

**Question 1.1**

An ion current of  $10^{-11}$  ampere ( $A = C\ s^{-1}$ ; Ampere = Coulomb per second) corresponds to 62,415,096 elementary charges arriving at the detector per second, taking the elementary charge of  $e = 1.6021765 \times 10^{-19}\ C$  into account. Assuming identical transmission between SEM and Faraday detectors, the ratios of the  $^{18}O$  and  $^{16}O$  ion beams are:

0.00206678 for glacial forams and  
0.00206346 for interglacial forams.

**Question 1.1.1 (5 points)**

Normalizing to the VPDB standard, the delta values for glacial and interglacial forams are -0.20 (-0.203) and -1.81 (-1.809) per mil.

The saturated mixing ratio at 20°C air temperature and 1000 mbar is 14.86 gram per kilogram. The saturated mixing ratios at -5°C and -22°C at the same pressure and starting temperatures (assuming saturation) are 2.63 grams/kg and 0.65 grams/kg. This means that the water vapor fractions remaining for both scenarios are 0.17698 (0.177) 0.04374 (0.044), respectively (calculated using the Mixing Ratio calculator at [www.srh.noaa.gov/epz/?n=wxcalc\\_mixingratio](http://www.srh.noaa.gov/epz/?n=wxcalc_mixingratio)).

**Question 1.1.2 (5 points)**

Note that the universal gas constant  $R$  needs to be in units of  $\text{cal mol}^{-1}\ \text{K}^{-1}$  (i.e. 1.9858775), and that the temperature values (in degree Celsius) need to be converted to Kelvin. The alpha values for the relevant temperatures are:

20°C 1.009201  
7.5°C 1.010421 (this is the mean temperature of 20°C and -5°C)  
-1°C 1.011316 (this is the mean temperature of 20°C and -22°C)  
-5°C 1.117563  
-22°C 1.013788,  
indicating greater fractionation at lower temperatures.

**Question 1.1.3 (5 points)**

Calculate delta values for the condensate from Willi Dansgaard's formula #6 in his 1964 Tellus (4, 436-468) article. These values (relative to SMOW) are:

-15.4 (-15.398) per mil for the Emiliani (cooling from 20°C to -5°C) case and  
-30.4 (-30.405) per mil for the Dansgaard & Tauber (cooling from 20°C to -22°C) case.

These values are the values of ice locked in the 130 meters of ice-equivalent water that melted since the last glacial maximum. The 69 meters of water-equivalent ice existing during the current interglacial is 5 per mil heavier, i.e.

-10.4 per mil for the Emiliani case

-25.4 per mil for the Dansgaard & Tauber case.

### Question 1.2 (20 points)

Charette and Smith (2010, *The Volume of Earth's Ocean*, Oceanography 23, No. 2) have determined the volume of the ocean at  $1.3324 \cdot 10^9 \text{ km}^3$  (area:  $361.84 \cdot 10^6 \text{ km}^2$ , mean depth: 3682.2 m). Neglecting changes in density, thermal expansion, topography and changes in the area of the ocean on G-IG time scales, 130 meter water-equivalent ice has a volume of  $47.04 \cdot 10^6 \text{ km}^3$ , whereas the remaining 69 meters of water-equivalent ice correspond to a volume of  $24.97 \cdot 10^6 \text{ km}^3$ . The remaining (IG) ice is 5 per mil heavier than the corresponding glacial ice.

The simple mass balance is then:

Emiliani: 
$$\Delta\delta^{18}\text{O}_{\text{sw}} = \frac{(47.04 * 15.4) + (24.97 * 5)}{(1332.4 - 47.04)} = 0.66 \text{ per mil}$$

Dansgaard & Tauber: 
$$\Delta\delta^{18}\text{O}_{\text{sw}} = \frac{(47.04 * 30.4) + (24.97 * 5)}{(1332.4 - 47.04)} = 1.21 \text{ per mil}$$

With a total change of 1.61 per mil, Emiliani's scenario attributes 41 (40.99) % to changes in ice volume and composition, whereas Dansgaard & Tauber argue that it is 75 (75.16) %.

### Question 1.3 (20 points)

The Erez & Luz (1983, best-fit constants below are from their table 2) equation for paleotemperature (in °C) is:

$$T (^{\circ}\text{C}) = 16.998 - 4.52 (\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{sw}}) + 0.028 (\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{sw}})^2$$

Note that this equation requires delta values normalized to VPDB, not VSMOW. The equation also relies on measurements of  $\text{CO}_2$  released from carbonates upon decomposition with phosphoric acid ( $\delta^{18}\text{O}_{\text{carb}}$ ), and on equilibrating  $\text{CO}_2$  with seawater ( $\delta^{18}\text{O}_{\text{sw}}$ ) at a constant temperature ( $\delta^{18}\text{O}$  of seawater is very difficult to measure directly, because water is such a sticky molecule in mass spectrometers). The  $\delta^{18}\text{O}_{\text{sw}}$  term in the equation (relative to VPDB) can be related to our VSMOW scale by:

$$\delta^{18}\text{O}_{\text{sw-VPDB}} = \delta^{18}\text{O}_{\text{sw-VSMOW}} - 0.27$$

The relevant differences (parentheses) in the Erez & Luz equation are therefore:

Interglacial:  $(\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{sw}}) = -1.539$

Emiliani glacial:  $(\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{sw}}) = -0.593$

Dansgaard & Tauber glacial:  $(\delta^{18}\text{O}_{\text{carb}} - \delta^{18}\text{O}_{\text{sw}}) = -1.143$

With this, the interglacial temperature is  $24.02^{\circ}\text{C}$ . The glacial temperature with the Emiliani scenario is  $19.69^{\circ}\text{C}$ , whereas the glacial temperature with the Dansgaard & Tauber scenario is  $22.20^{\circ}\text{C}$ . The glacial-interglacial temperature differences derived for these two scenarios are  $4.3^{\circ}\text{C}$  (Emiliani) and  $1.8^{\circ}\text{C}$  (Dansgaard & Tauber).

**Note:** the above conversion deal with measurements of CO<sub>2</sub> gas (real life, CO<sub>2</sub> measurements generated by reacting carbonate with phosphoric acid, or by equilibrating CO<sub>2</sub> gas with seawater at 25°C in so-called Kiel devices – originally developed at GEOMAR in Kiel, Germany), as our foram data were generated in this fashion. If you want to convert delta values from VPDB to VSMOW scales or vice versa, the following equations have to be used (the numbers in parentheses are alternative values – different conversion schemes have slightly different constants (i.e. 1.03086 (92) means that one study uses a value of 1.03086 whereas another uses a value of 1.03092), giving you a sense of the uncertainty associated with these conversions:

$$\delta^{18}\text{O}_{\text{VSMOW}} = 1.03086 \text{ (92)} \delta^{18}\text{O}_{\text{VPDB}} + 30.86 \text{ (30.92)}$$

$$\delta^{18}\text{O}_{\text{VPDB}} = 0.97006 \text{ (01)} \delta^{18}\text{O}_{\text{VSMOW}} - 29.94 \text{ (29.29)}$$

## Question 2 (15 points)

We start by realizing that the measurement will be limited by the count-rate of the less abundant isotope. This is  $C^{18}O^{16}O$ , which is 0.4% of the more abundant  $C^{16}O^{16}O$ . Put another way, the  $^{16}O$  count will be 250 times greater than the  $^{18}O$  count, and hence measured to 16 times greater accuracy. Considering the implied “imprecision” of the other factors given and the way errors propagate in the isotope ratio calculation, ignoring this contribution to measurement error is justified. Now since the measurement is ion current limited, and the target precision is 0.01‰ (one part in  $10^5$ ), it would at first seem that we would need to acquire  $10^{10}$  counts (recall that counting precision goes as  $N^{-0.5}$ ). However, since we need to measure both unknown and standard, we need to now both better due to the propagation of errors.

That is, we need to have a precision that is  $1/\sqrt{2}$  better for both. (Think about computing the ratio of the two and propagating the errors!) Thus we need to count *twice* as many ions for both standard and unknown. Inasmuch as the standard will likely be unlimited in size and we’re asked to determine how much unknown we need, we proceed with that. Working backwards from that, there will be approximately 250 ions delivered to the detectors for every one  $C^{18}O^{16}O$  ion received. Thus we need to deliver  $250 \times 2 \times 10^{10} = 5 \times 10^{12}$   $CO_2^+$  ions (remember the factor of two because of the standard/unknown symmetry. Now we need to feed the source 900 atoms for every ion sent to the detectors, so the requirement now becomes  $4.5 \times 10^{15}$   $CO_2$  molecules. Finally, the gas delivery system is only 50% efficient so we need to have  $9 \times 10^{15}$   $CO_2$  molecules in our sample. Given Avogadro’s number, this means that we require

$$S = \frac{9 \times 10^{15} \text{ atoms}}{6.025 \times 10^{23} \text{ atoms/mole}} = 1.5 \times 10^{-8} \text{ mole} = 0.015 \mu\text{mol}$$

Now the over-fastidious student might consider the contribution of  $C^{13}O^{16}O^{17}$  and  $C^{12}O^{17}O^{17}$  to the mass 46 channel. The presence of other ions, that can and would be subtracted, will “pollute” the ion counts and inflate the error. Fortunately, the contributions (an exercise to the student) are extremely small.

### Question 3 (15 points)

The first step is to list the isotopologues of  $N_2O$ , and then give the normalized ion currents, given by isotope ratios relative to the most abundant isotopes:

| Mass | Isotopologues                                                                       | Ratios                                                |
|------|-------------------------------------------------------------------------------------|-------------------------------------------------------|
| 44   | $^{14}N^{14}N^{16}O$                                                                | =1                                                    |
| 45   | $^{15}N^{14}N^{16}O + ^{14}N^{15}N^{16}O + ^{14}N^{14}N^{17}O$                      | $2 * R_{15/14} + R_{17/16}$                           |
| 46   | $^{15}N^{15}N^{16}O + ^{14}N^{15}N^{17}O + ^{15}N^{14}N^{17}O + ^{14}N^{14}N^{18}O$ | $R_{15/14}^2 + 2 * R_{15/14} * R_{17/16} + R_{18/16}$ |

Substituting the atmospheric isotopic ratios for  $^{15}N/^{14}N = 3.6765 \times 10^{-3}$ ,  $^{17}/^{16}O = 3.799 \times 10^{-4}$ , and  $^{18}O/^{16}O = 2.0052 \times 10^{-3}$ , we can substitute into the isotopologue list above to get

$$45/44 = 7.733 \times 10^{-3} \text{ and } 46/44 = 2.02151 \times 10^{-3} \text{ for the } N_2O \text{ distributions.}$$

This is what we actually measured. We then do the same for the  $CO_2$  distributions, which have a slightly greater number (5) of isotopologues at mass 46, we create the following equations:

$$45/44 = R_{13/12} + 2 * R_{17/16} = 3.65765 \times 10^{-3}$$

$$46/44 = 2 * R_{13/12} R_{17/16} + 2 * R_{18/16} + R_{17/16}^2 = 2.0052 \times 10^{-3}$$

This is two equations in three unknowns, so we need to use a third constraint to solve for all three variables, which is that since  $\delta^{17}O = 0.516 \delta^{18}O$ . Substituting into the definition of  $\delta$  referenced to SMOW, we have

$$\frac{(R_{17/16})_{Unknown}}{(R_{17/16})_{SMOW}} = 0.516 \frac{(R_{18/16})_{Unknown}}{(R_{18/16})_{SMOW}} + 0.484$$

And substituting in the values for SMOW, this reduces to

$$(R_{17/16})_{Unknown} = 0.095530 (R_{18/16})_{Unknown} + 1.8387 \times 10^{-4}$$

Now we have three equations in three unknowns, which can be solved either iteratively (the hard way), by substitution of the third equation into the first two combined with a little algebra, or with a non-linear equation solver (e.g., in MATLAB). We get

$$R_{13/12} = 0.00717 \Rightarrow \delta_{PDB}^{13}C = -359 \text{ ‰}$$

$$R_{18/16} = 0.001009 \Rightarrow \delta_{SMOW}^{18}O = -496 \text{ ‰}$$

You could also solve the above problem using 45/44 and 46/45, but it would be more complicated.

#### Question 4 (15 points)

I preface this solution with an apology: Kyrstin pointed out an error in the  $\Delta G$  units used (they were listed as kJ/mol) in the table, but they should be in the older units of kCal/mol. This means that those who did not receive correct guidance on the error were off by a factor of  $\sim e^4$ , or an order of magnitude. Students were not penalized for this, although I need a good flogging....

We first write out the reaction equation:  $H_2 + HDO \rightleftharpoons HD + H_2O$  which allows us to write the reaction constant as

$$K = \frac{R_{H_2}}{R_{H_2O}} = \frac{[H_2O][HD]}{[HDO][H_2]} = e^{\frac{-\Delta G}{RT}}$$

where the un-subscripted  $R$  is the gas constant (not to be confused with the isotope ratios). We can rewrite this as

$$\alpha = \frac{R_{H_2O}}{R_{H_2}} = e^{\frac{\Delta G}{RT}}$$

Now we can calculate from the table values that

$$\Delta G = \Delta G_f^0(HD) + \Delta G_f^0(H_2O) - \Delta G_f^0(H_2) - \Delta G_f^0(HDO) = 0.735 \text{ kCal/mol}$$

Substituting the value for  $RT$

$$RT = 1.987 \frac{\text{Cal}}{\text{mol} \cdot K} \times 298K = 0.5921 \frac{\text{kCal}}{\text{mol}}$$

we get

$$\ln(\alpha) = \frac{0.735}{0.5921} = 1.2413$$

$$\alpha = e^{1.2413} = 3.4603$$

Since the original gas has  $\delta D = -60\text{‰}$  with respect to VSMOW, its ratio is 0.940 (remember you should always convert to and work in terms of isotope ratios, and then compute delta values). This means the final ratio of the water vapor with respect to VSMOW is  $0.940 \times 3.4603 = 3.2526$  (note that this is a *huge* effect, while typical values for other isotopes are much closer to unity). That is, there is a strong affinity for D to concentrate preferentially in the water molecule. Using the delta notation, we arrive at

$$\delta D_{H_2O} = (3.2526 - 1) \times 1000\text{‰} = 2526\text{‰}$$

If you write the original equation in reverse, *i.e.*,  $HD + H_2O \rightleftharpoons H_2 + HDO$

it still works out the same because the different summation/difference would lead to the sign in the exponent for  $\alpha$  being the opposite and we would have to use  $1/\alpha$  to have the correct sense. That is, the equations have symmetry.