3. REVIEW OF FUNDAMENTAL GEOCHEMISTRY

3.1 Reading List

- (Freeze and Cherry 1979) Chapter 3 Groundwater Chemistry
  - 2.0 Chemical Principles and Properties
  - 2.1 Groundwater and Its Chemical Constituents
  - 2.8 Environmental Isotopes

- Papers to Review/Read on use of Isotopes:
  - (Fontes 1980), (Desaulniers, Cherry et al. 1981), (Fortin, Kamp et al. 1991), (Hendry and Wassenaar 1998), (Remenda, Kamp et al. 1996)

3.2 Introduction and Definitions

3.2.1 Significance and Applications

- Where can we apply Chemical Principles?
  - Source Characterization:
    - General characterization: redox conditions, speciation, leachability, weathering, etc.
  - Pathway:
    - Geochemical interactions: adsorption, redox reactions, precipitation, co-precipitation
    - Geochemical modelling
  - Receptor:
    - Mixing with surface water or groundwater sources

- Required Background:
  - Inorganic equilibrium chemistry, organic chemistry, fundamental / applied geochemistry, contaminant hydrogeology, chemical kinetics, microbiology

3.2.2 Water and Dissolved Solids:

- Water is a Solvent therefore … water contains solutes.
  - Total Dissolved Solids:
    - Measured by evaporation on filtered samples
    - Ms / Vt .... Units: kg/m3, gm/L, mg/L, ppm
    - Measured indirectly by electrical conductivity: mmhos/cm

- Chemical Constituents of Groundwater:
Cations: net positive charge / Anions: net negative charge

**Table 3.3 Classification of Dissolved Inorganic Constituents in Groundwater**
(Freeze and Cherry 1979 - SOURCE: Davis and De Wiest, 1966.)

<table>
<thead>
<tr>
<th>Major constituents (greater than 5 mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicarbonate</td>
</tr>
<tr>
<td>Silicon</td>
</tr>
<tr>
<td>Calcium</td>
</tr>
<tr>
<td>Sodium</td>
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<tr>
<td>Chloride</td>
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<tr>
<td>Sulfate</td>
</tr>
<tr>
<td>Magnesium</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Minor constituents (0.01-10.0 mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
</tr>
<tr>
<td>Nitrate</td>
</tr>
<tr>
<td>Carbonate</td>
</tr>
<tr>
<td>Potassium</td>
</tr>
<tr>
<td>Fluoride</td>
</tr>
<tr>
<td>Strontium</td>
</tr>
<tr>
<td>Iron</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Trace constituents (less than 0.1 mg/l)</th>
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</thead>
<tbody>
<tr>
<td>Aluminum</td>
</tr>
<tr>
<td>Molybdenum</td>
</tr>
<tr>
<td>Antimony</td>
</tr>
<tr>
<td>Nickel</td>
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<tr>
<td>Arsenic</td>
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<tr>
<td>Niobium</td>
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<tr>
<td>Barium</td>
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<tr>
<td>Phosphate</td>
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<tr>
<td>Beryllium</td>
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<tr>
<td>Platinum</td>
</tr>
<tr>
<td>Bismuth</td>
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<tr>
<td>Radium</td>
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<tr>
<td>Bromide</td>
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<tr>
<td>Rubidium</td>
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<tr>
<td>Cadmium</td>
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<tr>
<td>Ruthenium</td>
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<tr>
<td>Cerium</td>
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<tr>
<td>Scandium</td>
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<tr>
<td>Cesium</td>
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<tr>
<td>Selenium</td>
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<tr>
<td>Chromium</td>
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<tr>
<td>Silver</td>
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<tr>
<td>Cobalt</td>
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<tr>
<td>Thallium</td>
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<tr>
<td>Copper</td>
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<tr>
<td>Thorium</td>
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<tr>
<td>Gallium</td>
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<tr>
<td>Tin</td>
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<tr>
<td>Germanium</td>
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<tr>
<td>Titanium</td>
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<tr>
<td>Gold</td>
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<tr>
<td>Tungsten</td>
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<tr>
<td>Indium</td>
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<tr>
<td>Uranium</td>
</tr>
<tr>
<td>Iodide</td>
</tr>
<tr>
<td>Vanadium</td>
</tr>
<tr>
<td>Lanthanum</td>
</tr>
<tr>
<td>Ytterbium</td>
</tr>
<tr>
<td>Lead</td>
</tr>
<tr>
<td>Yttrium</td>
</tr>
</tbody>
</table>
In the equations below, 'volume' could be volume of solution or volume of solvent. There does not seem to be agreement in the literature as to the preferred form.

- (Fetter 1993) uses the volume of 'solvent'
- (Domenico and Schwartz 1998) and (Freeze and Cherry 1979) suggest that this is a solution volume.

### Concentration Units:

#### Mass Concentration:
- mass of solute / volume, e.g. gm/l

#### Molarity (Molar Concentration):
- # of moles of solute / volume, e.g. moles/l
- mass concentration / molecular weight

#### Equivalent units:
- # of equivalents/volume, e.g. meq/l
- molar concentration * valence

#### Molality:
- # of moles of solute / mass of solvent

#### Activity:
- Figure 3.3 (Freeze and Cherry 1979) p. 91
\[ a_i = m_i \gamma_i \]

where \( a_i \) is activity, \( m_i \) is molality, and \( \gamma_i \) is the activity coefficient.

\( \gamma_i \) is a unique function of the Ionic Strength (I) of the solution.

- Ionic Strength: \( I = \frac{1}{2} \sum m_i z_i^2 \) where \( z_i \) is the valence of the individual species in solution.

- In dilute solutions, molal concentrations can be used to determine equilibrium and solubility. For general case the activity coefficients, \( \gamma_i \), can be computed from concentration along with the theoretical relations such as the Debye-Hückel Equations. Empirical data developed over a small range of Ionic strengths is then extended using theoretical relationships.

### 3.3 Chemical Reactions: (see Fetter)

#### 3.3.1 Types of Reactions:

- 2 Types: Reversible and Irreversible
  - Reversible:
    - equilibrium with environment
    - subject to study in terms of kinetics and thermodynamic methods
  - Examples:
    - Disassociation (solution) \( \text{NaCl} \leftrightarrow \text{Na}^+ + \text{Cl}^- \)
    - Water bonds with Solid or Gas
♦ **Solid:** \[ \text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \]

♦ **Gas:** \[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]

(Water breaks into radicals when combining with species in solution)

- **Oxidation-Reduction reactions**
  - In the most simple of descriptions, REDOX reactions are reactions involving electron transfer. It is important to note that there can be no 'free' electrons in solution, consequently, the reaction must always involve an electron donor or receptor.
  - Example:
    \[ 4\text{Fe}^{2+} + 3\text{O}_2 + 8\text{e}^- \leftrightarrow 2\text{Fe}_2\text{O}_3 \] (Ferrous iron is oxidized to ferric iron by transfer of electron from iron to oxygen)

### 3.3.1.1 Reversible Equilibrium Reactions:

- **Law of Mass Action:**
  - Direction of Reversible Reaction?
  - Two reactions simultaneous
    \[ A + B \rightarrow C + D \]
    \[ C + D \rightarrow A + B \]
  - Equilibrium occurs when \( \text{rate of forward reaction} = \text{rate of reverse reaction} \)
  - Reaction represented as follows (stoichiometric):
    \[ aA + bB \leftrightarrow cC + dD \]
    - where; capital letter are constituent chemicals and small letters are coefficients representing moles of each species involved in the reaction.
  - The equilibrium constant for the reaction, \( K \), is:
    \[ K = \left( \frac{[C][D]^d}{[A]^c[B]^b} \right) \]
    - where [X] represents activity of the X ion.
    - \( K \) can be predicted at standard pressure and temperature (STP) from Gibb's Free Energy considerations. It can then be adjusted using Von't Hoff Equations for different temperatures. In complex geochemical modelling some empirical verification/determination of \( K \) is often usually required.
  - Example: (Concentration of pure liquid or solid is defined as 1).
    - **Example: Solubility of AgCl**
      - Reaction: \( \text{AgCl} \leftrightarrow \text{Ag}^+ + \text{Cl}^- \)
      - \( K_{sp} = [\text{Ag}^+][\text{Cl}^-] / [\text{AgCl}] \)
      - Experimentally determine solubility product: \( K_{sp} = 10^{9.8} \)
        Therefore; \( K_{sp} = [\text{Ag}^+][\text{Cl}] \)
Geochemical Modelling:

- Simplistically - geochemical models such as PHREEQE, MINTEQ, etc. are based on large thermodynamic data bases for a large number of reactions. The concentrations and chemical conditions (reactants) are put into these models and then the concentrations of the products is solved for based on the solution of the simultaneous equations knowing the equilibrium constants for every possible reactions.

- See References: (Plummer, Jones et al. 1976) and (Parkhurst, Thorstenson et al. 1980) for original papers.
3.4 Isotope Chemistry
(Much of this material has been adapted from (Fetter 1993) and from (Rose 1995).)

3.4.1 General Description of Isotopes:

- Isotopes of an element have the same atomic number but differ in terms of mass.
  - e.g. Hydrogen .... Note $^2_1\text{H}$ ....
    The 1 is the number of protons, 2 is the mass (neutrons and protons)

$^1_1\text{H} \quad \text{Hydrogen} \quad ^2_1\text{H} \quad \text{Deuterium} \quad ^3_1\text{H} \quad \text{Tritium}

- Stable isotopes: no natural radioactive decay
- Radioactive isotopes: spontaneous radioactive decay
- Radiogenic isotopes: stable product of radioactive decay

3.4.1.1 Brief Overview of Radioactive Decay Mechanisms:

Of the ~ 1700 nuclides (isotopes of all elements), most are radioactive and very short lived. Basic decay reactions are alpha and beta decay.

- Beta Decay:
  - Spontaneous release of an electron like particle ($\beta$ particle) from nucleus.
  - Transforms a neutron to a proton, atomic number of element increases by 1, but atomic mass stays the same.
  - Example: $^{40}_{19}\text{K} \rightarrow ^{40}_{20}\text{Ca} + \beta^- + \text{neutrino} + \text{Energy}
  - $^3\text{H}$ and $^{14}\text{C}$ decay by beta emission

- Alpha Decay:
  - 2 protons and 2 neutrons (a particle and helium nucleus) emitted from nucleus
  - Drops mass number by 4 units and atomic number by 2 units
  - Typical in uranium decay series (along with $\beta$ decay)
  - Example – production of Radium to Radon
    $^{226}_{88}\text{Ra} \rightarrow ^{222}_{86}\text{Rn} + ^4_2\alpha + \text{Energy}
    \text{note} \ ... ^4_2\alpha \text{ is a helium molecule.}$


3.4.2 Brief Overview of the Environmental Isotopes:

### Table 12.14
Isotopes of environmental significance and their relative abundances (modified from Fritz and Fontes, 1980)

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotopes</th>
<th>Average abundance % of stable isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$^1$H</td>
<td>99.984</td>
</tr>
<tr>
<td></td>
<td>$^2$H</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>$^3$H radioactive</td>
<td>$10^{-14}$ to $10^{-16}$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}$O</td>
<td>99.76</td>
</tr>
<tr>
<td></td>
<td>$^{17}$O</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>$^{18}$O</td>
<td>0.10</td>
</tr>
<tr>
<td>Carbon</td>
<td>$^{12}$C</td>
<td>98.89</td>
</tr>
<tr>
<td></td>
<td>$^{13}$C</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>$^{14}$C radioactive</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{32}$S</td>
<td>95.02</td>
</tr>
<tr>
<td></td>
<td>$^{33}$S</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>$^{34}$S</td>
<td>4.21</td>
</tr>
<tr>
<td></td>
<td>$^{36}$S</td>
<td>0.02</td>
</tr>
</tbody>
</table>

1. Deuterium, often referred to by D.
2. Tritium, often referred to by T.

(Dominco and Schwartz)

3.4.2.1 Applications of Isotope Hydrology

- To assess … TIME, PATHWAY, PROCESS
  - Sources of recharge, timing, rates
  - Effectiveness of confining beds (aquitards)
  - Sources of contamination, pathways
  - Residence time, fluxes
  - Chemical processes affecting water quality (fractionation)
  - Feasibility and effectiveness of remediation methods

- Interpretation must always be in terms of ‘multiple working hypothesis’, i.e., supported by:
  - Hydrogeologic interpretation and data
  - Geochemical interpretation and data.
3.4.2.2 Basic Groups of Environmental Isotopes

Of the approximately 1700 isotopes that exist in nature only a small number are used in environmental or hydrogeologic applications. The reason for this is that fractionation only affects lighter isotopes not heavier than Calcium (~ 40 atomic weight). 2 groups – Stable Isotopes and Radioactive Isotopes

**Stable Isotopes**

- **Hydrogen (\(^1\text{H}/\text{H} or \text{D}/\text{H})]**:
  - Along with \(^{18}\text{O}/^{16}\text{O} most studied stable isotopes – water itself.
  - Applications: interpretation of sources of water (recharge), physical processes affecting quality (e.g. evaporation), timing of hydrologic processes and mixing

- **Oxygen (\(^{18}\text{O}/^{16}\text{O})***: 
  - Water combinations (excluding rare \(^{17}\text{O})*; HH\(^{16}\text{O}, \text{DH}\(^{16}\text{O}, \text{DD}\(^{16}\text{O}, \text{HH}\(^{18}\text{O}, \text{DH}\(^{18}\text{O}, \text{DD}\(^{18}\text{O} (heaviest and very rare) (Note: \text{D}_2\text{O} is ‘heavy water’)
  - Applications – time and process

- **Carbon (\(^{13}\text{C}/^{12}\text{C})***: 
  - Applications: determine sources of inorganic carbon, organic carbon, and reduced carbon in natural waters. Required for dating water using \(^{14}\text{C}
  - Applications – time and process

- **Nitrogen (\(^{15}\text{N}/^{14}\text{N})***: 
  - Studied in determining sources of nitrogen compounds in nitrate contamination of natural water
  - Applications - process

- **Sulfur (\(^{34}\text{S}/^{32}\text{S})***: 
  - Study sources of sulfur in natural water
  - Applications - process

- **Strontium (\(^{87}\text{Sr}/^{86}\text{Sr})***: 
  - Both stable; however \(^{87}\text{Sr} derived from beta decay of \(^{87}\text{Sr}.

**Radioactive Isotopes:**

- **Hydrogen (\(^3\text{H} or \text{Tritium}) (t = 12.35 \text{ y})***: 
  - Cosmogenic – atmospheric testing of thermonuclear bombs in 1950’s-1960’s
  - Tracer for ‘modern’ water

- **Carbon (\(^{14}\text{C})(t=5730 \text{ y})***: 
  - Ubiquitous in organisms and atmosphere (produced by neutron bombardment of nitrogen)
  - Used to date water as old as 50,000 bp – but requires sophisticated testing and ‘corrections’
Krypton ($^{85}$K) ($t=10.6\text{y}$)
- Rare cosmogenic isotope – can be produced by fission in nuclear reactors – tracer for hydrogeologic investigations near reactors

Chlorine ($^{36}$Cl) ($t=3.08\times10^5 \text{y}$)
- Study hydrogeologic processes on scale of 25,000 to $2\times10^6 \text{y bp}$
- Dating very old waters where $^{14}$C no longer effective – v. sophisticated methods

3.4.2.3 Relative Abundance of Isotopes: (Table 12.14 [Domenico, 1990 #156] p. p464)

3.4.3 Basic Principles:

3.4.3.1 Fractionation:

- Physical process and chemical reactions
  - organic, inorganic or biochemical serve to alter isotopic ratios

- Examples:
  - Isotope exchange, evaporation, condensation, mineral precipitation, aqueous oxidation-reduction, molecular or ionic diffusion, surface reactions (adsorption), biochemical reactions in metabolism

- Signature:
  - process produces characteristic shift in isotopic ratios.

- Cause:
  - Motion of molecules due to translation, rotation, and vibration. Vibration is most important relative to bond breaking and making. Chemical bond for heavy isotope has lower vibrational frequency than equivalent bond for lighter isotope, therefore they are more stable. In fact there is no discernable ‘fractionation’ between isotopes of same element for atomic number greater than 40(calcium). Energy difference miniscule between isotopes of different weight.
    - Think about ‘big’ people and ‘little’ people dancing on an enormous trampoline
  - Examples:
    - Evaporation – remove the lighter $^1$H, and leave the heavier, $^2$H
    - Biological – Bugs eating N – eat the lighter $^{14}$N, leave the heavier, $^{15}$N

- Factors effecting fractionation:
  - Temperature – fractionation is inversely related to temperature. Opposite to effect of temperature on reactions. Reason – at high temperatures – less ‘difference’ in vibrational energy for heavy and light. At boiling point – little difference in isotopic composition of vapour and fluid.
3.4.3.2 Detection: Mass spectrometer
- Sample is collected and physically or chemically converted to a gas
- Gas is ionized using filament and accelerated under high voltage field
- Ionized gases are swept under vacuum through large magnetic field – heavier ions accelerate along greater radial path than lighter.
- Charge particles collected and detected – voltage measured as ratio for each isotope
- Results given as ratio of the ‘relative abundance’ of one isotope to another. Absolute number of atoms is not measured by MS

3.4.3.3 Terminology:
The relative abundance of isotopes to the non-isotopic element is very low. So much so that measuring and reporting ‘concentrations’ of isotopes in a conventional manner would be very difficult to work with. Consequently, a ‘relative’ concentration is used to highlight changes in the ratio of the relative abundance due to TIME, PROCESS or PATHWAY.

‘Del’ notation: (δ):
- the per mil difference between the isotopic ratio of a sample to a standard
  - Equation: \( \delta^{18}E (\%) = \left( \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \) where;
    - δ is ‘del’ meaning difference as in ‘delta’
    - H refers to heavy stable isotope of element ‘E’
    - E is an element with at least two stable isotopes
    - % designate ‘per mil’ or 1/1000 (1/10 of %)
    - R is the ratio of heavy to light isotopes from a sample or standard
      - sample is analyte, standard is agreed upon reference – sample with a well defined ‘R’, example Standard Mean Ocean Water (SMOW)
      - Example: \( \delta^{18}O (\%) = -6\% \) means that sample is 0.6 % lighter than standard.
- Example:
  - R of standard was .00015/1 and R measured was .00014/1
  - Calculation: \( \delta^{18}E (\%) = \left( \frac{.00015/1 - .00014/1}{.00015/1} \right) \times 1000 = -70 \% \)

Fractionation Factor: (\( \alpha \)):
- Equilibrium ratio of a given stable isotope pair in two different phases. Value of unity indicates no fractionation as isotope exchanged between phases. ‘A’ and ‘B’ used to refer to 2 phases.
  \( \alpha_{A,B} = \frac{R_A}{R_B} = \frac{1000 + \delta_A}{1000 + \delta_B} \)
- Example: Exchange of sulfur between pyrite and aqueous sulfate
Fe^{34}S + ^{32}\text{SO}_4^2^- = Fe^{32}S + ^{34}\text{SO}_4^2^- \\
\alpha_{A:B} = (Fe^{32}S)(^{34}\text{SO}_4^2^-)/(Fe^{34}S)(^{32}\text{SO}_4^2^-) or = (^{34}\text{Sulphate}/^{32}\text{Sulphate})/(^{34}\text{Pyrite}/^{32}\text{Pyrite})

- Reasonable value ~ 1.030. Suggests that sulfate has slightly higher affinity for heavy sulphur isotope. More energetically favorable to break bond with heavier Sulfur in pyrite.

- Temperature dependency:
  - \[ 1000 \ln \alpha_{A:B} = a + bT^{-1} = cT^{-2} \]
  where a, b, c are constants for specific system. Note inverse ratio to temperature.

- Similar term: ‘Enrichment’
  - \[ \varepsilon_{A:B} = (\alpha_{A:B} - 1) \times 1000 \]
  or ~ 1000 \ln \alpha_{A:B} \sim \alpha_A - \alpha_B

**Reporting Components:**
- \(\alpha\) value
- standard reference (SMOW – standard mean ocean water, SLAP – standard light arctic precipitation)
- degree of precision – requires replicates and deriving spread around mean. Often expressed as ± 1 or 2 standard deviations.

### 3.4.4 Key Behavior of Isotopes:

#### 3.4.4.1 Stable Isotopes of Hydrogen and Oxygen

- ‘water’ is best tracer for ‘water’
- Shallow groundwater has low degree of fractionation – assumption- that isotopic composition of ground water represents isotopic concentration of recharge (meteoric) water.
- Relative mass difference between Hydrogen isotopes >> than relative mass difference between Oxygen isotopes, therefore, greater fractionation for Hydrogen over Oxygen

**Relative Abundance:**
- 3 stable Oxygen: \(^{16}\text{O}, ^{17}\text{O}, ^{18}\text{O}\) and 2 stable Hydrogen: \(^2\text{H}\) (or D), and \(^1\text{H}\).
- \(^{17}\text{O}\) insignificant, \(^{16}\text{O}\) and \(^{18}\text{O}\) represent 99.63% and .19% of all oxygen
- \(^1\text{H}\) and \(^2\text{H}\) make up 99.9852% and 0.0158% of hydrogen in hydrosphere

**Measurement Considerations:**
- Oxygen not directly measured by Mass Spectrometer.
  - Water is equilibrated with carbon dioxide gas at fixed temperature.
  - The \(^{18}\text{O}/^{16}\text{O}\) measured on \text{CO}_2, since \(\alpha\) known for \text{H}_2\text{O}/\text{CO}_2 then original isotopic composition of water can be calculated.
- Hydrogen ratios (D/H)
  - Reduce sample to hydrogen gas and measure ratio with mass spec.
Requires passing sample over heated uranium metal at high temperature and numerous ‘cold traps’ to separate hydrogen.

Expensive, resulting in more studies of oxygen isotopic ratios than hydrogen.

- **Note:** You will see in some papers that they only measure $^{18}\text{O}/^{16}\text{O}$, inferring the D/H values from the meteoric line.

Standards:

- SMOW – Standard mean ocean water – however this does not have ‘del’ of zero. Original standard no longer exists – instead comparison is made to National Bureau of Standards sample NSB-1 and corrected to SMOW.

**Fractionation of Hydrogen and Oxygen**

Key mechanism is Raleigh type of process ~ distillation. $^{16}\text{O}$ and $^{1}\text{H}$ have a higher vapour pressure than $^{18}\text{O}$ and $^{2}\text{H}$ resulting in water vapour being isotopically lighter than original. As water evaporates and then re-condenses in atmosphere, then re-evaporates and condenses, it continues to be isotopically depleted, more in hydrogen than oxygen.

In general the degree of fractionation increases with latitude due to 2 reasons; most of evaporation occurs globally near equator and then works its way poleward, and the fractionation factor increases as temperatures decrease towards the poles.

(Temperature change … attitudinally, latitudinally, seasonally (continentally))

Collection of data from around the world has created the ‘meteoric line’. (Figure 12.12 [Domenico, 1990 #156], p. 466) with the equation of:

$$\delta D = 8.17 \delta ^{18}\text{O} + 10.56 \%$$

**Applications:**

- Example Fortin et al 1991 also Desauliniers and Hendry and Waasenauer
- Sources of Recharge or relative contribution of various water sources to aquifers:
  Compare isotopic composition of groundwater to regional precipitation (including different elevations)
- Seasonality of Recharge: (Figure 9 - (Desaulniers, Cherry et al. 1981), (Hendry and Wassenaar 1998))
- Leakage between aquifers:
- Sources of salinity: was water salinized after recharge (evaporation from ponds or playas) or was it generated as result of salt dissolution.

**3.4.4.2 Tritium**

**Sources:**

- $^3\text{H}$ is rarest hydrogen isotope. It is present naturally as a ‘cosmogenic’ isotope, produced by neutron-bombardment of nitrogen:
\[ ^{14}\text{N} + n \rightarrow ^{12}\text{C} + ^{3}\text{H} \]

- 'Technogenic' tritium also produced by nuclear reactors (leaks) and for 'liquid crystals' used in indoor illumination signs (EXIT) used.

- Primary tritium in hydrogeologic studies is due to atmospheric testing of nuclear devices over past 40 years. Water with appreciable tritium levels are referred to as 'modern' or 'post-bomb'.
  - Changes in Atmospheric Tritium (Nuclear Testing post 1950’s)
  - Figure 3.11 Freeze and Cherry (1979), p. 137
  - Distinguish between “Modern” (post 1952) and “old” (pre-1952) waters.

  > Example: Desaulniers et al (1981)

**Applications:**
- Tracer for mass balance studies in stream-flow generation studies
- Identification of sources of recharge, quantify infiltration/recharge rates in the vadose zone
- Quantify ‘dispersion’ parameters
- Quantify residence time for groundwater in basins

**Measurement**
- Tritium decays (half life ~ 12.3 y) through beta emission:
  \[ ^{3}\text{H} \rightarrow ^{3}\text{He} + \beta^{-} \]
- Very low concentrations, consequently, special unit used in measurement:
  Tritium unit (T.U. or TU) defined as one \(^{3}\text{H}\) per \(10^{18} \text{H atoms}\).
  1 TU ~ 3.2 picoCuries per liter (1 pCi = \(10^{12}\) Curies)
  EPA health standard is 20,000 pCi/L (~ 6250 TU)
- Measurement difficult. Uses scintillation counting of \(\beta^{-}\) emission
- Detection limits: Non-enriched sample ~ 100 TU, too high for most natural waters
- Enrichment – ‘electrolytic enrichment’ in which heavier \(^{3}\text{H}\) moved towards one pole of an electrode system. Final sample ~ 250-500 ml. Detection limit ~ 1 TU with precision of ± .5-1 TU
- Alternate measurement – monitoring helium growth – requires long analytic time (6 mo.) but only small sample volumes required (~ 20ml).

**Interpretation:**
- < 1 TU – groundwater has not been influenced by recharge over last 40-50 years. Age undetermined – better to try carbon-14
- Low TU, 0-5 TU; At some locations (high latitudes) suggests pre-modern and some degree of mixing with post-bomb water occurred. However some coastal locations have had < 10 TU over past 10 years.
- TU > present day rainfall; generally imply bomb-pulse component of recharge
• TU ~ present day rainfall; recent or fortuitous ‘mixing’

3.4.4.3 *Carbon-14 and Carbon-13*

• Based on interpretation of Carbon Cycle (carbon transfers within/from atmosphere, living organisms, rock, to groundwater)
• Interpretation complicated about whether the cycle is ‘closed’ or ‘open’. Leaky egg-timer.

**Carbon 13 and 14 Sources:**

- Half-life is 5730 ± 40 years.
- Produced in upper atmosphere by bombardment of 14N with cosmic ray neutrons:
  - $^{14}\text{N} + n \rightarrow ^{14}\text{C} + p$ but $^{14}\text{C}$ is unstable and decays by $\beta$ emission $^{14}\text{C} \rightarrow ^{14}\text{N} + \beta^-$
- Transferred to groundwater by physicochemical (diffusion), biochemical and microbial metabolic processes.
- Nuclear testing has increased $^{14}\text{C}$ activity – although fossil fuel emissions have only been of ‘dead’ carbon (old), therefore lacking in $^{14}\text{C}$.
- Stable Isotopes (12 and 13):
  - Fractionation occurs as a result of numerous kinetic and equilibrium processes (Rightmire and Hanshaw 1973):
    - Photosynthesis – enrichment of light carbon in organism as plants take in atmospheric carbon ($\delta^{13}\text{C}$ of atmospheric carbon \ldots -7‰) to produce $\delta^{13}\text{C}$ of -24 to -34 ‰ or -6 to -19‰ for desert plants (different types of photosynthesis)
    - Soil CO2 release from plant respiration and bacterial respiration typically -20 to -25‰
    - Dissolution of carbonate rocks usually causes increase in $\delta^{13}\text{C}$
      - $^{12}\text{CO}_2 + ^{13}\text{CO}_3 \rightarrow ^{13}\text{CO}_2 + ^{12}\text{CO}_3$
      - Tendency for aqueous phase to be ‘heavier’ - carbonate dissolution results in ‘heavier’ groundwater
    - Example: (Rightmire and Hanshaw 1973) noted:
      - +23 ‰ for soil organic matter, -18.2‰ to -29.5‰ for litter samples (Calvin and Hatch-Slack cycle plants) -14.7‰ to -21.3‰ for soil CO2 (consistent with litter)
- Example: Remediation – organic contaminants should cause DIC to become ‘lighter’ while methane production under reducing conditions should ‘enrich’ the DIC as microbes prefer lighter C-12.
- Case History: Waste Rock - to be collected from Dr. Hendry

3.4.4.4 *Nitrogen-15*

- 2 isotopes of Nitrogen:
  - $^{14}\text{N}$ (99.63% of all N) and $^{15}\text{N}$
R standard is atmospheric nitrogen

Fractionation occurs in non-equilibrium manner as the result of biochemical alteration of nitrogen compounds producing various ‘signatures’ associated with the process

Example: Nitrate (NO3-)
- contaminant has a limit of 45 mg/L or 10 mg/L as Nitrogen
- sources: natural soil organic matter, livestock waste, sewage (tanks, pipe, septic fields) and fertilizers

Groundwater compared to atmospheric to locate source of contamination. (e.g. fertilizer)

Examples
- (Bottcher, Strebel et al. 1990)
  - Nitrogen and Oxygen isotopes compared in upgradient wells, and agricultural land
  - High nitrate concentrations associated with low d15N and low d18O values and vice versa
  - Ratio of d15N/d18O shows linear increase (slope 1:2.1)
- Example: (Kreitler, Ragone et al. 1979) Shifts in δ15N as follows
  - inorganic fertilizer -3‰ to +2‰, unfertilized cultivated fields +2‰ to +8‰, animal wastes (+10‰ to +20‰)

Interpretation:

Nitrogen cycle: Nitrogen has 5 out of 8 electrons in outer shell – therefore important element in way organism (particularly microorganisms) obtain energy:
- 1) Nitrogen fixation (mediated by bacteria)
  \[ \text{N}_2 (0) \text{ atmospheric} \text{ ----- Organic nitrogen (NH}_3\text{)} (-2) \]
- 2) Ammonification
  \[ \text{NH}_2 (-2) \text{ (organic nitrogen)} \text{ ----- NH}_4^+ \text{ (Aqueous ammonia)} (-3) \]
- 3) Nitrification (bacterial oxidation):
  \[ \text{NH}_4^+ (-3) \text{ (Ammonia) ----- NO}_2^- \text{ (Nitrite)} (+3) \text{ ----- NO}_3^- \text{ (Nitrate)} (+5) \]
- 4) Denitrification (bacterial reduction in reducing waters): Nitrate ---- Nitrite ---- N2
- 5) Volatilization of Ammonia:
  \[ \text{NH}_4^+ (-3) \text{ ----- bacterial breakdown of organic matter \text{ ----- NH}_3 (-3) \text{ (gaseous ammonia)} \]
- 6) Fertilizer production: \text{N}_2 \text{ (from air) (0) \text{ ------ Ammonium salts} (-3) \]

Complex set of biologically mediated redox reactions

Range of δ15N in Nitrates:
- Source: Range of δ15N:
  - Uncontaminated soil/water 0 to +11
Animal and human wastes +10 to +22
Cesspool wastes +18 to +25
(heaviest probably due to more volatilization depleting $^{14}$N)
Unfertilized Fields/Fertilizer -3 to +2
(difficult to distinguish from normal soil)

Example: (Kreitler, Ragone et al. 1979)

Case History: (Bottcher, Strebel et al. 1990)
- note separation of agricultural sources from other using 15N and 18O
- copy equation 1 and Figure 2

3.4.4.5 Sulphur-34

Sulphur cycle (Figure in (Rose 1995))

Commonly Observed Ranges:
- Meteorite (standard): 0 in FeS
- Granitic rocks and sulfate derived from these: 0 to +10
- Native sulfur: -10 to -20
- Pyrite: -30 to +4 (large variation results from source of sulphur in pyrite)
- Modern seawater (+20)
- Ancient evaporites (+10 to +30)
- Rainfall (+0 to +20) depending on location
- Sulfides from mafic igneous rock: -5 to +10
- Sedimentary sulfate: -35 to +42 (variety of sources)

Dissolution of gypsum enriches, oxidation of reduced sulfur will result in enrichment of S32