LAB GUIDE

Rayleigh Isotope Effect in the Oceans: Building Glaciers

GROUP LAB WRITE-UP INCLUDES: Hypothesis, Methods, Results (*including calculations outlined here)*, Discussion, and Conclusion.

DUE: Turn in your lab report at the start of the lab period on __________________. You can find the white paper describing the instrument, and a paper on measurement of temperature dependent fractionation factors for H and O isotopes (Horita and Wesolowski, 1994) in the assignment folder for this lab in the class dropbox.

STABLE ISOTOPES IN THE ENVIRONMENT

Water is composed of a mixture of molecules with the chemical composition H_2O, but there are multiple stable isotopes of H and O, resulting in water molecules that differ in their isotopic composition (and mass). We call these different molecules, ***isotopologues***. For the purpose of this lab, we will ignore the differences in the mass contributions from the **H** isotopes, and focus on the differences in the oxygen molecules. (Why might this be justified?) In this way, we see that water will have three isotopologues with respect to oxygen: $\mathbf{H_2{}^{16}O}$, $\mathbf{H_2{}^{17}O}$, and $\mathbf{H_2{}^{18}O}$, with relative abundances that are proportional to the isotopic abundance of $\mathbf{^{16}O}$, $\mathbf{^{17}O}$, $\mathbf{^{18}O}$. The most abundant of these isotopes is $\mathbf{^{16}O}$ (99.76%), the second most abundant is $\mathbf{^{18}O}$ (0.20%), while $\mathbf{^{17}O}$ (0.038%) is found in relatively low abundance and like H's effect on water mass, can be neglected to first order. That leaves us with water mostly composed of $\mathbf{H_2{}^{16}O}$ and $\mathbf{H_2{}^{18}O}$. If the water in a reservoir has more $\mathbf{H_2{}^{18}O}$, it has a higher $\boldsymbol{\delta^{18}O}$ value as we discussed in lecture. If in contrast, it has more $\mathbf{H_2{}^{16}O}$, it has a lower $\boldsymbol{\delta^{18}O}$ value. Isotope geochemists also use the terms ***heavy*** for an isotope with more mass than other stable isotopes of the same element and ***light*** for an isotope with less mass than other stable isotopes of the same element.

Stable isotopic fractionation is the separation or partitioning of a substance's stable isotopes due to a variety of processes that depend on relative differences in the mass of the isotopes (***equilibrium isotopic fractionation***), or other processes that involve rate-dependent transfers or site-specific binding effects, for example, during the synthesis of organic molecules (***kinetic isotopic fractionation***).

Isotopic fractionation takes place when water changes phase through evaporation and condensation. While condensation is associated with an equilibrium fractionation factor, evaporation is an example of a rate-dependent, kinetic fractionation. Water and water vapor can be in isotopic equilibrium if they are in contact with each other and given enough time with constant conditions (like temperature) to equilibrate. If all of the water in a reservoir is evaporated, and then condensed, there would be no fractionation expressed because there would have been no separation of materials between reservoirs (i.e., complete transfer of matter from one reservoir to another). This is an important point. Regardless of how large a fractionation factor is it will not be expressed if there is no separation of the material between different phases or reservoirs. When considering phase transitions, such as the transformation from liquid water to water vapor during evaporation, a useful rule of thumb to remember is that the heavier isotopes (with higher masses) are more easily held in the most tightly bound phase than the lighter, lower mass isotopes. This is true because it take more energy to transform the more massive $H_2{}^{18}O$ from a liquid to a vapor (i.e., to evaporate it), than the less massive $H_2{}^{16}O$.

The expression of an isotope fractionation is called an ***isotope effect***. For evaporation/precipitation of water, an isotope effect can be expressed, which we refer to as ***Rayleigh*** (pronounced RAY-lee) ***distillation***, the separation of $H_2{}^{16}O$ and $H_2{}^{18}O$ as part of the hydrologic cycle. However, if all of the water in a reservoir is evaporated, and then condensed without loss, there would be no fractionation expressed because there would have been no separation of materials between reservoirs (i.e., complete transfer of matter from one reservoir to another).

You will be performing a simple batch distillation experiment for this lab to simulate the isotope effect (Rayleigh distillation) in the oceans due to the removal of water by evaporation, its transfer by atmospheric circulation to land, and its storage on the continents in glaciers and ice sheets. The atmospheric transfer part is important. If the water evaporates, but then rains back into the ocean, there will be no isotopic effect in the ocean because the ^{18}O-depleted water that evaporated, is then rained back down to the ocean. The storage part is also important because if the water just runs off the land and back into the ocean, then there will be no isotope effect expressed in the oceans. To record an isotope effect in the oceans then, there must be a both an isotopic fractionation, and a separation of the material fractionated from the initial reservoir.

During interglacial times, much of the water that precipitates over land flows back to the sea, resulting in no net change in sea level due to evaporation (Figure 1A). During glacial periods however, more of the water that evaporated from the ocean was stored on land to create vast ice sheets. This resulted in lower sea level. Because the water that evaporated from the ocean was fractionated (had relatively lower $H_2{}^{18}O/H_2{}^{16}O$), when this water accumulated on land as snow and ice, it left the oceans depleted in $H_2{}^{16}O$. Consequently, during ice ages, the $\delta^{18}O$ of the ocean increased (Shackleton, 1967; Figure 1B).

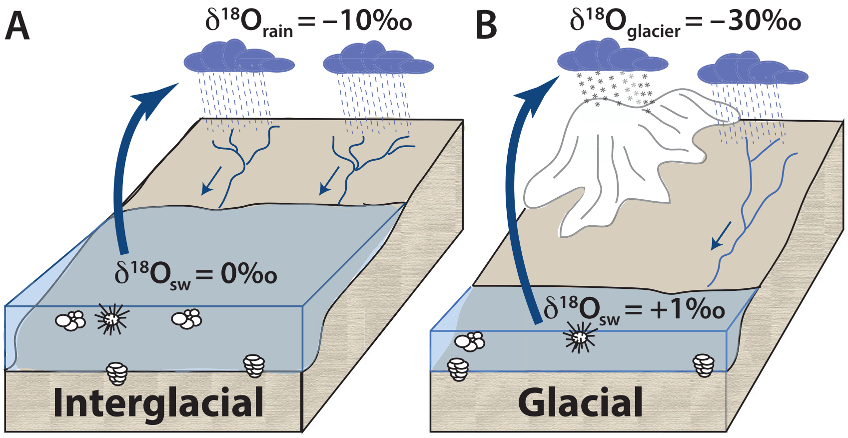
Unfortunately, we can't directly measure the $\delta^{18}O$ of glacial ocean water through time because the isotopic composition of the sea has been slowly shifting through time and is not directly preserved. Therefore, we rely on indirect (*proxy*) measurements from components of marine sediment that record the isotopic composition of seawater, such as calcifying marine organisms, with an isotopic offset that is dependent on temperature and metabolic processes (collectively known as "vital effects"). With independent measurements of temperature from other proxies and knowledge of an organism's vital effects, it is possible to constrain the variations in seawater isotopes and extract information about variations in global ice volume. Because the ice volume signal relates to global changes in sea level, it is also an extremely powerful tool for stratigraphic reconstruction (for additional details and references see Sharp, 2007).

It is interesting to note that the transport of moisture from the equator to the poles where ice typically accumulates also affects the isotopic composition of that ice (following similar Rayleigh distillation). This results in an empirical relationship between temperature and the isotopic composition of ice, which can be useful for paleoclimatic studies (Dansgaard, 1964).

Isotopic data ($\delta^{18}O_{water}$) from a simple batch distillation experiment will be modeled using open system Rayleigh isotopic fractionation. An ***open system*** is one in which the reactant and product become separated. An 'ideal' Rayleigh distillation following Equation 1 below is applied to an open system where the reactant reservoir is finite and well-mixed and does not re-react with the product (Clark and Fritz, 1997). In this open system, material is removed continuously under condition of a constant fractionation factor, α (Kendall and McDonnell, 1998).

$$\frac{R}{R_o} = f^{\alpha-1} \tag{1}$$

where R = ratio of the isotopes (e.g., $^{18}O/^{16}O$) in the reactant, R_o = initial ratio, f = fraction of material remaining in the reservoir, and α is the fractionation factor. Remember that $\alpha_{A\text{-}B} = R_A/R_B$, where R is the isotope ratio of interest (e.g., $^{18}O/^{16}O$) of substance A and B.



Isotopic balance: water with light isotopes evaporates preferentially from the ocean and returns via rivers

Glaciers expand, forming a new reservoir of isotopically light water on the continents: sea level drops, ocean becomes isotopically heavy

FIGURE 1. Comparison of the isotopic composition of seawater with respect to oxygen during interglacial and glacial times.

In delta notation, for Rayleigh fractionation associated with ***evaporation***, Equation 1 reduces to

$$\delta_l = [\delta_{l,o} + 1{,}000]\, f^{\alpha-1} - 1{,}000 \tag{2}$$

where o stands for the initial δ-value of the liquid (l) for the case when α is the fractionation factor between vapor and liquid $\alpha_{vapor\text{-}liquid}$, and f is the fraction of liquid remaining (for more details see Sharp, 2007). In Figure 2, the fractionation factor is associated with the phase transition during evaporation, $\alpha_{vapor\text{-}liquid} = 0.990$ at 25°C (i.e., the newly formed vapor is 10‰ lighter than the residual water).

The simple Rayleigh fractionation model we use is only valid for a single fractionation step due to evaporation, as water goes from the liquid to the vapor phase. But in our experiment, the situation is a bit more complex. The water in the reservoir is affected by evaporation only, but the condensate is the product of two steps (evaporation ***and*** condensation), each with its own fractionation factor, which is beyond the scope of this exercise. To address this, we will focus on modeling the isotopic fractionation due only to evaporation from the water reservoir. Water vapor is continuously removed from the reservoir (i.e., isolated from the initial water) following a constant evaporative fractionation factor. We can compare the initial and final values from the reservoir with the condensate values qualitatively and graphically. By measuring the initial and final volume of the reservoir and condensate we obtain f and its error, the amount of liquid or vapor lost during the experiment. We then apply the Rayleigh fractionation model by comparing the initial isotopic composition of the water before we start the experiment with the isotopic composition of the water remaining in the reservoir at the end of the run. However, in the natural system it is the condensation and precipitation (or rain-out) that follows open system Rayleigh behavior and not the ocean "water reservoir" because the ocean is so large (for more details, see Sharp, 2007).

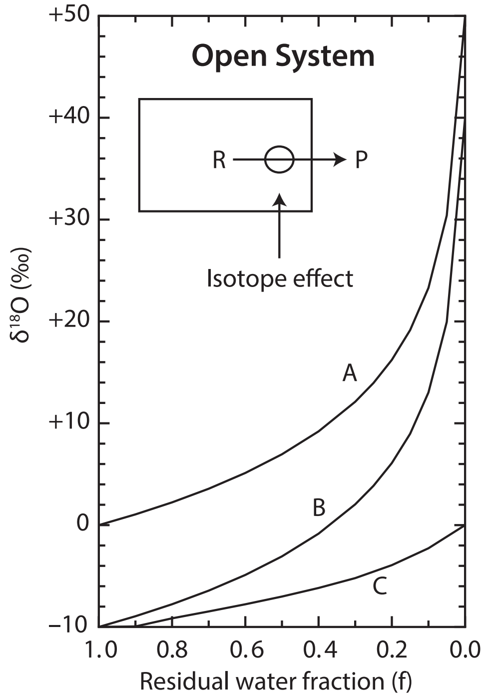


FIGURE 2. Isotopic change under open system Rayleigh conditions for evaporation with a fractionation factor α = 0.990 for an initial liquid composition of $\delta^{18}O = 0$. The $\delta^{18}O$ of the remaining water (line A), the instantaneous vapor being removed (line B), and the accumulated vapor being removed (line C) all increase during single-phase, open-system, evaporation under equilibrium conditions. Schematic of the relationship and isotope effect between a reactant (R) and product (P) in an open system. *Modified from Kendall and McDonnell (1998)*

HYPOTHESIS

After reading through the analytical and experimental methods, what are the questions that you could test with a distillation experiment? What would you expect to happen?

ANALYTICAL METHOD

The white paper from Picarro that you were given provides information regarding how the instrument works. You should include **a short paragraph in your report** describing this in your own words. Dr. J will explain the analytical steps required to run the instrument when you visit her lab. We will start the lab together, but you must sign up for a time to meet with Dr. J to understand how the measurements are made. Some of the distillation experiments could take slightly longer than the lab period. Please make arrangements for at least part of your lab group to remain to complete the experiment.

Indicate which time that you will meet with Dr. J to measure your samples below:

Date	**Time**	**Place**	**Yes! We'll be there! (Write your group number, a.m. or p.m. lab, and member names here)**
Friday	2:30-4:00 pm	Room 123	
Monday	2:00-4:00 pm	Room 123	

EXPERIMENTAL METHOD: SIMPLE BATCH DISTILLATION

Morning Lab

Group 1: Starting volume in reservoir: **80 mL;** Ending volume in condensate: **60 mL (record actual)**
Group 2: Starting volume in reservoir: **60 mL;** Ending volume in condensate: **30 mL (record actual)**
Group 3: Starting volume in reservoir: **60 mL;** Ending volume in condensate: **20 mL (record actual)**
Group 4: Starting volume in reservoir: **100 mL;** Ending volume in condensate: **20 mL (record actual)**

Afternoon Lab

Group 5: Starting volume in reservoir: **80 mL;** Ending volume in condensate: **60 mL (record actual)**
Group 6: Starting volume in reservoir: **60 mL;** Ending volume in condensate: **30 mL (record actual)**
Group 7: Starting volume in reservoir: **60 mL;** Ending volume in condensate: **20 mL (record actual)**
Group 8: Starting volume in reservoir: **100 mL;** Ending volume in condensate: **20 mL (record actual)**

The experimental set-up will look similar to Figure 3. Note temperature will be measured with an IR thermometer:

1. Measure the given initial volume for your initial reservoir using the water provided in your squirt bottle and a **dry** 100 mL volumetric cylinder and pour into round bottom flask. (*Instructor Note: Choose a range of volumes for the initial reservoir and final volume to enable graphic representation of the results.*) Also fill a **labeled** (with IR Group #) 20 mL scintillation vial with water from the same source until overflowing with the water so that when sealed there is little or no air trapped in the vial.
2. Place the reservoir, which you filled with the measured amount of water on the distillation apparatus, and be sure it is in contact with the hotplate (Figure 3).
3. Turn on the water to the condensing column and adjust the flow so that there are no bubbles visible.

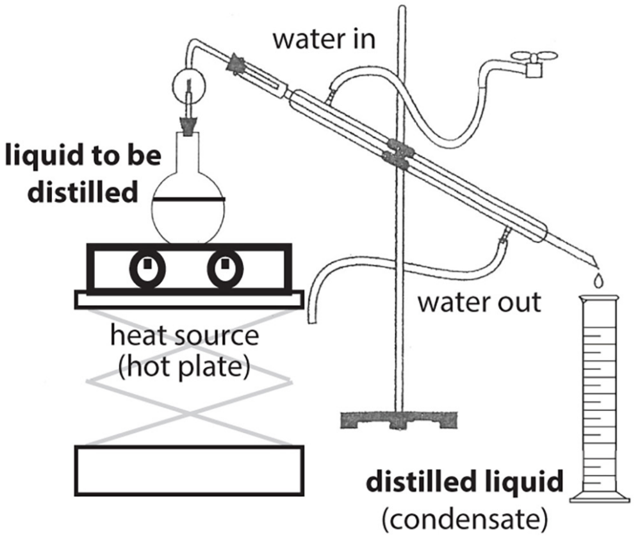


FIGURE 3. Distillation experiment and measurement laboratory setup.

4. Be sure that you have a **dry** 50 or 100 mL volumetric cylinder placed inside a 1L beaker filled with ice and situated to catch the condensate. Adjust the apparatus so all the connections are tight to prevent water vapor loss during the experiment.
5. Turn on the hotplate, set it to medium high or high, and wait for the water in the reservoir to boil, indicating the temperature has reached 100°C.
6. Maintain a constant 100°C boiling temperature for the water in the reservoir by adjusting the temperature on the hotplate. Measure the temperature at ~5-minute intervals using the IR thermometer, and turn the heat source up or down as needed.
7. Collect the condensate into the volumetric cylinder, keeping track of the volume to ensure that you ***stop the experiment when you have reached the target ending volume.*** Measure and **record** the ending volume of condensate when it reaches the value desired (as it might be slightly different than the target value).
8. At the end of the experiment, turn off hot plate and lower it out of position using the scissors jack. Remove the hot plate carefully using the insulated gloves. Take care not to remove the boiling flask yet. You want to prevent any additional evaporative loss, so cool the water in the reservoir before disassembling the distillation apparatus by placing a bucket filled with cool water under the flask. When the flask cools to room temperature, measure the volume of the final reservoir using a **dry** 50 or 100 mL graduated cylinder and record the result.
9. Now, pour the water from the final reservoir into a **labeled** (with FR Group #) 20 mL scintillation vial. Be careful not to lose any of the water remaining in the reservoir and not to contaminate it with water from the cooling bath. If any condensate remains in the distillation column, pour it into the graduated cylinder with the condensate and revise your volume measurement as needed.

10. Next, pour the ending condensate into a different **labeled** (with C Group #) 20 mL scintillation vial. ***Fill each scintillation vial until overflowing so that when it is sealed, little or no air is trapped in the vial***. You might have extra water from the reservoir or condensate that does not fit into the scintillation vials. That is ok; it can be discarded as long as you have first measured the volume of the condensate and the final reservoir. You will now have three filled, labeled scintillation vials: initial reservoir, final reservoir, and condensate.

ANALYSIS OF RESULTS

An Excel spreadsheet with data from 8 experiments will be provided to you in the dropbox prior to the start of the second lab period. You are required to write up your report using all of these results. Make sure that you show all your work in the Excel spreadsheet that your group turns in. You will not get credit for your work if you provide an answer without the equations you used to complete the calculation.

You are required to complete the following calculations and discuss the results.

1. Using the mass balance equation below

$$\delta^{18}O_{initial\ reservoir} = \delta^{18}O_{final\ reservoir}(f) + \delta^{18}O_{condensate}(1-f) \tag{3}$$

   where f = fraction of reactant (reservoir) remaining, what is the theoretical (expected) isotopic composition of the initial reactant (our initial reservoir)? You will have one experimental value from each group. What is the average value and standard deviation for the calculated initial reservoir? How does this ***calculated*** $\delta^{18}O_{initial\ reservoir}$ compare with the ***measured*** $\delta^{18}O_{initial\ reservoir}$? What is the propagated error (the square root of the sums of squares of the standard deviations of the ***measured*** $\delta^{18}O_{final\ reservoir}$ and $\delta^{18}O_{condensate}$) for the ***calculated*** $\delta^{18}O_{initial\ reservoir}$?

2. Create a figure in Excel with two sets of data on the same plot (like Figure 2). Plot $\delta^{18}O_{final\ reservoir}$ (the reactant) vs. f, and $\delta^{18}O_{condensate}$ (the cumulative product) vs. f, where f = fraction of reactant remaining (on the x-axis). Be sure both are labeled correctly.

3. Fit natural log curves to the $\delta^{18}O_{final\ reservoir}$ (reactant) vs. f and $\delta^{18}O_{condensate}$ (cumulative product) vs. f. Display the equations for the curves, which should have the form of $\delta^{18}O_w = a*\ln(f) + b$. What trends do you see?

4. Using a derivation of the Rayleigh equation applying the measured $\delta^{18}O$ values given in the equation that follows, calculate the fractionation factor ($\alpha_{vapor\text{-}liquid}$) between vapor and liquid during evaporation.

$$\frac{1{,}000 + \delta^{18}O_{final\ reservoir}}{1{,}000 + \delta^{18}O_{initial\ reservoir}} = f^{(\alpha_{vapor\text{-}liquid}-1)} \tag{4}$$

   You will have one value of $\alpha_{vapor\text{-}liquid}$ from each group. What is their average value and standard deviation? How does this compare to published measurements of the equilibrium fractionation factor for evaporation using much more sophisticated equipment: $\alpha_{v\text{-}l} = 0.996$ at 100°C or $\alpha_{v\text{-}l} = 0.990$ at 25°C from Horita and Wesolowski (1994)? What role does temperature play?

5. The accuracy of our results depends in part on how much sample is lost during the experiment. Calculate the difference between the published measurement of $\alpha_{v\text{-}l} = 0.996$ at 100°C and the experimental measurement of $\alpha_{v\text{-}l}$ from each group. Plot the difference vs. the percent of water lost by each group; do you see a trend?

DISCUSSION AND CONCLUSIONS

*Be sure to address the points below as part of your **Discussion** section and be sure to include a **Conclusions** section based on your **Results** in the lab write-up you turn in for credit.*

Students need to answer the following questions when discussing their results:

1. If we compare our reactant and condensate to the natural system in Figure 1, which parts of the hydrologic cycle do they represent?

2. What are the key factors controlling the isotopic composition of seawater in the ocean during a glacial period? How is this recorded in marine carbonates? What other factors influence the recording phase(s) in the geologic record?

3. What influences the isotopic fractionation factor that you calculated using your data from the distillation experiment? What physicochemical processes are occurring? Do the experiments fall precisely on the exponential curve? If not, why?

4. If this experiment were done with seawater, what effect would you see in the salt content of the seawater (i.e., ocean "water reservoir")? How would salt content (salinity) vary with $\delta^{18}O_w$ given this observation? Would this effect for surface waters be different at low vs. high latitudes? What else could affect surface $\delta^{18}O_w$ of low vs. high latitudes?

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