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Mimicking the Rayleigh Isotope Effect in the Ocean

By Elizabeth M. Griffith, Joseph D. Ortiz, and Anne J. Jefferson

PURPOSE OF ACTIVITY

This activity provides hands-on exploration of the impact of Rayleigh distillation on the isotopic composition of water in different experimental reservoirs. Similar experimental methods have been a primary source of information for understanding isotopic variations in the natural system. Students are exposed to fundamentals of isotope geochemistry, isotope measurement using a cavity ring down spectroscopy (CRDS) instrument (e.g., Picarro, Los Gatos Research), or an isotope ratio mass spectrometer (IRMS) and associated calculations. Archived data from this project are available for instructors who wish to use the lab but lack access to a CRDS or IRMS instrument. This activity builds a foundation for exploration of stable isotope geochemistry appropriate for students in numerous courses.

AUDIENCE

This activity is appropriate for upper class majors or first-year graduate students with backgrounds in oceanography, atmospheric science, or the Earth sciences. It has been taught several times at two different institutions. Students in post-course interviews noted that lab experiences are critical for learning in the geosciences and that, when organized to encourage the development of questions and hypotheses, lab experiences increase motivation and depth of content knowledge.

BACKGROUND

Stable Isotopes of Water in the Ocean

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 molecules that differ in their isotopic composition (and mass), referred to as *isotopologues* (Sharp, 2007, and references therein). Water has many isotopologues; three of them differ in their oxygen isotopic composition, $H_2^{16}O$, $H_2^{17}O$, and $H_2^{18}O$, and their relative abundances are proportional to the isotopic abundance of ^{16}O , ^{17}O , and ^{18}O . The most abundant of these isotopes is ^{16}O (99.76%), the second most abundant is ^{18}O (0.20%), and ^{17}O (0.038%) is found in relatively low abundance.

For the purpose of this focused activity, we'll neglect the H isotopes of water, but the exercise could be expanded to explore these variations as well (see Possible Modifications to Activity). We thus consider water as composed of $H_2^{16}O$ and $H_2^{18}O$. The delta notation ($\delta^{18}O$) can be used to compare water with differing isotopic compositions to a standard, such as Standard Mean Ocean Water, and reported as differences in a tenth of a percent or per mil (‰). Water in a reservoir with more $H_2^{18}O$ has a higher $\delta^{18}O$ value. In contrast, water with more $H_2^{16}O$ has a lower $\delta^{18}O$ value.

Useful Definitions: *Fractionation* is the separation of a substance's stable isotopes due to processes that depend on relative differences in the masses of the isotopes (*equilibrium isotopic fractionation*), or that involve rate-dependent exchange or site-specific binding effects (*kinetic isotopic fractionation*), such as during the synthesis of organic molecules. The expression of an isotopic fractionation is called an *isotope effect*. The magnitude of an isotope effect is measured by a *fractionation factor* (α).

Isotopic fractionation takes place when water changes phase through evaporation or condensation (Urey, 1947). When considering phase transitions, such as the transformation from liquid water to water vapor during evaporation, a useful rule of thumb is that typically the higher mass isotopes are more easily held in the lower energy phase than the lower mass isotopes. It takes more energy to evaporate the more massive $H_2^{18}O$ molecule, transforming it from a liquid to a vapor, than the less massive $H_2^{16}O$. While condensation is associated with an equilibrium fractionation factor, evaporation is associated with an equilibrium fractionation factor *and* a rate-dependent, kinetic fractionation, and both depend on temperature (Urey, 1947; Dansgaard, 1964). Water and water vapor can reach isotopic equilibrium if they are in contact for sufficient time under constant conditions of temperature and humidity. For evaporation and subsequent precipitation of water, an additional isotope effect can be expressed, which we refer to as *Rayleigh* (pronounced RAY-lee) *distillation*, which quantifies the relative separation of $H_2^{16}O$ and $H_2^{18}O$ within 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).

This hands-on lab activity is a batch distillation experiment to simulate the isotope effect (Rayleigh distillation) in the ocean 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 isotope effect in the ocean because the ^{18}O -depleted water that evaporates from it returns to it. The storage part is also important because if the water just runs off the land and back into the ocean, there will also be no isotope effect expressed. To record an isotope effect in the ocean then, there must be 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 evaporates from the ocean is stored on land, creating vast ice sheets. This results in lower sea level. Because the water that evaporates from the ocean is fractionated and contains more H_2^{16}O than H_2^{18}O , when this water accumulates on land as ice sheets, it leaves the ocean depleted in H_2^{16}O . Consequently, during ice ages, the $\delta^{18}\text{O}$ of the ocean increased (Shackleton, 1967; Figure 1B).

Unfortunately, we can't directly measure the $\delta^{18}\text{O}$ of glacial ocean water. 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).

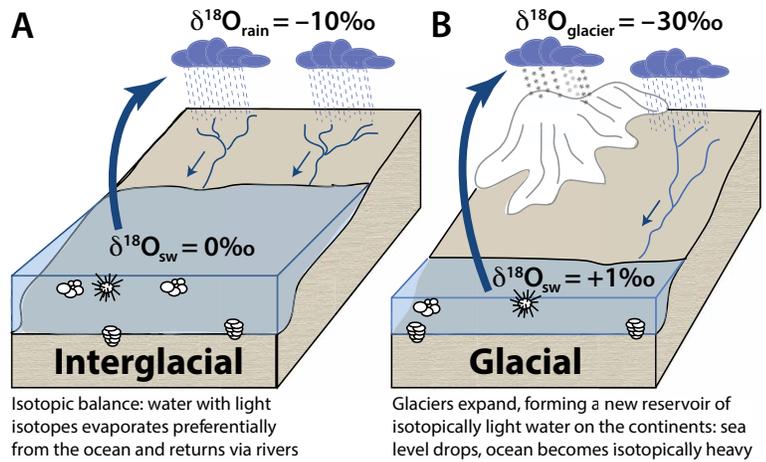


FIGURE 1. Comparison of the isotopic composition of seawater with respect to oxygen during interglacial and glacial times.

Rayleigh Isotope Effect in the Ocean

Students model the isotopic data ($\delta^{18}\text{O}_{\text{water}}$) from a simple batch distillation experiment using open system Rayleigh isotopic fractionation. An *open system* is one in which the reactant and product become separated (Figure 2). An "ideal" Rayleigh distillation following Equation 1 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):

$$\frac{R}{R_o} = f^{\alpha-1} \quad (1)$$

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

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

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

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 ($\alpha_{\text{vapor-liquid}}$), 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, $\alpha_{\text{vapor-liquid}} = 0.990$ at 25°C (i.e., the newly formed vapor is 10‰ lower 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

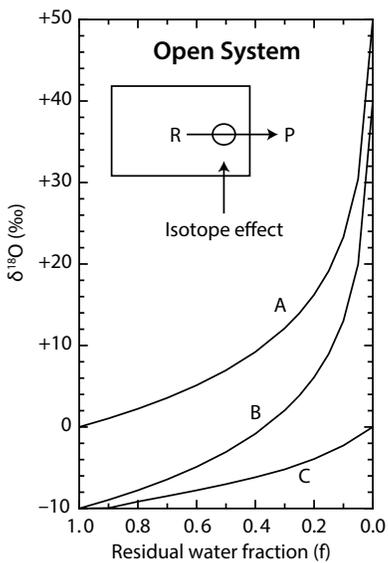


FIGURE 2. Isotopic change under open system Rayleigh conditions for evaporation with a fractionation factor $\alpha = 0.990$ for an initial liquid composition of $\delta^{18}\text{O} = 0$. The $\delta^{18}\text{O}$ of the remaining water (line A), the instantaneous vapor being removed (line B), and the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

(evaporation and condensation), each with its own fractionation factor, which are beyond the scope of this exercise. To address this issue, 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 the final volumes 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).

ACTIVITY

- 1. Lecture** presentation of isotope theory given to the class using PowerPoint (75-minute class). Two class periods would be better to cover more completely the fundamental concepts and analytical methods, including examples from isotope hydrology, stratigraphy, and/or paleoclimatology.
- 2. Distillation experiment** completed within a class or lab period (~2 hours with additional 30–45 minutes to set up and clean up). However, a longer time period of up to 2½ hours would be better. The experiment is summarized with step-by-step instructions in the following section. The lab guide (online supplementary material) includes guided questions to prompt the students to construct testable hypotheses, summarize analytical methods, and discuss conclusions that could be drawn from the experiments. An approximate budget is also provided (see online supplementary Table S1).

3. Stable isotope measurements on the Picarro CRDS (Figure 3), which measures vibrational differences between isotopologues to infer the isotopic composition of a sample (Woelk, 2009). An instructor who operates the instrument supervised two two-hour time slots scheduled outside of class time for the students to assist with sample loading and to learn how to set up a measurement run. The instructional sessions included 30 minutes of instruction and ~1½ hours of machine time. Instrument run time was approximately one day, but it can vary with the number of samples analyzed. The instructor (or technician) assembled isotope data for distribution to students prior to the next lab period (one to two hours). A list of isotope labs that can provide analyses is also provided in the online supplementary Table S2. This is a starting place for instructors without access to instrumentation or for times when the instrument is not available (which happened to us during one class). Because expedited services are typically required, our experience has been that many of these labs will help if they can.

4. Analytical lab for students to work in their lab groups to analyze data set under supervision of instructor and teaching assistant using Excel spreadsheets (~2 hours).

5. Report writing by individuals or lab groups done outside of classroom time for homework as indicated by instructor (two to four hours). This lab report was turned in the following week and graded using a rubric.

MATERIALS AND SUPPLIES

Distillation Equipment

- Hotplate
- Scissors jack (8" × 8")
- Deluxe distillation apparatus kit: stand and clamp, round bottom boiling flask, Kieldahl bulb, Liebig condenser
- Condenser accessory kit: condenser hoses and connect for faucet
- 1 L beaker (2)
- Plastic box with ice to cool the round bottom boiling flask and the graduated cylinder that collects the condensate

Measurement Equipment

- 100 mL volumetric cylinder (2) – to measure initial and/or final reservoir volume
- 50 mL volumetric cylinder (2) – to collect condensate and measure final reservoir volume
- IR thermometer to measure temperature of boiling water

Safety Equipment

- Safety glasses
- Latex or vinyl gloves
- Insulated gloves for handling hot distillation equipment

Other Supplies

- 250 mL squirt bottle with deionized water for initial reservoir
- 20 mL scintillation vials (3)
- Label tape (1 roll)
- Sharpie (1)

DISTILLATION EXPERIMENT: STEP-BY-STEP INSTRUCTIONS

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.
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 all the completed experiments is provided to the students prior to the start of the second lab period. They should discuss their results within their group. The students are asked to do the exercises listed below and answer the accompanying analytical and research questions using data from all groups, not just their own group.

1. Using the mass balance equation

$$\delta^{18}\text{O}_{\text{initial reservoir}} = \delta^{18}\text{O}_{\text{final reservoir}}(f) + \delta^{18}\text{O}_{\text{condensate}}(1 - f) \quad (3)$$

where f = fraction of reactant (reservoir) remaining, determine the theoretical (expected) isotopic composition of the initial reactant (your initial reservoir). You will have one

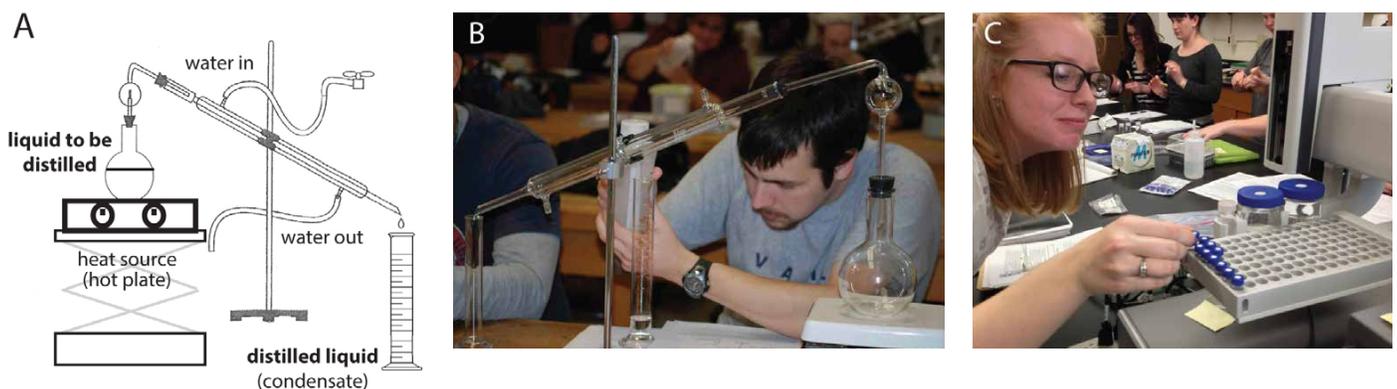


FIGURE 3. Distillation experiment and measurement: (A) Laboratory setup. (B) Student measuring initial water with distillation setup in standard classroom. (C) Student loading autosampler for Picarro water isotope analyzer.

experimental value from each group. What is the average value and standard deviation for the calculated initial reservoir? How does this **calculated** $\delta^{18}\text{O}_{\text{initial reservoir}}$ compare with the **measured** $\delta^{18}\text{O}_{\text{initial reservoir}}$? What is the propagated error (the square root of the sums of squares of the standard deviations of the measured $\delta^{18}\text{O}_{\text{final reservoir}}$ and $\delta^{18}\text{O}_{\text{condensate}}$) for the **calculated** $\delta^{18}\text{O}_{\text{initial reservoir}}$?

2. Create a figure in Excel with two sets of data on the same plot (Figure 4). Plot $\delta^{18}\text{O}_{\text{final reservoir}}$ (the reactant) vs. f , and $\delta^{18}\text{O}_{\text{condensate}}$ (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 $\delta^{18}\text{O}_{\text{final reservoir}}$ (reactant) vs. f and $\delta^{18}\text{O}_{\text{condensate}}$ (cumulative product) vs. f . Display the equations for the curves, which should have the form of $\delta^{18}\text{O}_w = a \cdot \ln(f) + b$. What trends do you see?
4. Using a derivation of the Rayleigh equation and applying the measured $\delta^{18}\text{O}$ values given in the equation that follows, calculate the fractionation factor ($\alpha_{\text{vapor-liquid}}$) between vapor and liquid during evaporation.

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

You will have one value of $\alpha_{\text{vapor-liquid}}$ 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: $\alpha_{v-l} = 0.996$ at 100°C or $\alpha_{v-l} = 0.990$ at 25°C from Horita and Wesolowski (1994)? What role does temperature play?

5. The accuracy of your results depends in part on how much sample is lost during the experiment. Calculate the difference between the published measurement of $\alpha_{v-l} = 0.996$ at 100°C and the experimental measurement of α_{v-l} from each group. Plot the difference vs. the percent of water lost by each group; do you see a trend? (See Figure 4 for example of results.)

RESEARCH QUESTIONS

In the Discussions and Conclusions section of the lab report, students answer the following questions, which connect the experiment to the natural earth system and to paleoclimate.

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?

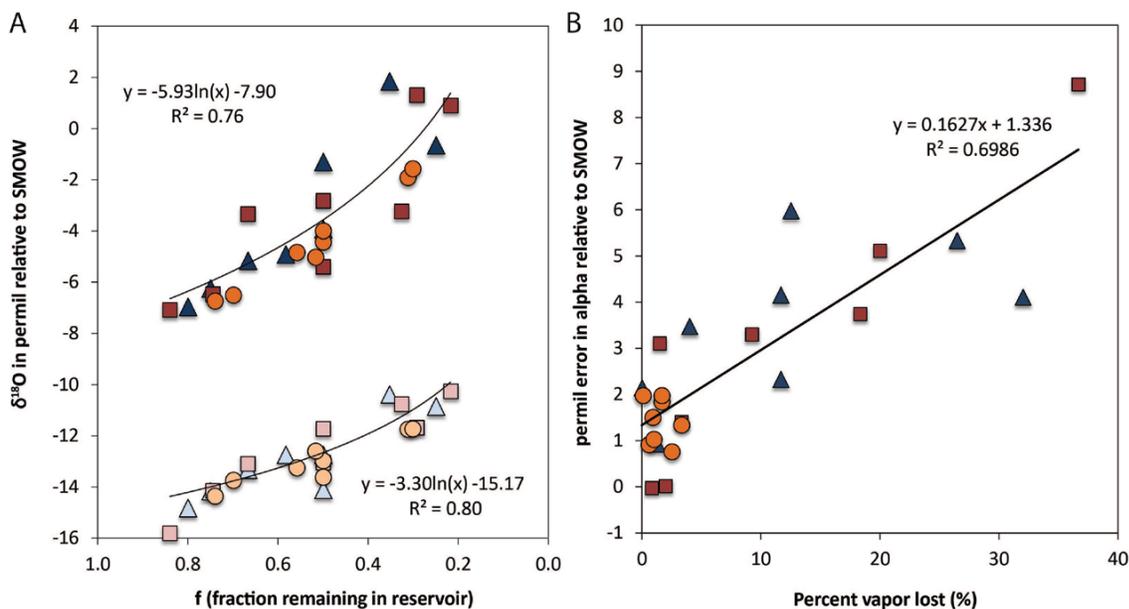


FIGURE 4. Results from three classes (more than 20 experiments) with variable fractions evaporated from the initial reservoir. Offsets between the original water used for each class are removed so that the data can be plotted together as regional differences are seen in the initial $\delta^{18}\text{O}$ water. (A) Reservoir (reactant) in solid dark symbol and condensate (product) in light symbols for each experiment evaporating various fractions in per mil (‰) relative to standard mean ocean water (SMOW). (B) Percent vapor lost compared to the per mil (‰) error in fractionation factor (α) for evaporation at 100°C . Results from each class are plotted with different symbols. The analytical uncertainty for $\delta^{18}\text{O}$ is $\pm 0.08\text{‰}$, which is less than the size of the symbols plotted. The reported uncertainty is based on a combined standard uncertainty including uncertainty associated with IAEA standards, with calibration of internal standards, and with variability between instrument runs, providing a level of confidence of approximately 95%.

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”)? Given this observation, how would salt content (salinity) vary with $\delta^{18}\text{O}_w$? Would this effect for surface waters be different at low vs. high latitudes? What else could affect surface $\delta^{18}\text{O}_w$ of low vs. high latitudes?

POSSIBLE MODIFICATIONS TO ACTIVITY

As part of a three-year, National Science Foundation-funded Geoscience Education project, we conducted this lab in a variety of ways at multiple institutions and in different classes (paleoceanography, environmental geochemistry, sedimentology and stratigraphy) to explore how student learning is impacted by different styles of delivery (Griffith et al., 2014; Jefferson et al., 2014). The exercise as described here requires (1) lab space with sinks and running water for each student group to operate the distillation apparatus, and (2) access to an instrument to make isotope measurements. Depending on available resources and infrastructure, we suggest the following modifications:

- The experiment can be modified to include analysis of H isotopes in addition to O isotopes. Plotting δD vs. $\delta^{18}\text{O}$ for the experimental data along with a local or meteoric water line (if available) allows for interpretation of the experimental data as an evaporative line and discussion of the regional hydrologic cycle. Furthermore, deuterium (^2H or D) excess could be calculated and discussed as it is related to humidity at the moisture source (see Clark and Fritz, 1997).
- A standard classroom with tables, but no running water, can be used by wrapping bags of ice around the distillation column to condense the water vapor. Loss of water vapor during the experiment would be significant, but trends would be measurable and predictable following the analysis as it is outlined here.
- The experimental setup could be simplified using a standard lab beaker and hotplate, rather than employing a distillation apparatus. This modification would be simple, fast, and less expensive, but it prevents isotopic analysis of the condensate, which reinforces the fundamental concept of isotopic fractionation because the condensate is so much lighter isotopically than the initial reservoir or final reservoir.
- Isotopic measurements could be conducted with either an in-house CRDS or IRMS system, or arrangements could be made to analyze at an external laboratory with sufficient time to provide results immediately to the students (see online supplementary Table S2 for list of possible labs).
- The lab can be run as a “pen and paper” lab using archived measurements presented here and available at: <https://sites.google.com/a/kent.edu/d-edgeo>. Alternatively, the experimental activity could be incorporated into a nontraditional lab format that ties it to a modern problem like sea level change. 

SUPPLEMENTARY MATERIALS

The following supplementary materials are available online at <http://dx.doi.org/10.5670/oceanog.2015.89>.

Lab Guide. The group lab guide, *Rayleigh Isotope Effect in the Oceans: Building Glaciers*, includes the lab hypothesis, methods, results (including calculations), discussion, and conclusion.

Table S1. Approximate activity budget (compiled in 2015).

Table S2. Selection of stable isotope laboratories that provide commercial analysis (costs based on 2015 rates).

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