ESS 312 Geochemistry Tutorial on Stable Isotopes

(1) Isotopic compositions – the "δ" value.

Differences in the $^{18}O/^{16}O$, D/H or $^{13}C/^{12}C$ ratio among natural substances are small. Moreover, these absolute isotopic ratios are seldom measured. Instead, measurements are made by comparing the ion beams from a sample and an appropriate standard in a mass spectrometer. Hence the isotopic composition of a sample is determined relative to a standard material. A convenient way to express these relative differences in large, easy-to-remember numbers is the "δ" notation:

$$\delta^{18}O_{sample-standard} = 1000\left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample} - \left(\frac{^{18}O}{^{16}O}\right)_{standard}}{\left(\frac{^{18}O}{^{16}O}\right)_{standard}}\right)$$

$$= 1000\left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample}}{\left(\frac{^{18}O}{^{16}O}\right)_{standard}} - 1\right).$$

Likewise:
$$\delta^{13}C_{sample-standard} = 1000\left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample} - \left(\frac{^{13}C}{^{12}C}\right)_{standard}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}}\right),$$

and:
$$\delta D_{sample-standard} = 1000\left(\frac{\left(\frac{D}{H}\right)_{sample} - \left(\frac{D}{H}\right)_{standard}}{\left(\frac{D}{H}\right)_{standard}}\right).$$

The standard values in these expressions are the $^{18}O/^{16}O$, $^{13}C/^{12}C$ and D/H ratios of the standards:

Standard mean ocean water (SMOW or V-SMOW): $^{18}O/^{16}O = 0.0020052$
$D/H = 0.00015576$

and for C isotopes, the "Pee Dee belemnite" (PDB): $^{13}C/^{12}C = 0.011238$.

These "δ" values are stated in parts per thousand, or "per mil", which is written "‰". In effect, the $\delta^{18}O$ value of a substance is the difference in parts per thousand between its $^{18}O/^{16}O$ ratio and that of the relevant standard (generally SMOW). A substance with a higher $^{18}O/^{16}O$ ratio than SMOW will have a positive δ value. If the $^{18}O/^{16}O$ ratio of the substance is lower than the $^{18}O/^{16}O$ ratio of SMOW, its δ value will be negative. Occasionally a substance with a higher isotopic ratio than the standard is referred to as isotopically "heavy", because it is richer in the heavy isotope (^{18}O, ^{13}C, D ...) than the standard. Conversely, a substance with a negative δ value (i.e. depleted in the heavy isotope) is sometimes referred to as "isotopically light". The delta values of SMOW (O and H isotopes) and PDB (C isotopes) are zero, by the definitions above.

The following calculations will give you some practice in using the δ notation:

(i) The pyroxene and plagioclase feldspar in a gabbro have $\delta^{18}O$ values relative to the SMOW standard of 7‰ and 7.7‰ respectively. Calculate the absolute $^{18}O/^{16}O$ ratios of these two minerals. Notice how small the difference is.

(ii) A sample of Antarctic snow has an $^{18}O/^{16}O$ ratio of 0.0019250 and a D/H ratio of 0.00010747. What are its $\delta^{18}O$ and δD values?

(iii) A sample of coral has a $\delta^{18}O$ value relative to the SMOW standard of 26‰. What is its absolute $^{18}O/^{16}O$ ratio ?

(iv) Labs that make O isotope measurements of marine carbonates (foraminifera, coral, limestones, etc) find it handy to use the PDB standard for <u>both</u> O and C measurements. The $\delta^{18}O$ value of PDB calcite relative to the SMOW standard is 30.9‰. Calculate the absolute $^{18}O/^{16}O$ ratio of PDB calcite. Now use this to calculate the $\delta^{18}O$ value of the coral sample from question (iii) above <u>relative to the PDB standard</u>. Add the $\delta^{18}O$ value of PDB calcite relative to SMOW to the $\delta^{18}O$ value of the coral relative to PDB (i.e. $\delta^{18}O_{PDB\text{-}SMOW} + \delta^{18}O_{coral\text{-}PDB}$). How close is the result to $\delta^{18}O_{coral\text{-}SMOW}$?

(2) <u>Isotopic fractionation between substances at equilibrium</u>.

O-bearing compounds in chemical equilibrium with one another generally <u>do not</u> have the same O isotopic composition. Instead, differences in the bonding environment of O in the two compounds result in a slight enrichment of ^{18}O in one compound relative to the other. This is usually described as a "fractionation" of ^{18}O between the two compounds. As a result, the two compounds have different $^{18}O/^{16}O$ ratios, hence different $\delta^{18}O$ values (by the definition in part 1). The situation is identical for the fractionation of C, H, N ... isotopes between compounds containing those elements.

The fractionation of ^{18}O between the compounds can be described by an equilibrium constant, which you'll generally see written as "α":

For an isotope exchange reaction such as $^{12}CO_2 + {}^{13}CH_4 = {}^{13}CO_2 + {}^{12}CH_4$,

α is written in the usual way:

$$\alpha_{CO_2-CH_4} = \frac{\left({}^{13}CO_2\right)\left({}^{12}CH_4\right)}{\left({}^{12}CO_2\right)\left({}^{13}CH_4\right)} = \frac{\left(\frac{{}^{13}CO_2}{{}^{12}CO_2}\right)}{\left(\frac{{}^{13}CH_4}{{}^{12}CH_4}\right)} = \frac{\left(\frac{{}^{13}C}{{}^{12}C}\right)_{CO_2}}{\left(\frac{{}^{13}C}{{}^{12}C}\right)_{CH_4}}.$$

Note that the ratios of the activity coefficients for the isotopic variants of each compound are equal to 1. For an isotopic substitution reaction, the equilibrium constant is just a statement about how the isotopes distribute themselves between the compounds. Typical values for α are between 0.95 and 1.05.

Now express the $^{13}C/^{12}C$ ratios of the two compounds in terms of their δ values. (Notice that the term $(^{13}C/^{12}C)_{PDB}$ cancels out top and bottom):

$$\alpha_{CO_2-CH_4} = \frac{\left(1+\frac{\delta^{13}C_{CO_2}}{1000}\right)}{\left(1+\frac{\delta^{13}C_{CH_4}}{1000}\right)}$$

Taking the natural log of both sides and multiplying by 1000 gives:

$$1000\ \ln\left(\alpha_{CO_2-CH_4}\right) = 1000\ \ln\left(1+\frac{\delta^{13}C_{CO_2}}{1000}\right) - 1000\ \ln\left(1+\frac{\delta^{13}C_{CH_4}}{1000}\right).$$

Now here's the trick: To a very good approximation, 1000 ln (1.00X) ≈ X (try it on your calculator with a number like 1.005), so we can replace the $1000\ \ln\left(1+\frac{\delta^{13}C}{1000}\right)$ terms above by the δ values for CO_2 and CH_4 to get:

$$1000\ \ln\left(\alpha_{CO_2-CH_4}\right) \approx \delta^{13}C_{CO_2} - \delta^{13}C_{CH_4}.$$

This gives us a very simple relationship between the δ values of a pair of compounds and the equilibrium constant for isotopic partitioning between them. It says that a line showing 1000 ln (α) vs T for a pair of compounds can be read as the difference between the δ values of the compounds as a function of T. This is handy, because it is the δ values that we get directly from mass spectrometer measurements. We refer to the

difference in δ values of magnetite and quartz as the "oxygen isotopic fractionation" between them. The following exercise will help you understand the relationship between α and δ values and how we can put measurements of $\delta^{18}O$ to work to estimate equilibration temperatures:

Famous geochemist Bob Clayton runs some experiments in which he synthesizes magnetite plus quartz at various temperatures. He separates the two minerals from the reaction products and measures their $\delta^{18}O$ values relative to the SMOW standard. He gets the following results:

T °C	T K	$10^6/T^2$	$\delta^{18}O_{qtz\text{-}SMOW}$	$\delta^{18}O_{mt\text{-}SMOW}$	$\alpha_{qtz\text{-}mt}$	1000 ln α	$\delta^{18}O_{qtz} - \delta^{18}O_{mt}$
500			+1.02	-9.16			
700			+0.64	-5.79			
900			+0.45	-3.98			
1100			+0.33	-2.91			

Calculate the exact value of the equilibrium constant α at each temperature and add it to the table. You will need to convert the $\delta^{18}O$ values to isotopic ratios. Take $(^{18}O/^{16}O)_{SMOW} = 0.0020052$. Fill in the rest of the table . Compare the value of 1000 ln $\alpha_{qtz\text{-}mt}$ at each temperature to the difference between the δ values of the two minerals. What do you notice ?

Draw a plot of 1000 ln $\alpha_{qtz\text{-}mt}$ vs $10^6/T^2$ and draw a line through the data. Note that a plot of $\delta^{18}O_{qtz} - \delta^{18}O_{mt}$ would have given you essentially the same diagram.

Plots of this type allow you to predict the difference in δ values between minerals, fluids and gases in equilibrium. Any pair of substances give a line on the diagram. For example, the line for quartz-pyroxene would have approximately 1/3 the slope of the quartz-magnetite line. At any given temperature, the difference in $\delta^{18}O$ values between pyroxene and quartz will be ~1/3 as large as the difference in $\delta^{18}O$ values of magnetite and quartz.

We can use these kinds relationships to determine temperatures of equilibration:

(i) Quartz and magnetite in a banded iron formation come to isotopic equilibrium at 700°C. The quartz has a $\delta^{18}O_{SMOW}$ value of +10‰. What $\delta^{18}O_{SMOW}$ value would be measured on the magnetite ? If the $\delta^{18}O_{SMOW}$ value of the quartz were +15‰, what would the $\delta^{18}O_{SMOW}$ value of the magnetite be ?

(ii) O isotopic analyses of minerals from the granitic host rock of a porphyry copper deposit give $\delta^{18}O_{SMOW}$ values of +11.1‰ for quartz and +7.0‰ for magnetite. What temperature did these minerals equilibrate at ?

The relationship between the O isotopic compositions of quartz and feldspar in equilibrium is given by the equation:

$$1000 \ln \alpha_{qtz\text{-}albite} = 0.97 (10^6 / T^2)$$

(iii) Feldspar in the granitic rock described in question (ii) has a $\delta^{18}O_{SMOW}$ value of +10.45‰. Calculate the temperature of equilibration between quartz and feldspar. Did feldspar crystallise in equilibrium with quartz and magnetite ?

(iv) The granite is cross-cut by quartz-feldspar veins in which

$$\delta^{18}O_{qtz\text{-}SMOW} = 4.1‰$$

$$\delta^{18}O_{albite\text{-}SMOW} = 2.25‰$$

What temperature did the quartz-feldspar veins form at ? Did they form during the high-temperature crystallisation of the granite ?

(v) The bulk $\delta^{18}O$ value of the granite must lie somewhere between the $\delta^{18}O$ value of its magnetite and the $\delta^{18}O$ value of its quartz. Likewise the bulk $\delta^{18}O$ value of the quartz-feldspar veins must lie between the $\delta^{18}O$ values of the two minerals they contain. Can the two rock types have the same bulk oxygen isotopic composition? Can the veins have formed from the same magma as the granite, or were they formed from some unrelated source ?

(vi) Over the range 200°C - 500°C the isotopic relationships between quartz and water and albite (feldspar) - water are given by the equations:

$$1000 \ln \alpha_{qtz\text{-}water} = 4.1 (10^6 / T^2) - 3.7, \quad \text{and}$$

$$1000 \ln \alpha_{albite\text{-}water} = 3.13 (10^6 / T^2) - 3.7.$$

Suppose the quartz-feldspar veins were formed from a hydrothermal solution percolating through cracks in the granite. Calculate the $\delta^{18}O$ value of hydrothermal water that would have been in equilibrium with quartz and feldspar in the veins, at the temperature you calculated in (iv) above. Is the water isotopic composition you calculate the same in both cases? (Thus, even though you can't

sample the water the veins were deposited from, you have a way to cross-check whether the two minerals reached equilibrium with the fluid, which can give you confidence in your estimate of the formation temperature).

(vii) Considering the isotopic composition you just calculated, what fluid might have been involved in generating the copper deposit ?

This is a realistic geological example. Many volcanic islands in the SW Pacific host young porphyry copper deposits which are only just emerging from beneath the ocean (due to tectonic uplift). A good example is the Ok Tedi deposit in Papua-New Guinea, which formed below sea level only a few million years ago, but has since been uplifted and exposed at an altitude of > 2000m in the Star Mtns.