EOS 240: Lab Assignment 7

Measuring Stable Isotopes

Due: 2:30 pm March 21, 2024 (Th section)
Due: 1:30 pm March 22, 2024 (F section)

You have one week to complete this assignment. You should submit your response to the course Brightspace page as a single PDF file. **Additionally, we ask that you upload a copy of the scripts, code, or spreadsheets you used to complete the assignment. These documents will help us track down mistakes.** Responses to questions should be typed, using complete sentences and standard grammar. If you choose to support your answers with hand-drawn illustrations or hand-written calculations, you should scan or photograph the written work and integrate it into your PDF file as a figure. Double check that your image resolution is high enough to read. A google search of 'PDF combiner' will return a number of webpages that allow you to upload individual images and combine them into a single .pdf file (example: combinepdf.com). There are also a number of good apps for mobile phones. If you write your response in a word processor, please export to .PDF before submitting your response.

You are not excluded from working with others (pairs are recommended), but each person will submit their own copy of the assignment. In your submission, include the names of anyone you worked with on the assignment.

To answer the questions, you can perform calculations and make figures using Excel (an open source alternative: www.libreoffice.com), or with a program or programming language of choice.

Name : _____

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Marks:	5	10	5	20
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Question 1   (20)
ANALYZING $CaCO_3$

Speleothems are cave formations that form as calcium and carbon rich groundwater reaches a cave and begins to equilibrate with air inside. This process leads to degassing and the precipitation of $CaCO_3$:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$

Stalagmites are a type of speleothem that grow upwards from the floor of a cave as groundwater drips down from the cave ceiling. The growth of stalagmites can take hundreds to thousands of years and layers within the stalagmite can record changes in the isotopic composition of the dripping ground water as well as changes in the cave temperature. You have micro-drilled and collected two $CaCO_3$ powders from a stalagmite in your favorite local cave, one sample from the base (older) and one sample from the top (younger). You bring these samples to the gas-source mass spectrometer in SEOS at UVic and plan to determine if the isotopic composition of the stalagmite has changed over the duration of its growth.

To analyze your carbonate ($CaCO_3$) powders, you must first dissolve the powder with an acid to create CO_2 gas.

$$3CaCO_3(s) + 2H_3PO_4(aq) \rightarrow Ca_3(PO4)_2(aq) + 3CO_2(g) + 3H_2O(l)$$
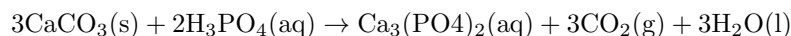
This CO_2 gas is then ionized in the *source* of the mass spectrometer using a high voltage, and then the CO_2^+ ions are accelerated down a flight tube where the charged particles are deflected by a magnetic field. Particles are deflected according to their mass to charge ratio. Variations in the mass of carbon and oxygen are called *isotopes*, and the following table describes the naturally occuring abundance of the stable isotopes of these two elements.

Element	Stable Isotope Masses	Fractional Abundance
Carbon	12, 13	0.9893, 0.0107
Oxygen	16, 17, 18	0.99757, 3.8 x 10^{-4}, 2.05 x 10^{-3}

(a) (3 points) Variations in the isotopic composition of CO_2^+ are called *isotopologues*. Use the carbon and oxygen *isotope* table above to determine the possible configurations of CO_2^+ isotopologues and the relative abundance of each unique mass. I have provided the first two for you. *Hint: the fractional abundance of an isotopologue is equal to the product of the fractional abundances of each isotope in the isotopologue.*

Mass	Isotopologues	Fractional Abundance
44	$^{16}O^{12}C^{16}O$	0.9845
45	$^{16}O^{13}C^{16}O$, $^{17}O^{12}C^{16}O$, $^{16}O^{12}C^{17}O$	0.0114
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Your mass spectrometer is tuned to analyze the three most abundant masses of CO_2^+: 44, 45, and 46. Beams of these singly-charged CO_2^+ particles are focused into three conductive metal cylinders, called Faraday cups. When the charged particles hit the conductive metal cup, they are neutralized, transfering their charge to the metal. The cup is then discharged to produce a current that is proportional to the number of charged particles in the beam. Each collector is fitted with appropriate resistor so that the output voltage (current) of each ion beam are close to the same.

(b) (2 points) In the *dataset.csv* file you will find time series of voltages recorded by your mass spectrometer as the CO_2^+ from your sample is analyzed. Make a figure showing a time series (time on the x-axis) of the mass 44, 45, and 46 voltages that correspond to your sample from the bottom of the stalagmite.

You should find that there is a high signal plateau in the middle of your time-series, and that plateau is surrounded by low background noise associated with the electronics in your machine. The high voltage plateau corresponds to the time when the CO_2^+ beam was hitting the Faraday cup. You will use ratios of the high-signal voltage to determine the relative abundance of each charged particle beam. However, first you must clean up the signal by removing the background noise. To remove this noise, subtract the average of the low signal noise on each side of your sample peak from the average voltage of the sample peak.

(c) (2 points) What are the average voltages of your cleaned signal for the stalagmite bottom sample?

You now want to convert these voltages to ratios of ^{13}C to ^{12}C and ^{18}O to ^{16}O. To solve this problem, first we must define some standard notations. We use the letter $\mathbf{R}$ to designate the ratio of a particular isotopic species to the related isotopic species of the lowest mass:

$$^n R = \frac{\text{mols of isotopic species of mass n}}{\text{mols of base species related to n}}$$

For example, the base species for ^{13}R is ^{12}C and the base species for ^{46}R is $^{12}C^{16}O_2$. We use the letter $\mathbf{F}$ to describe the fractional abundances of an isotopic species or isotopologue:

$$^n F = \frac{\text{mols of isotopic species of mass n}}{\text{sum of species related to n}}$$

You already calculated CO_2 fractional abundances in part (a) as a function of the individual carbon and oxygen isotope fractions (e.g., ^{13}F and ^{16}F). For example:

$$^{45}F = ^{13}F \cdot {}^{16}F \cdot {}^{16}F + 2 \cdot {}^{12}F \cdot {}^{16}F \cdot {}^{17}F$$

(d) (3 points) What are the corresponding expressions for ^{44}F and ^{46}F?

(e) (2 points) If you divide your expressions for ^{46}F and ^{45}F by ^{44}F, you should get a new expression in terms of isotopic ratios, $\mathbf{R}$. What are the expressions for ^{45}R, and ^{46}R? *Hint: there should be no* F *remaining in these expressions.*

^{45}R and ^{46}R are equal to the corresponding ratio of voltages collected by your mass spectrometer. In other words, the voltage of mass 45 divided by the voltage of mass 44 should be equal to ^{45}R. You can use your expressions in the previous question to solve for the ^{13}R and ^{18}R of each sample. For simplicity, for the rest of the problem set we will assume that $^{17}R = 0$ (in the real world, we have to account for trace amounts of ^{17}O, but the challenge of solving that problem is beyond the scope of this assignment).

(f) (2 points) What is ^{13}R and ^{18}R of each of your samples, as measured in the SEOS lab?

(g) (1 point) For quality control, you send your samples to a colleagues lab to be measured in exactly the same way. What is ^{13}R and ^{18}R of each of your samples, as measured in your colleagues lab?

(h) (1 point) What is the difference in the absolute ratio, ^{13}R, for your bottom sample when comparing the SEOS lab to your colleagues lab?

Large differences in raw measured ratios exist between labs due to the unique conditions and components of each mass spectrometer and the partial pressure of the CO_2^+ delivered to the flight tube. While the raw ratios may differ greatly, the measured difference between two samples should be consistent from lab to lab. We introduce delta notation to describe the isotopic composition of samples relative to each other (or relative to a widely distributed sample material). Delta notation:

$$\delta^n X_{STD} = 10^3 \cdot \left(\frac{^n R_{sample}}{^n R_{standard}} - 1 \right)$$

(i) (2 points) Using your bottom sample as our reference standard, what is the $\delta^{13}C_{bottom}$ and $\delta^{18}O_{bottom}$ of your top sample (provide the solutions from each lab).

(j) (2 points) What processes do you think are responsible for the change in $\delta^{13}C_{bottom}$ and $\delta^{18}O_{bottom}$ you observe in this stalagmite?