamic Equation Of Seawater - 2010
• Absolute Salinity will:
  • end the ongoing debate in the oceanographic literature about the use of “psu” or “pss”
  • make research papers more readable to the outside scientific community
  • be consistent with SI

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

• The value of $S_R$ can be related to Practical Salinity $S$ by
  $$S_R = \left( \frac{35.165}{35} \right) \text{g kg}^{-1} \times S$$

• Salinity can still be measured by conductivity, then corrected to a reference composition and for variation in composition ($S_A = S_R + \delta S_A$)

• An algorithm will account for the variation of seawater composition from the standard composition – using either measured parameters (e.g., total alkalinity, silicate and nitrate, Pawlowicz et al., 2010) or simply the spatial location (longitude, latitude and pressure, McDougall et al., 2009)
Why are major ion distributions so consistent?

Source of major ions to ocean is continental weathering

Reservoirs and fluxes

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean</td>
<td>$1.4 \times 10^{21}$ L</td>
</tr>
<tr>
<td>Evap from ocean</td>
<td>$43 \times 10^{16}$ L yr$^{-1}$</td>
</tr>
<tr>
<td>Precip over ocean</td>
<td>$38 \times 10^{16}$ L yr$^{-1}$</td>
</tr>
<tr>
<td>Precip over land</td>
<td>$11 \times 10^{16}$ L yr$^{-1}$</td>
</tr>
<tr>
<td>River flow</td>
<td>$3.7 \times 10^{16}$ L yr$^{-1}$</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>$0.017 \times 10^{16}$ L yr$^{-1}$</td>
</tr>
</tbody>
</table>

Residence time:

$$\tau_i = \frac{C_i \cdot V_o}{\sum I_i}$$
Continental materials are unlike seawater or river water

Most common ions in seawater and river water and the elemental composition of the Earth’s crust* listed in order of abundance

<table>
<thead>
<tr>
<th>Seawater (as ions)</th>
<th>Earth’s crust (as elements)</th>
<th>River water (as ions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride (Cl(^{-}))</td>
<td>Silicon (Si)</td>
<td>Bicarbonate (HCO(_3^{-}))</td>
</tr>
<tr>
<td>Sodium (Na(^{+}))</td>
<td>Aluminium (Al)</td>
<td>Calcium (Ca(^{2+}))</td>
</tr>
<tr>
<td>Sulphate (SO(_4^{2-}))</td>
<td>Iron (Fe)</td>
<td>Silicate (SiO(_2))</td>
</tr>
<tr>
<td>Magnesium (Mg(^{2+}))</td>
<td>Calcium (Ca)</td>
<td>Sulphate (SO(_4^{2-}))</td>
</tr>
<tr>
<td>Calcium (Ca(^{2+}))</td>
<td>Sodium (Na)</td>
<td>Magnesium (Mg(^{2+}))</td>
</tr>
<tr>
<td>Potassium (K(^{+}))</td>
<td>Potassium (K)</td>
<td>Potassium (K(^{+}))</td>
</tr>
<tr>
<td>Bicarbonate (HCO(_3^{-}))</td>
<td>Magnesium (Mg)</td>
<td>Sodium (Na(^{+}))</td>
</tr>
<tr>
<td>Bromide (Br(^{-}))</td>
<td>Titanium (Ti)</td>
<td>Iron (Fe(^{3+}))</td>
</tr>
<tr>
<td>Borate (H(_2)BO(_3^{-}))</td>
<td>Manganese (Mn)</td>
<td></td>
</tr>
<tr>
<td>Strontium (Sr(^{2+}))</td>
<td>Phosphorous (P)</td>
<td></td>
</tr>
</tbody>
</table>

* Excluding oxygen
Marcet’s Principle:
Marcet’s Principle: exceptions

- Coastal regions
- Anoxic basins
- Hydrothermal vents
- Sea ice
- Calcareous shells
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) in mid-latitudes due to net evaporation
  - Low at high latitudes (to ~33 above 40°N and S) and at the equator (~35) due to net precipitation
Global Evaporation - Precipitation
Annual salinity [PSS] at the surface.

Min Value= 5.0
Max Value= 40.4
Contour Interval= 0.2

World Ocean Atlas 2005
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
Most ocean water falls in a narrow salinity range

Temperature and salinity of 99% (75%) of the ocean water are represented by points within the blue (red) area. (After Gross, 1993).
Temperature and salinity are fingerprint characteristics of seawater origin.

Data from Chris Measures
also see Libes, Fig 4.19

Libes, Fig 4.14
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
Summary

• Residence time (inventory/inputs)
• Major ions in seawater: found in constant proportions (Marcet’s Principle)
• Techniques of measuring salinity
  • Absolute salinity (SI units)
• Evaporation/precipitation and salinity variability