Geobiology Spring 2013
Isotope Problem Set Solutions

1. **Identify and calculate the exact molecular weights of all the isotopologues of CO_2 and H_20. Calculate their relative abundances in a sample of seawater assuming all atoms are at their natural abundances and there are no isotope effects.**

   I calculated the solutions in an excel file using the following information about exact mass and natural abundance:

	Exact Mass	Natural Abundance (%)
^{1}H	1.007825	99.985
^{2}H	2.014102	0.015
^{12}C	12	98.89
^{13}C	13.003355	1.11
^{16}O	15.994915	99.759
^{17}O	16.999131	0.037
^{18}O	17.999159	0.204

   Notice that both CO_2 and H_2O are symmetrical molecules, so we need to multiply by 2 for isotopologues that can be created in 2 equally likely ways. For example: $^{16}O=^{12}C=^{18}O$ vs. $^{18}O=^{12}C=^{16}O$ are 2 ways of constructing $^{12}C^{16}O^{18}O$ whereas there is only one way to make $^{12}C^{16}O^{16}O$. The isotopologues that had an additional factor of two due to symmetry consideration are marked in green. Check to make sure your percentages add up to 100.

multipled by a factor of 2 (symmetry considerations)

Water	Exact Mass	Percent
1H 1H 16O	18.010565	99.729
1H 2H 16O	19.016842	0.0299
2H 2H 16O	20.023119	2.245E-06
1H 1H 17O	19.014781	0.0370
1H 2H 17O	20.021058	1.11E-05
2H 2H 17O	21.027335	8.325E-10
1H 1H 18O	20.014809	0.20394
1H 2H 18O	21.021086	6.119E-05
2H 2H 18O	22.027363	4.59E-09

Carbon Dioxide	Exact Mass	Percent
12C 16O 16O	43.98983	98.414
12C 16O 17O	44.994046	0.073
12C 16O 18O	45.994074	0.402
12C 17O 17O	45.998262	1.35E-05
12C 17O 18O	46.99829	1.49E-04
12C 18O 18O	47.998318	0.00041
13C 16O 16O	44.993185	1.10466
13C 16O 17O	45.997401	0.00082
13C 16O 18O	46.997429	0.00452
13C 17O 17O	47.001617	1.52E-07
13C 17O 18O	48.001645	3.04E-07
13C 18O 18O	49.001673	4.62E-06

2. **A ratio of $^{32}S/^{34}S$ of 20.031 was measured for a sample of sulfate. The same ratio in the Canyon Diablo Triolite is 22.22. What is the δ34S value for the sulfate sample?**

Given:
Sulfate Sample: $^{32}S/^{34}S$= 20.031
Canyon Diablo Triolite (CDT): $^{32}S/^{34}S$= 22.22

Definition:
$\delta^{34}S_{Sample}$= [($^{34}R_{sample}/^{34}R_{CDT}$) - 1]*1000 where $^{34}R_X=[^{34}S/^{32}S]_x$ (note this is the inverse of how the ratio is given in the problem, so we will need to take the inverse of what's given)

$^{34}R_{Sample}$= 1/20.031= 0.0499226
$^{34}R_{CDT}$= 1/22.22= 0.0450045

$\delta^{34}S_{Sample}$=[(0.0499226/0.0450045) – 1]*1000 =109.28 permil

3. **A sample of diamond has a $\delta^{13}C$ value relative to the lab standard. The lab standard has a $\delta^{13}C$ value of -6.50 relative to VPDB. What is the diamond relative to VPDB?**

Given:
$\delta^{13}C_{Std, VPDB}$=-6.50 permil
$\delta^{13}C_{DMD, Std}$=X
$\delta^{13}C_{DMD, VPDB}$=Y

where Std. is the lab standard, VPDB is the official standard, and DMD is the diamond sample.

Write these in terms of the definition:

$\delta^{13}C_{Std, VPDB}$= [($^{13}R_{Std}/^{13}R_{VPDB}$) - 1]*1000 = -6.50 permil (1)
$\delta^{13}C_{DMD, Std}$= [($^{13}R_{DMD}/^{13}R_{Std}$) - 1]*1000 = X permil (2)
$\delta^{13}C_{DMD, VPDB}$=[($^{13}R_{DMD}/^{13}R_{VPDB}$) - 1]*1000 = Y permil (3)

Solve for $^{13}R_{Std}$ using equation 1:
$^{13}R_{Std}$= [($\delta^{13}C_{Std, VPDB}$/1000) + 1]* $^{13}R_{VPDB}$
= [(-6.50/1000) +1] * $^{13}R_{VPDB}$ where * $^{13}R_{VPDB}=1.12372*10^{-2}$ (can look this up in class notes or on the internet)
$^{13}R_{Std}$= 0.01116416

Now substitute and rearrange equation 2 for $^{13}R_{DMD}$:
$^{13}R_{DMD}=1.116416*10^{-5}*\ \delta^{13}C_{DMD, Std} + 0.01116416$

Substitute into equation 3 and simplify:
$\delta^{13}C_{DMD, VPDB}=0.9935*\ \delta^{13}C_{DMD, Std} - 6.4998$

Would need either a value for $\delta^{13}C_{DMD, Std}$ or $^{13}R_{DMD}$ to be given in order to get a numerical value for $\delta^{13}C_{DMD, VPDB}$.

4. **A bacterium fixes carbon autotrophically and produces biomass with a $\delta^{13}C$ value of -31.6 per mil VPDB starting with atmospheric CO2 having a delta value of -7.8 per mil VPDB. Speculate about the type of isotope effects that might operate and propose possible carbon assimilation pathways. What are the alpha and epsilon values for the sum of the processes.**

Given:
Atmospheric CO_2: $\delta^{13}C$ = -7.8 permil
Autotrophic Biomass: $\delta^{13}C$ = -31.6 permil

Assumptions:
Autotrophic Biomass is fixing inorganic C from atmospheric CO_2 or an inorganic C source with the same isotopic value of atmospheric CO_2. Note: dissolved inorganic C (DIC) species in the oceans have a different isotopic composition compared to the atmospheric C, so calculating the isotopic fractionation using DIC while taking into account carbonate equilibrium considerations instead of atmospheric C will yield a different result.

$\varepsilon_{Prod/Reac} \approx$ -31.6 – (-7.8) = -23.8 permil (*this is an approximation*)
Note that -23.8 permil is close to the isotope effect associated with cyanobacterial Rubisco 2 according to the class notes.

$(\alpha-1)*1000 = \varepsilon$ (*this is the strict definition*)

Solve for α using the $\varepsilon_{Prod/Reac}$ approximated above:

$\alpha_{Prod/Reac} = [\varepsilon/1000]+1 = 0.9762$

The values you get here will depend on how you define epsilon and alpha (ie whether it's product/reactant or reactant/product). Either convention is valid as long as it's specified and consistent throughout the problem.

The above solution is most accurate for an autotrophic organism fixing atmospheric C. Alternatively, you could get a more accurate value for a marine autotrophic organism using bicarbonate. If the atmospheric CO_2 $\delta^{13}C$ = -7.8 permil, then the marine bicarbonate pool will be roughly 0 permil because of equilibrium between atmospheric CO_2 and dissolved CO_2 as well as the additional carbonate species (H_2CO_3*, HCO_3^-, CO_3^{2-}). You can confirm that bicarbonate would be roughly 0 permil by looking at the class slide displaying the natural variability in bulk C isotopes. If the autotroph was using only bicarbonate the you can make the following calculation:

$\varepsilon_{Prod/Reac} \approx -31.6 - (-0) = -31.6$ permil (*this is an approximation*)

where you can solve for alpha in the same way above to yield the following result:

$\alpha_{Prod/Reac} = [\varepsilon/1000]+1 = 0.968$

This value is more like Rubisco 1 for plants and algae.

5. **Inorganic carbon delivered to the ocean/atmosphere system by volcanism and weathering has the $\delta^{13}C$ value of -5 per mil.**

   a) **Calculate the isotopic composition of carbonate minerals precipitated from the seawater, stating your assumptions about different burial fractions and the fractionation by primary producers.**

   $\delta_{in}=f_{Carb} * \delta_{Carb} + f_{Org} * \delta_{Org}$ (1)
   where $f_{Carb} + f_{Org} = 1$

   According to figures in lecture slides based on Des Marais, 2002:

   $f_{Carb} = 0.8$ and $f_{Org} = 0.2$ in the modern

   Given:
   δ_{in}= -5 permil

   Assume:

δ_{Org}= -25 permil

Then substitute into equation 1:

-5= (.8* δ_{Carb}) + (.2*-25)
δ_{Carb} = 0 permil

This value fits within the range of isotopic values for modern carbonates.

b) Carbonate rocks that have a $\delta^{13}C$ value of + 9 per mil are common in the Neoproterozoic. What would you expect f_{org} to have been during the deposition of these carbonates?

Given:

δ_{in}= -5 permil
δ_{Carb}= 9 permil

Assume:

δ_{Org}= -25 permil

Solve for f_{Org} by substituting equation 1 into equation 2:

f_{Carb}= 1- f_{Org} (1)
δ_{in}=f_{Carb} * δ_{Carb} + f_{Org} * δ_{Org} (2)

Inserting known values gives f_{org}=0.41 so f_{Carb}= 0.59.

Hence there were intervals of greater C_{Org} burial in the past relative to the modern.

c) Carbonate rocks that have a $\delta^{13}C$ value of -8 per mil can also be found in a number of Neoproterozoic successions. Which ε and f_{org} can explain the deposition of these carbonates? Propose a mechanism that delivered inorganic carbon with very low $\delta^{13}C$ value to these rocks.

First notice that the carbonate rocks are lighter than the canonical isotopic values of C source from volcanoes and weathering. Therefore, we will need to invoke a source of isotopically light C, such as organic C or methane.

More specifically, if you take a typical value for δ_{Org} (-25 permil) and the volcanic and weathering input value of -5 permil, then you get a *negative* f_{org} unless you choose an unrealistic value of $\varepsilon_{Biomass/DIC}$. This isn't physically possible.

Alternatively, if you have a light C source, say something similar to marine algal biomass (-20 permil):

δ_{in}=f_{Carb} * δ_{Carb} + f_{Org} * δ_{Org}
-20= (1-f_{Org})(-8) + f_{Org} (-25)

f_{Org}= 0.71

This solution allows for a reasonable photosynthetic fractionation and a positive fraction of organic C burial.

d) If carbonate rocks are deposited in areas with a strong delivery of inorganic carbon from carbonate weathering ($\delta^{13}C$ value of + 3 per mil), what would you expect their $\delta^{13}C$ value to be? State your assumptions.

Given:
δ_{in}= 3 permil

Assume:
Same f_{Org} and f_{Carb} as given in slide based on Des Marais 2002.
δ_{Org}= -25 permil

Again use the following equation:
$\delta_{in}=f_{Carb} * \delta_{Carb} + f_{Org} * \delta_{Org}$

Plug in the values to get δ_{Carb} = 10 permil

Note that you could make other assumptions to get different answers to most parts of this problem, but be sure to check that your assumptions are reasonable and give reasonable values.

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