INSTRUCTIONS TO STUDENTS: READ THE FOLLOWING. ANSWER THE QUESTIONS AS YOU GO ALONG. USE THE ANSWER SHEET PROVIDED AND SHOW YOUR WORK.

An Introduction to Stable Isotope Geochemistry with Application to Metamorphic Rocks

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Part 1.

Introduction

Isotopes refer to varieties of an element that differ in their atomic mass. Each element has a unique number of protons in its nucleus, that is its atomic number. Hydrogen is one, helium is two, lithium is three, and so on. Different isotopes of an element have differing numbers of neutrons in their nucleus. ^{12}C (pronounced carbon-12) has six protons (atomic number 6 in the periodic table of the elements) and six neutrons. ^{13}C (carbon-13) has six protons (same element), but seven neutrons. ^{14}C (carbon-14) has six protons (still carbon), but eight neutrons.

Because the nucleus of ^{14}C is not stable, it radioactively decays into ^{14}N with a half-life of 5730 years. That makes ^{14}C useful for age determinations, but that is not the topic of this unit. The other isotopes of carbon are stable and do not radioactively decay through time. Furthermore, no other element decays radiogenically into either ^{12}C or ^{13}C. Therefore, the $^{13}C/^{12}C$ ratio of naturally-occurring materials is constant through time and this ratio can be used as a geochemical marker.

Isotopes of the same element act identically as far as their chemical behavior is concerned. Their electron configuration is identical and this is what controls their behavior in chemical reactions. However, the difference in mass between isotopes results in small variations in natural materials. These variations are referred to as **mass-dependent fractionations**. Let's look at an example. CO_2 in the atmosphere is in equilibrium with seawater bicarbonate by the reaction,

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+. \quad (1)$$

At any point in time, some carbon is moving into the carbon dioxide reservoir and some into the bicarbonate reservoir. From an isotopic perspective, this exchange equilibrium can be written,

$$^{13}CO_2 + H^{12}CO_3^- \leftrightarrow {}^{12}CO_2 + H^{13}CO_3^- \quad (2)$$

The net result of this reaction is one atom of ^{12}C trades places with one atom of ^{13}C. The CO_2 and the bicarbonate both contain ^{12}C and ^{13}C, but in equilibrium at seawater temperatures, the $^{13}C/^{12}C$ ratio of the bicarbonate anion will be slightly greater than that of the CO_2. The heavier ^{13}C has a slight "preference" for the bicarbonate anion over the CO_2 molecule. Equation 2 is perfectly analogous to a cation exchange reaction such as Fe-Mg exchange between garnet and biotite.

The fractionation of a heavy isotope into one compound over another correlates with the bond strength. Heavier isotopes form slightly stronger bonds and are preferentially fractionated into the compound with stronger bonding. Thus, in general, heavier isotopes are fractionated into a solid phase over a liquid phase, and a liquid phase over a vapor phase. This is evident in the evaporation of seawater. The lighter isotopes of hydrogen and oxygen are favored in the water vapor evaporated from the ocean and, therefore, meteoric water (water derived from precipitation) is isotopically lighter than seawater.

The magnitude of isotopic fractionations depends on temperature. This is really useful! For example, the isotopic composition of precipitation depends in part on the temperature. Seawater has essentially the same isotopic composition everywhere, but as one travels north or south from the equator, the precipitation becomes isotopically lighter. The glacial ice that has built up on Greenland from precipitation over the past 100,000 years contains a record of isotopic variation that corresponds to fluctuations in climate. Quaternary geologists read the climate history of the ice ages in the isotope record of the ice.

Isotopic fractionations should decrease to zero, theoretically, as temperature increases to infinity. At infinite temperature, the vibrational energy and strain on bonds would be so great that it wouldn't matter which isotope is present[1]. So isotopic fractionations tend to be largest at low temperatures. The temperature dependence of isotope fractionations allows stable isotopes to be used for geothermometry, that is, the isotopic composition of two phases assumed to be in exchange equilibrium can reveal the temperature of their equilibrium exchange.

Summary of Main Points So Far

Mass-dependent fractionations result in different isotopic ratios in different compounds in equilibrium. Stable isotopes are useful in two important ways. One is as a geochemical tracer. As elements cycle through various reservoirs of natural systems, the isotopic ratio of an element in rocks or other material can elucidate the movement of elements through these reservoirs. Secondly, stable isotope ratios of two substances can be used to constrain the temperature of their exchange, if one can assume equilibrium.

Stable Isotope Fundamentals

Delta-notation

The stable isotope systems that are most useful are the light stable isotopes, including H, C, N, O, and S. Other systems are becoming more useful as analytical methods improve, for example ^{54}Fe and ^{56}Fe. However, mass dependent fractionations are small to begin with and are really tiny when the mass differences are smaller. The mass difference between ^{54}Fe and ^{56}Fe is less than 4%, and between ^{204}Pb and ^{206}Pb is less than 1%. In contrast, the mass difference between ^{12}C and ^{13}C is about 8%. The light stable isotopes and their abundances are summarized in Table 1. Note that the light isotope is by far the most abundant for these elements of interest.

Stable isotope ratios are reported using **delta notation (δ)**. This notation compares the ratio of the heavier isotope to the lighter isotope in a sample to that of a standard. Because the variations are small, we multiply by 1000 and the resulting **delta value** is therefore in permil (‰). Delta values are defined as follows:

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[1] This is also true of cation exchange thermometers, such as garnet-biotite. The distribution coefficient approaches a value of one (i.e., no fractionation) as temperature approaches infinity.

$$\delta \mathrm{D} = \frac{(\mathrm{D/H})_{sample} - (\mathrm{D/H})_{SMOW}}{(\mathrm{D/H})_{SMOW}} \times 1000 \tag{3}$$

$$\delta^{13}\mathrm{C} = \frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{sample} - (^{13}\mathrm{C}/^{12}\mathrm{C})_{PDB}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{PDB}} \times 1000 \tag{4}$$

$$\delta^{18}\mathrm{O} = \frac{(^{18}\mathrm{O}/^{16}\mathrm{O})_{sample} - (^{18}\mathrm{O}/^{16}\mathrm{O})_{SMOW}}{(^{18}\mathrm{O}/^{16}\mathrm{O})_{SMOW}} \times 1000 \tag{5}$$

An equivalent way to write the delta expression is

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000\,, \tag{6}$$

where R represents the isotopic ratio of the sample or standard. From inspection of these delta definitions, you can see that a negative δ value means that the sample has less of a heavy isotope (ratio) than the standard, and a positive δ value means more heavy isotope than the standard. A δ of zero means an isotopic ratio equal to that of the standard. Given these definitions we should expect that the δ^{18}O (pronounced delta Oh-18) of seawater will always be near 0‰ relative to SMOW, and the δ^{13}C of marine carbonates will generally be close to 0‰ relative to PDB, a marine carbonate fossil.

Table 1. Light Stable Isotope Systems.

	abundance†	notation	standard used
H†† D	99.985 0.015	δD	SMOW, Standard Mean Ocean Water
^{12}C ^{13}C	98.892 1.108	δ^{13}C	PDB, Peedee formation belemnite, S.C.
^{14}N ^{15}N	99.635 0.365	δ^{15}N	N_2-atm, Air nitrogen
^{16}O ^{17}O ^{18}O	99.759 0.037 0.204	δ^{18}O	SMOW, Standard Mean Ocean Water or PDB, Peedee formation belemnite, S.C.
^{32}S ^{33}S ^{34}S ^{36}S	95.018 0.750 4.215 0.017	δ^{34}S	CDT, Canyon Diablo Troilite (FeS), an iron meteorite

† Approximate abundances, small variations are the basis for the use of stable isotopes (VG Instruments Fact Sheet).

†† Note: hydrogen is the only element for which its isotopes have a separate name, i.e., deuterium and tritium for ^{2}H and ^{3}H.

Fractionation factors (α) and Δ factors

The equilibrium fractionation of isotopes between two substances can be determined experimentally or theoretically. The fractionation factor, α, is defined as $\alpha = \frac{R_A}{R_B}$, where R is the isotopic ratio of the element of interest in substances A and B. Because isotopic variations are small, α factors are generally close to 1.0. They also depend on temperature. For example, the fractionation factor for oxygen between calcite and H_2O ($\alpha_{Cc\text{-}H_2O}$) = 1.015 at 120°C, 1.012 at 160°C, and 1.007 at 260°C.

Fractionation factors are often portrayed in the form $10^3 \ln\alpha$, as in Figure 1. This is convenient because $10^3 \ln\alpha_{A\text{-}B} \approx \delta_A - \delta_B$. The difference in δ values between any two substances is defined as $\mathbf{\Delta_{A\text{-}B} = \delta_A - \delta_B}$. Capital delta ($\Delta$), or simply "big delta", is commonly used to denote a difference between two numbers. It is unfortunate that in stable isotope convention we have two uses of delta, but if one specifies "Delta calcite-water", then it is clear to mean $\Delta_{Cc\text{-}H_2O}$.

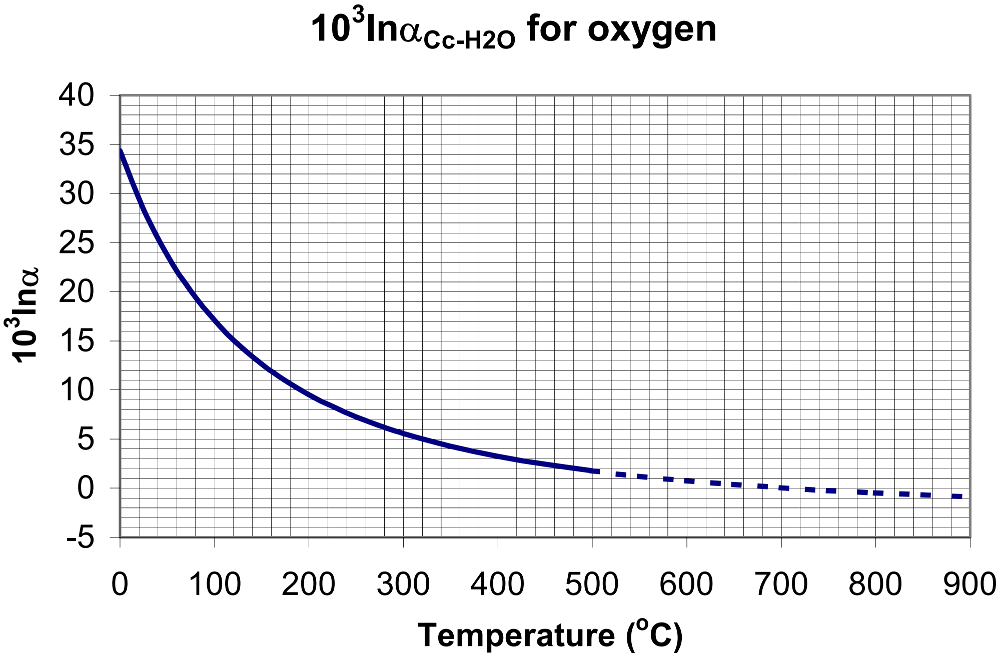

Figure 1. Fractionation of oxygen isotopes between calcite and water as a function of temperature(0-500°C). From O'Neil et al. (1969), updated by Friedman and O'Neil (1977), $10^3\ln\alpha_{Cc\text{-}H_2O} = 2.78(10^6 T^{-2}) - 2.89$, T in Kelvin in this equation.

The relationship between α factors and the δ values of two substances, A and B, are given by,

$$\alpha_{(A-B)} = \frac{1 + \frac{\delta_A}{1000}}{1 + \frac{\delta_B}{1000}} \quad \text{or equivalently,} \quad \alpha_{(A-B)} = \frac{1000 + \delta_A}{1000 + \delta_B} \qquad (7)$$

So $10^3 \ln\alpha_{A\text{-}B} \approx \Delta_{A\text{-}B}$, and $\Delta_{A\text{-}B} = \delta_A - \delta_B$. The reason $10^3 \ln\alpha_{A\text{-}B} \approx \Delta_{A\text{-}B}$ is simply from the properties of natural logarithms, namely ln(1.005) ≈ 0.005, and ln(1.003) ≈ 0.003. Thus 10^3ln(1.00X) ≈ X. But this approximation breaks down as X becomes larger than ten or so. Table 2 show the relationships among Δ, $10^3 \ln\alpha$, and α. Note that $10^3 \ln\alpha_{A\text{-}B} \approx \Delta_{A\text{-}B}$, but the approximation becomes less good as $\Delta_{A\text{-}B}$ gets larger than ~10.

Table 2. Some examples for comparison among values of Δ, $10^3 \ln\alpha$, and α.

δ_A	δ_B	$\Delta_{A\text{-}B}$	$10^3 \ln\alpha_{A\text{-}B}$	α
1.00	0	1.00	1.00	1.00100
5.00	0	5.00	4.99	1.00500
10.00	0	10.00	9.95	1.01000
15.00	0	15.00	14.89	1.01500
20.00	0	20.00	19.80	1.02000
30.00	0	30.00	29.56	1.03000
30.00	29.00	1.00	0.97	1.00097
30.00	25.00	5.00	4.87	1.00488
30.00	20.00	10.00	9.76	1.00980
30.00	10.00	20.00	19.61	1.01980
0	10.00	-10.00	-9.95	0.99010
0	20.00	-20.00	-19.80	0.98039

IMPORTANT NOTE: Reproducibility of stable isotope analyses is generally ±0.1 to 0.2‰. Differences in that range or less are not significant.

Examples and Problem Assignments I

Suppose one finds calcite with $\delta^{18}O = 5‰$. Suppose further that fluid inclusion evidence indicates the calcite formed from hydrothermal fluid at 120°C. What was the $\delta^{18}O$ of the hydrothermal water?

All you need to know to answer this question is $\Delta_{Cc\text{-}H_2O}$, then you can use $\Delta_{Cc\text{-}H_2O} = \delta^{18}O_{Cc} - \delta^{18}O_{H_2O}$ to find the answer. Since $10^3 \ln\alpha_{Cc\text{-}H_2O} \approx \Delta_{Cc\text{-}H_2O}$, one can use figure 1 to find that $10^3 \ln\alpha = 15.0$ at 120°C. Thus, $15 \approx 5 - \delta^{18}O_{H_2O}$ and $\delta^{18}O_{H_2O} \approx -10.0‰$. Water with $\delta^{18}O_{H_2O}$ of –10‰ is almost certainly meteoric water, so if this were a real example, it would reveal useful information about the hydrothermal system.

If you are bothered by the approximation in this example, we can find $\alpha_{Cc\text{-}H_2O}$ from $10^3 \ln\alpha$ and determine the exact solution as follows: $10^3 \ln\alpha = 15.0$, so $\ln\alpha = 0.0150$, and $\alpha = 1.0151$ (recall that, by definition, if $\ln\alpha = x$, then $e^x = \alpha$. Most calculators have both a ln function and an e^x function, so this is an opportunity to use that nice calculator you own!) Inserting $\delta^{18}O_{Cc} = 5‰$ and $\alpha_{Cc\text{-}H_2O} = 1.0151$ into equation 7 gives $\delta^{18}O_{H_2O} = [(1000 + 5) \div 1.0151] - 1000 = -9.95‰$. Because analytical reproducibility in stable isotope analyses is at least ±0.1‰, the approximation in the first calculation gave a perfectly acceptable answer.

Now here are two sample problems for you to solve (use the Sample Problem Worksheet provided and show your work).

Problem 1. Suppose the $\delta^{18}O$ value of a calcite sample is 16.2‰ and fluid inclusion data indicates that this calcite formed at 260°C. What must the $\delta^{18}O$ value of the water have been? Please provide both the approximate and the exact solutions.

Problem 2. Suppose heated seawater ($\delta^{18}O$ = 0.0‰) near a mid-oceanic spreading axis precipitates calcite at 260°C. What will the $\delta^{18}O$ value of the calcite be? (approximate solution only, please)

More Examples and Problem Assignment II

Delta notation for stable isotopes allows simple addition of materials, as long as this is done on a molar basis (that is, a per atom basis). So, for example, if you add 1 mole of calcite with $\delta^{18}O$ = 0‰ to 1 mole of calcite with $\delta^{18}O$ = 10‰ and somehow allowed them to equilibrate, you would have 2 moles of calcite with $\delta^{18}O$ = 5‰.

Here's a more interesting problem. Suppose you add 1 mole of calcite with $\delta^{18}O$ = 10‰ and 1 mole of H_2O with $\delta^{18}O$ = 0‰ and allow these to equilibrate, then what would you have? The answer is .... ha! Trick question! First, you would need to know the temperature at which they equilibrate because you need to know the fractionation, $10^3\ln\alpha_{Cc-H_2O}$. So let's assume a temperature of 500°C. From figure 1, $10^3\ln\alpha_{Cc-H_2O} = 1.8$ at 500°C (the calcite is heavier than the water by 1.8‰). We start with 3 moles of oxygen from the calcite ($CaCO_3$) with $\delta^{18}O$ = 10‰, and 1 mole of oxygen from the H_2O with $\delta^{18}O$ = 0‰, so the mixture contains 4 moles of oxygen and the bulk $\delta^{18}O$ value of the mixture = [(3mol × 10‰ + 1mol × 0‰) ÷ 4mol] = 7.5‰.
We have two unknowns, δ_{Cc} and δ_{H_2O}, related by two equations,

$$\delta_{Cc} - \delta_{H_2O} = 1.8, \text{ and} \qquad (8)$$

$$(3 \times \delta_{Cc} + 1 \times \delta_{H_2O}) \div 4 = 7.5‰. \qquad (9)$$

If we rearrange the first equation to $\delta_{Cc} - 1.80 = \delta_{H_2O}$ and replace δ_{H_2O} in the second equation,
we get, $(3 \times \delta_{Cc} + 1 \times (\delta_{Cc} - 1.80‰)) \div 4 = 7.50‰$.
This rearranges to $4\delta_{Cc} - 1.80‰ = 4 \times 7.50‰ = 30.0‰$,
and thus, $4\delta_{Cc} = 31.80‰$, so $\delta_{Cc} = 7.95‰$,
and $\delta_{H_2O} = 7.95 - 1.80 = 6.15‰$.

That is one approach to solving this problem. You might find a different way! We can check our answer for consistency by noting that the bulk $\delta^{18}O$ still equals 7.5‰. Specifically, [(3 × 7.95) + (1 × 6.15)] ÷ 4 = 7.5.

Problem 3. 1 mole of calcite ($\delta^{18}O$ = 10‰) equilibrates with 1 mole H_2O ($\delta^{18}O$ = 0‰) at 300°C. What is the final $\delta^{18}O$ value of both the calcite and the water? Show your work on the answer sheet.

Problem 4. 2 moles of calcite ($\delta^{18}O$ = 25.0‰) equilibrates with 1 mole of water ($\delta^{18}O$ = 5‰) at 320°C. What is the final $\delta^{18}O$ value of both the calcite and the water? Show your work on the answer sheet.

I noted earlier that stable isotopes can be used to infer the transfer of elements through different geochemical reservoirs. The following figures illustrate some important reservoirs for oxygen and carbon. Reservoirs and compositional ranges are available for other stable isotopic systems as well (for example, see Hoefs, 1997).

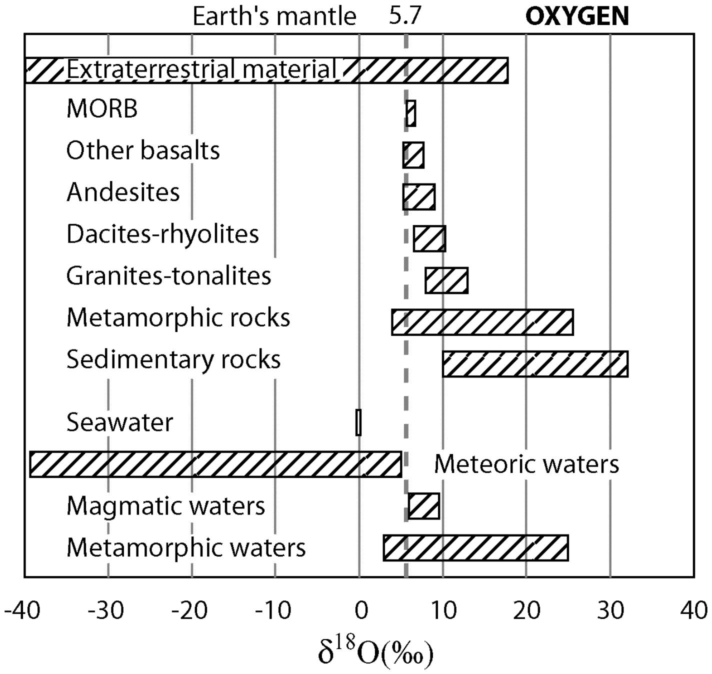

Figure 2. Typical oxygen isotopic composition of selected natural materials. Dashed line represents the earth's mantle. Modified from Hoefs (1997) and Best (2003). Igneous rock values exclude hydrothermally altered rocks.

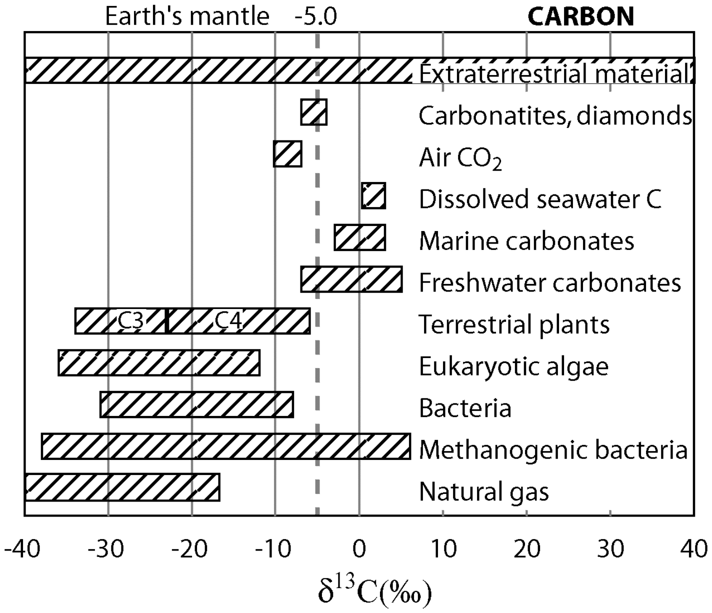

Figure 3. Typical carbon isotopic composition of selected natural materials. Dashed line represents the earth's mantle. Modified from Hoefs (1997). Terrestrial plants include ranges for C3 and C4 plants that use different photosynthetic pathways.

Sample Problem Worksheet
Stable Isotope Assignment

Name ______________________________

Problem 1. Suppose the $\delta^{18}O$ value of a calcite sample is 16.2‰ and fluid inclusion data indicates that this calcite formed at 260°C. What must the $\delta^{18}O$ value of the water have been? Please provide both the approximate and the exact solutions.

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PART 2.

Stable Isotopes in Metamorphic Rocks

So far we have considered only the case for a single mineral, calcite, and coexisting water at a fixed temperature. Metamorphic rocks, however, generally consist of several minerals, and metamorphic reactions among minerals may either produce water or consume water, and carbonate-bearing rocks might also produce carbon dioxide. The expulsion of volatiles such as H_2O and CO_2 can alter the C, O, or H isotopic composition of the rock if the escaping fluid has fractionated the isotopes in any way (which generally will be the case). The effect might be negligible or significant, depending on the fractionation and quantity of the element removed. Also, if fluid expelled from one rock infiltrates another rock, fluid-rock exchange could alter the isotopic composition of the infiltrated rock. Thus, stable isotopes can be a powerful tool for recognizing processes that involve fluids in rocks.

The stable isotope composition of a metamorphic rock depends on three factors, (1) the isotopic composition of the protolith, (2) the effects of removing the element of interest (for example, by volatilization), and (3) exchange with infiltrated fluids. Protolith composition can often be assumed, but with a fair amount of uncertainty depending on the rock type. The effect of volatilization depends on the fractionation factors and the amount of volatile lost, and the effect of infiltration depends on the fractionation factors and the isotopic composition of the infiltrating fluid.

Protolith

The stable isotope composition of most igneous and sedimentary rocks can be quite variable, for example see Figures 2 and 3. If metamorphic processes modify the stable isotopes of a particular rock by an amount less than the typical initial variation, then it can be difficult or impossible to recognize. Contact metamorphism is the most conducive to the study of purely metamorphic effects, because one has the opportunity to analyze the unmetamorphosed equivalent for comparison.

Volatilization

Consider a rock containing calcite and quartz. If heated to a high enough temperature, these minerals react to form wollastonite and CO_2 by the reaction

calcite + quartz = wollastonite + carbon dioxide. (10)
$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$

As the CO_2 is produced, it is likely to be expelled. The removal of carbon and oxygen will alter the $\delta^{18}O$ and the $\delta^{13}C$ of the rock. Because CO_2 fractionates both heavy oxygen and heavy carbon, the $\delta^{18}O$ and the $\delta^{13}C$ values of the rock will decrease from this decarbonation process.

The amount of CO_2 produced and expelled by this reaction depends on how much calcite and quartz are in the rock initially. If the reaction goes to completion, either the calcite or the quartz will be completely consumed and the final rock will consist of either wollastonite + quartz (if calcite was the limiting reactant) or wollastonite + calcite (if quartz was the limiting reactant), plus other minerals not involved in the reaction. If calcite is the limiting reactant (i.e., all the calcite is reacted) and there are no other carbon-bearing minerals present, then all of the carbon may be removed from the rock. However, there will always be substantial oxygen remaining in the rock after reaction is complete. Notice that even if the maximum reaction possible occurs (calcite and quartz are in equal molar amounts and no other oxygen-bearing minerals are present), 60% of the oxygen remains in the wollastonite after reaction (see reaction 10). This same reaction, however, removes all of the carbon. This decoupling of the oxygen and the carbon is discussed by Valley (1986). He refers to the remaining oxygen as "the calc-silicate limit," meaning that the removal of oxygen in calc-silicate rocks and marbles is always limited. For this reaction, 60% is the calc-silicate limit for oxygen. Most reactions remove less oxygen than this, so this can be viewed as a limiting case.

Geochemists use the variable "F" to represent the fraction of an element remaining in the rock during a fractionation process such as the decarbonation reaction being considered here. The F value for oxygen starts at 1.0, before reaction begins, all the oxygen is in the initial rock. F decreases to 0.6 when the reaction reaches completion for the case of the calc-silicate limit. At the same time the F value for carbon starts at 1.0 and decreases to 0 when reaction is complete (no carbon remains in the rock).

Removing CO_2 by this reaction will have an effect on the stable isotopes of carbon and oxygen. However, the magnitude of the effect depends upon how the process proceeds. Let's consider two different processes, batch volatilization and Rayleigh volatilization (Valley, 1986). In batch volatilization the CO_2 produced stays within the system as the mineral reaction proceeds, and remains in isotopic equilibrium with the rock until the reaction is complete. The δ value of the rock at any point (δ_f) will depend on the rock's initial value (δ_i), the fractionation factor ($10^3 \ln\alpha_{CO_2-Rock}$), and the proportion of oxygen or carbon still in the rock relative to the oxygen or carbon in the fluid (F). This relationship is given by

$$\delta_f = \delta_i - (1 - F)\, 10^3 \ln\alpha_{CO_2-Rock} \qquad (11).$$

In contrast, the Rayleigh volatilization process involves continuous loss of CO_2 as it forms. In this scenario the CO_2 does not continue to exchange and equilibrate with the rock after it forms. This results in the relationship given by

$$\delta_f - \delta_i = 10^3(F^{(\alpha - 1)} - 1) \qquad (12).$$

Equation 11 can be used to calculate the effect on $\delta^{18}O$ or $\delta^{13}C$ for the batch volatilization process, provided one can make assumptions about the initial isotopic composition, the fractionation factor for oxygen or carbon, and the F value for oxygen or carbon. The same assumptions are needed for applying equation 12 to calculate the effect of Rayleigh volatilization. The isotopic effect of volatilization by batch and Rayleigh volatilization is illustrated in Figure 4 for selected fractionation factors. The fractionation factor used must be approximate because α will depend on the minerals in the rock and the temperature, both of which may vary as reaction proceeds.

Volatilization in real systems is likely to be somewhere between these two end-member processes, but closer to Rayleigh volatilization because the batch model requires a substantial volume increase to accommodate all of the CO_2 produced. As CO_2 is produced, pressure will build up locally until it becomes sufficient to force the fluid out of the area. Successive pulses of build-up and expulsion of volatiles by reaction will mimic Rayleigh volatilization. In Rayleigh processes the steps, or increments, are infinitesimally small.

Note from Figure 4 that the isotopic effects due to the batch and Rayleigh volatilization models are approximately the same for F-carbon values ≥ 0.5. By either process 50% carbon loss only shifts $\delta^{13}C$ by ~-1.5‰. The corresponding F-oxygen would be 0.8 (20% oxygen loss) and the resulting shift in $\delta^{18}O$ would be -1.5 to -2.5‰. The difference in $\delta^{18}O$ between the batch and the Rayleigh models is pretty small, even at $F_{carbon} = 0.05$, whereas the difference in $\delta^{13}C$ at $F_{carbon} = 0.05$ is large, over 4‰.

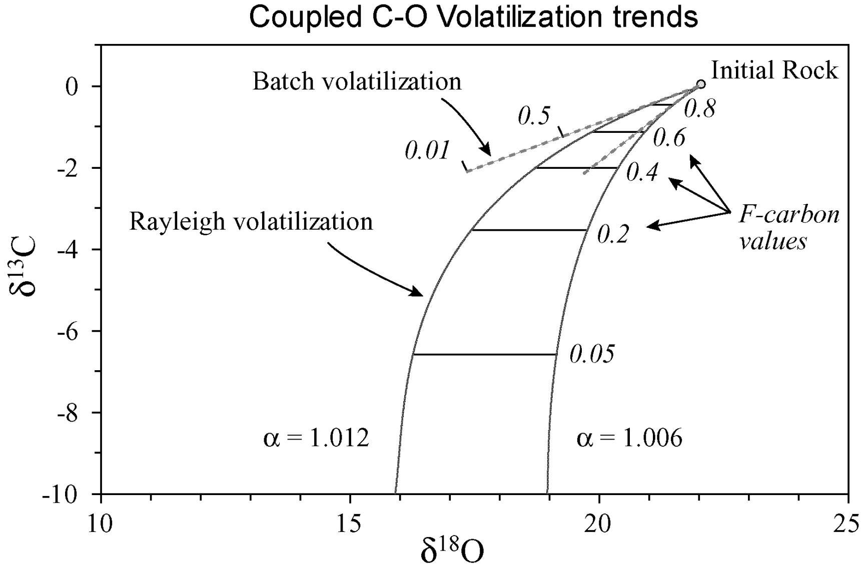

Figure 4. $\delta^{18}O$ versus $\delta^{13}C$ for volatilization (CO_2-loss) of a rock with initial $\delta^{18}O$ = 22‰ and $\delta^{13}C$ = 0‰. Two values of α for oxygen (CO_2-rock) are shown for both Rayleigh (solid lines) and batch (dashed lines) processes, $\alpha_{carbon} = 1.0022$. F values shown are for carbon. The F values for oxygen are related by $F_{oxygen} = 0.4F_{carbon} + 0.6$, which is the calc-silicate limit discussed in the text. (modified from Valley, 1986)

The fractionation factors used in Figure 4 are selected to illustrate the effect of volatilization by the batch and Rayleigh models. Larger values of α will produce larger isotopic effects. This can be seen by the two values of α_{oxygen} shown in Figure 4. The mineralogy of the rock and the temperature will determine the actual $\alpha_{CO_2\text{-rock}}$ for oxygen, as can be deduced from Figure 5. The horizontal line at zero in Figure 5 represents no fractionation (although this line is not labeled in Fig. 5, one could think of it as the position of calcite itself). Curves above that line (dolomite, quartz, and CO_2) indicate greater $^{18}O/^{16}O$ ratios than coexisting calcite, below that line calcite has the greater $^{18}O/^{16}O$ ratio. The value of $\alpha_{CO_2\text{-rock}}$ at any temperature depends on the mole fraction abundance of the oxygen-bearing minerals in the rock. The values of $\alpha_{CO_2\text{-rock}}$ used in Figure 4 are 1.012 and 1.006. These approximately correspond to $10^3\ln\alpha$ values of 12 and 6. For a rock composed only of calcite, dolomite, and quartz, a $10^3\ln\alpha_{CO_2\text{-rock}}$ value of 6 is pretty good if the reaction is near 500°C (see figure 5). A $10^3\ln\alpha_{CO_2\text{-rock}}$ value of 12 would require considerable other silicates. Wollastonite and tremolite have fractionations similar to that of diopside in Figure 5, so a rock dominated by either of these silicates might approach a $10^3\ln\alpha_{CO_2\text{-rock}}$ value of 12.

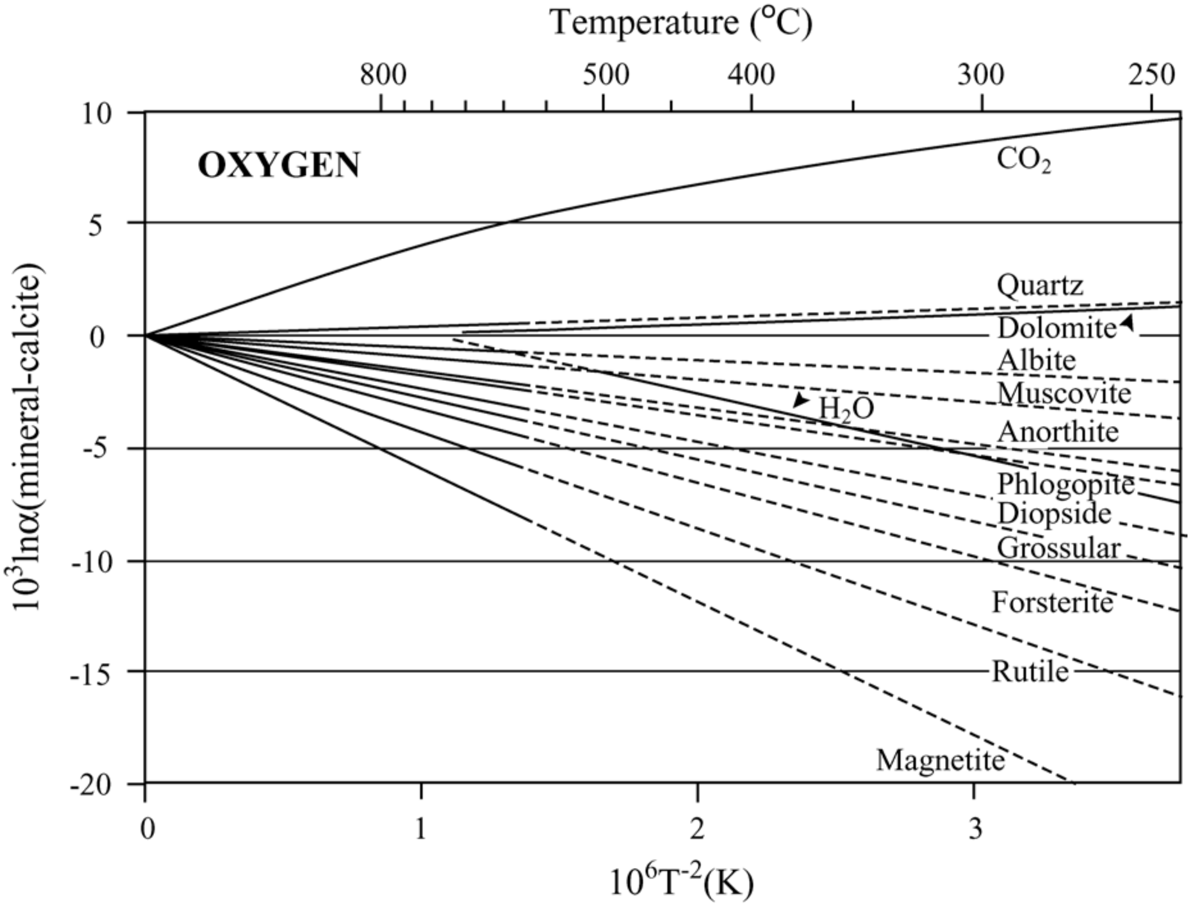

Figure 5. Fractionation of oxygen isotopes between selected minerals (and volatiles) and calcite. $10^3\ln\alpha$ between solids is normally assumed to be linear with $1/T^2$ as shown. Dashed lines are projected outside their experimental temperature range. Fractionation factors used are from various studies summarized in Chacko et al., 2001. H_2O-calcite is from O'Neil et al. (1969), updated by Friedman and O'Neil (1977), dolomite-calcite is from Sheppard & Schwarz (1970).

The $\alpha_{CO_2\text{-rock}}$ value applied for carbon also depends on the mineralogy of the rock and the temperature of volatilization (Figure 6). In this case, the CO_2-calcite curve does not change very much over the temperature range 400-600°C. Figure 4 applied a $\alpha_{CO_2\text{-rock}}$ value of 1.0022, or $10^3\ln\alpha_{CO_2\text{-rock}}$ of 2.2. A value in excess of 3 would be more representative of calcite- and dolomite-rich rocks. Graphite is the only other common carbon-bearing phase in marbles and it is rarely abundant enough to significantly change the $\alpha_{CO_2\text{-rock}}$ value, although it would increase the bulk $\alpha_{CO_2\text{-rock}}$ value, but the greater effect of abundant graphite would be to diminish the F_{carbon} value and thereby decrease the overall isotopic effect of volatilization.

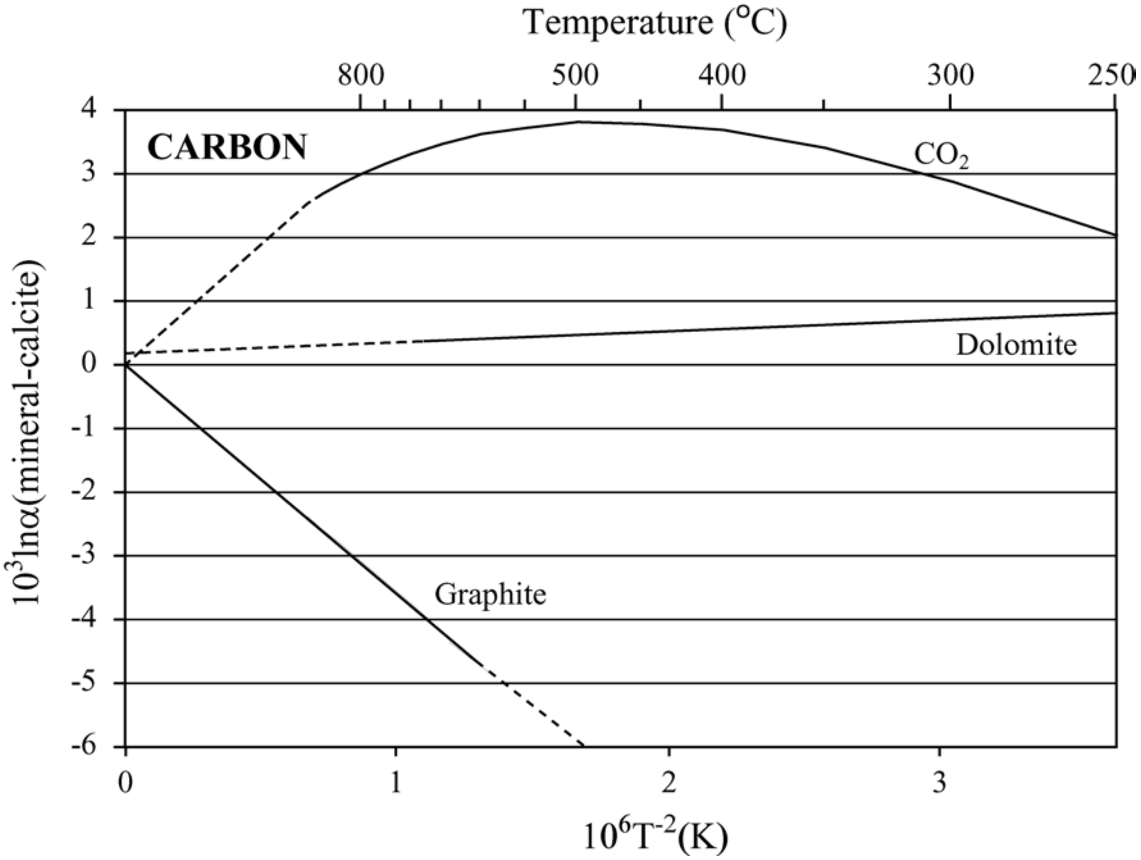

Figure 6. Fractionation of carbon isotopes between selected minerals (and CO_2) and calcite. Curves are dashed outside their experimental range (graphite-calcite is an empirically derived relationship, Kitchen and Valley, 1995). Dolomite-calcite is from Sheppard & Schwarz (1970) and CO_2-calcite is from Chacko et al (1991) as given in Chacko et al. (2001).

To summarize, volatilization of CO_2 in metamorphic rocks should result in a modest decrease in $\delta^{18}O$ values. The effect on $\delta^{13}C$ values can be greater, but only after significant CO_2 loss. Interestingly, most studies of C-O isotopic trends in marbles that have undergone volatilization from metamorphic reactions in contact aureoles do not follow the trend shown in Figure 4 (Valley, 1986). Instead, marble in contact aureoles typically show a *greater* decrease in $\delta^{18}O$ values than can be explained by volatilization. Substantial $\delta^{18}O$ depletions require exchange with either magmatic fluid expelled by the crystallizing pluton or hydrothermal fluid associated with the hot aureole. Let's now consider infiltration of fluid as a mechanism for isotopic change.

Fluid Infiltration

Imagine a column of homogeneous rock with a small amount of interconnected porosity through which a fluid might move under a pressure gradient of some kind. As fluid enters one end of the column, it pushes whatever fluid is in the pore space down stream, displacing the fluid in each adjacent volume of the rock. Assume the entering fluid is out of isotopic equilibrium with the rock, and that once fluid enters the rock isotopic exchange is rapid relative to the fluid migration. Thus, fluid in the pore space of any particular volume of rock at a given time will be in equilibrium isotopic exchange. Let's consider an example for oxygen. Assume that the rock is initially 25‰ ($\delta^{18}O$), the fluid 10‰, and the $\alpha_{rock\text{-}fluid}$ = 6‰. As fluid flow begins, the first aliquot of fluid to enter the rock will fill the pore space and exchange with the rock to attain equilibrium. If the pore space is small relative to the rock volume, then the fluid will be brought up to a $\delta^{18}O$ value near 19‰ and the $\delta^{18}O$ value of the rock will decrease by a very small amount. This particular batch of fluid will have negligible isotopic effects on the next volume of rock it encounters downstream. But the next aliquot of fluid to enter our original volume of rock will bring down the rock $\delta^{18}O$ value by another small increment, and each subsequent pulse of fluid will do the same. Eventually, after enough fluid has passed, this volume of rock will be brought down to a value of 16‰. At 16‰ we would describe the oxygen in that part of the column as "fluid dominated" (Figure 7).

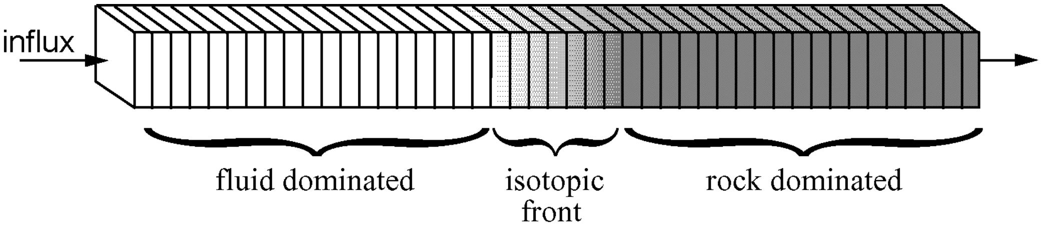

Figure 7. Illustration of a column of rock undergoing infiltration and exchange as described in the text. The light region is "fluid-dominated" and the dark region is "rock-dominated." The "isotopic front" (or exchange front) moves in the direction of fluid flow and is a measure of the cumulative fluid flux.

Prior to starting the flow, fluid already occupying the rock pore space would have $\delta^{18}O$ = 19‰ and would already be in isotopic equilibrium with the rock. As this fluid is displaced downstream, it will have no isotopic effect whatsoever on the rock it passes through. Similarly, new fluid that has entered the system, but has exchanged with enough rock to have attained an isotopic composition of 19‰, cannot have any further effect. The infiltration of fluid already in

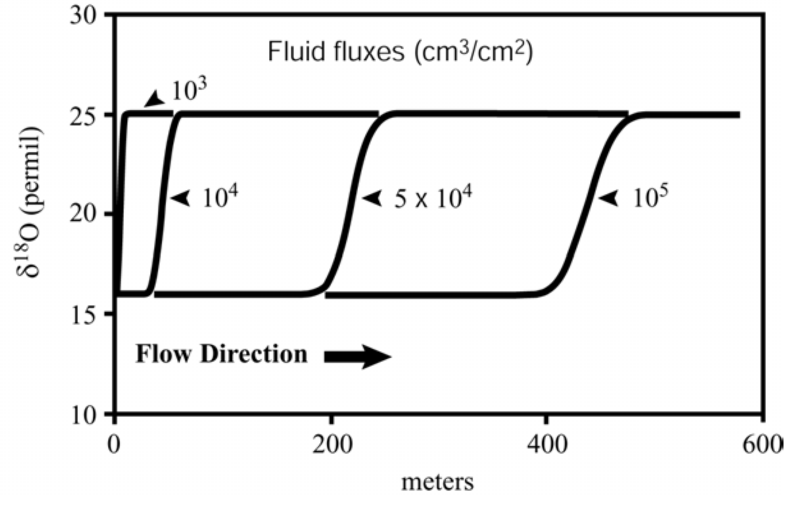

Figure 8. $\delta^{18}O$ value of model rock as a function of distance along the flow path. Isotopic fronts are displaced in the direction of fluid flow with increasing fluid flux. In this model the initial rock is 25‰, the fluid enters from the left at 10‰, and $\Delta_{rock\text{-}fluid}$ = 6‰.

equilibrium with the rock is not detectable. The part of the flow path that still retains its original isotopic character is the rock-dominated part of the system. Between the fluid-dominated and rock-dominated parts of the column is the isotopic front, where the fluid is brought into isotopic equilibrium with the rock. The position of the isotopic front is a function of the fluid flux that has passed through the column (Figure 8). An isotopic front may be sharp (i.e., occur over a short distance) or broad (occurring over a larger distance), depending on factors such as the rock porosity, whether fluid disperses laterally (in and out of "columns"), and whether exchange is rapid relative to the rate of fluid flow.

In natural systems, rocks are not idealized columns and temperatures are not steady-state. Fluid flow will be focused into more permeable layers or fractures or shear zones. Depending upon the scale of observation, fluid flow may be considered pervasive (flowing through the rock and exchanging at the granular level) or it may be channelized. A so-called isotopic front may actually be a "side", depending on the three-dimensional aspect of the flow system. Geologists are generally viewing, at best, a two-dimensional representation, which is the exposed erosion surface.

Isotopes are not the only aspect of a rock that will be affected by fluid flow as described here. Every element has some solubility in a given fluid and will be transported by fluid flow. Geochemical fronts may pertain to any element and will depend on the concentration of the element in the fluid, the concentration of the element in the rock (that is, in each mineral of the rock), and the fractionation factor of the element between the fluid and the rock. Chemists and geochemists call this process **chromatography**. When a mineral reaction results from fluid flow, then one may find a **reaction front**.

Part 2 Problems

1.) Figure 4 used a value for $\alpha_{CO_2\text{-rock}}$ (carbon) of 1.0022. From inspection of Figure 6, suggest a more appropriate $\alpha_{CO_2\text{-rock}}$ value for a dolomite marble undergoing CO_2 volatilization at ~500°C. Explain how this new choice of $\alpha_{CO_2\text{-rock}}$ (carbon) would change the shape of the Rayleigh volatilization curves.

2.) Use Excel spreadsheet, or other software of your choice, to construct a new set of Rayleigh volatilization curves using the value of $\alpha_{CO_2\text{-rock}}$ (carbon) that you suggest in #1 (above). (Keep the same values of $\alpha_{CO_2\text{-rock}}$ (oxygen) as in Figure 4 and try to label F-carbon values.)

3a.) A typical shale contains ~5 wt.% H_2O, a portion of which is lost during metamorphism. What do you need to know in order to calculate the effect of dehydration on the $\delta^{18}O$ value of the resulting rock?

3b.) Determine the direction of the shift in $\delta^{18}O$ by dehydration of a rock at 400°C if the rock is equal parts quartz and muscovite (use Figure 5). Determine the direction of the shift in $\delta^{18}O$ if the rock is equal parts of muscovite and phlogopite (Mg-biotite) and the dehydration occurs at 500°C.

3c.) Calculate the magnitude of the shift in the $\delta^{18}O$ value for dehydration at 500°C of a rock that is equal parts muscovite and phlogopite. Assume $F_{oxygen} = 0.9$. Show your work. (Note: loss of 5 <u>wt.%</u> H_2O is approximately 9 <u>mol%</u> of the oxygen because 89% of the H_2O is oxygen by weight whereas only about 50% of silicate minerals are oxygen by weight. Thus loss of 5 wt% H_2O corresponds to an F_{oxygen} of ~0.9).

PART 3.

The Alta Contact Aureole

Southeast of Salt Lake City, Utah, near the Alta ski area, is the Alta stock. This Tertiary granodiorite pluton intruded Paleozoic sedimentary rocks, including quartz-bearing dolomites (Figure 9). Prograde metamorphism of the siliceous dolomite resulted in a sequence of mineral reactions that increase in grade approaching the contact. Moore and Kerrick (1976) recognized the importance of mineral-fluid equilibria in the development of these reactions. The mineral isograds approaching the contact are based on the first appearance of talc, tremolite, forsterite, and periclase (an isograd on the north side involving clinohumite is not considered here). The temperature and fluid composition controls on these minerals can be seen in a $T\text{-}X_{CO_2}$ diagram (Figure 10). $T\text{-}X_{CO_2}$ diagrams plot fluid composition on the x-axis, pure H_2O fluid is on the left, pure CO_2 on the right. Mineral reactions that either consume or produce H_2O-CO_2 fluid will be affected by the relative abundance of these components (refer to your favorite petrology textbook for more information on $T\text{-}X_{CO_2}$ diagrams). The reactions in Figure 10 are shown in complete form in Table 3.

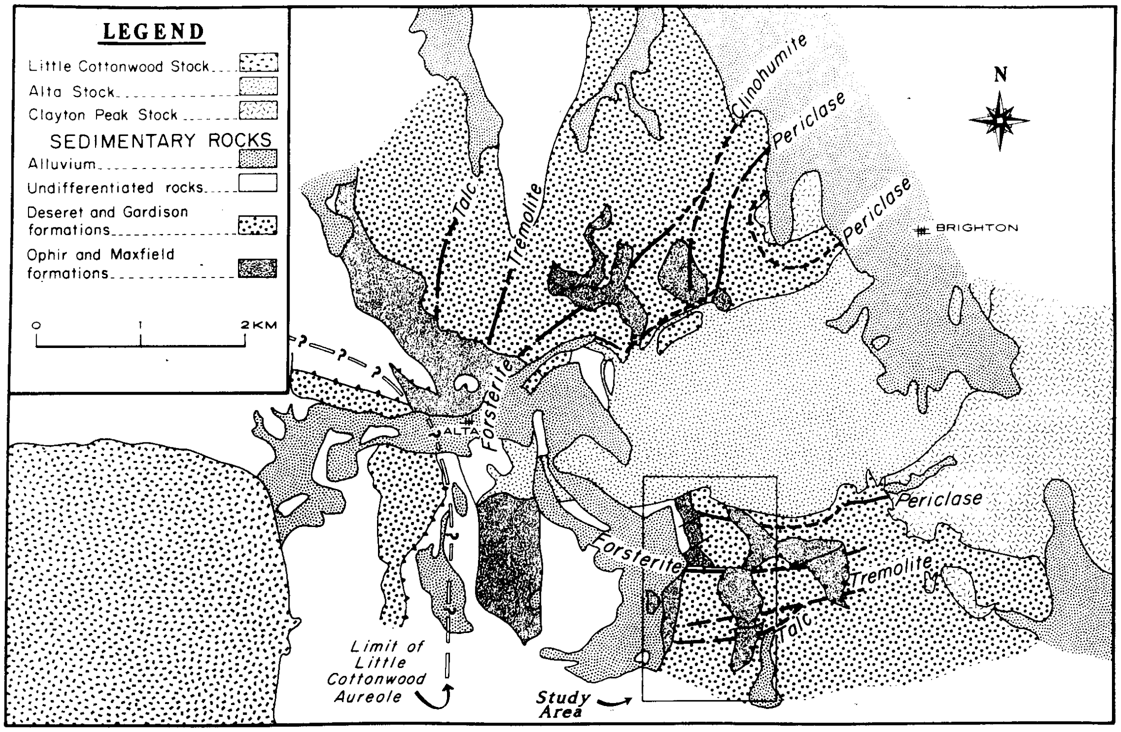

Figure 9. Geologic map of the Alta area, Utah (from Moore and Kerrick, 1976). Mineral reaction isograds surround the Alta stock within siliceous dolomites of the Mississippian Deseret and Gardison formations. The study area within the southern contact aureole is from Bowman et al. (1994).

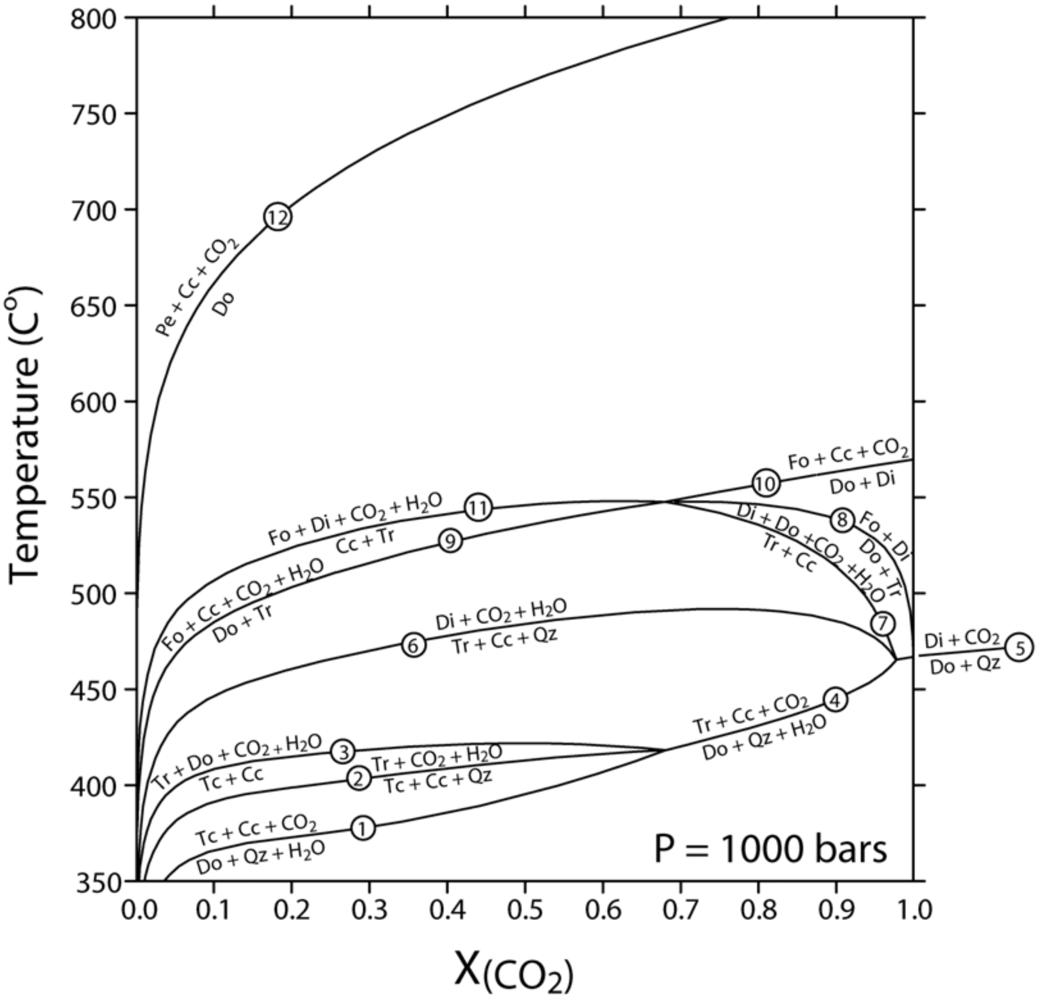

Figure 10. T-X_{CO_2} diagram for selected reactions in the system CaO-MgO-SiO_2-H_2O-CO_2 at 1 kbar, generated with the Ge0-Calc computer program (Berman & Perkins, 1987) using the thermodynamic data of Berman (1988). Complete reactions and abbreviations are in Table 3.

Table 3. Reaction list for T-X(CO_2) diagrams, mineral formulas and abbreviations.

1. 3 Do + 4 Qz + H_2O = Tc + 3 Cc + 3 CO_2
2. 6 Cc + 4 Qz + 5 Tc = 3 Tr + 2 H_2O + 6 CO_2
3. 3 Cc + 2 Tc = Tr + Do + H_2O + CO_2
4. 5 Do + 8 Qz + H_2O = Tr + 3 Cc + 7 CO_2
5. Do + 2 Qz = Di + 2 CO_2
6. Tr + 2 Qz + 3 Cc = 5 Di + 3 CO_2 + H_2O
7. Tr + 3 Cc = Do + 4 Di + H_2O + CO_2
8. 5 Do + 4 Tr = 6 Fo + 13 Di + 4 H_2O + 10 CO_2
9. 11 Do + Tr = 8 Fo + 13 Cc + H_2O + 9 CO_2
10. 3 Do + Di = 4 Cc + 2 Fo + 2 CO_2
11. 5 Cc + 3 Tr = 2 Fo + 11 Di + 3 H_2O + 5 CO_2
12. Do = Pe + Cc + CO_2

Cc = calcite, $CaCO_3$
Do = dolomite, $CaMg(CO_3)_2$
Di = diopside, $CaMgSi_2O_6$
Fo = forsterite, Mg_2SiO_4
Pe = periclase, MgO
Qz = quartz, SiO_2
Tc = talc, $Mg_3Si_4O_{10}(OH)_2$
Tr = tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$

Mineral assemblages constrained by the metamorphic reactions are (1) dolomite + quartz, (2) talc + calcite, (3) tremolite + calcite, (4) forsterite + calcite, and (5) periclase + calcite. These assemblages indicate increasing temperature (Figure 11). The peak metamorphic temperatures are known from calcite-dolomite geothermometry (Cook and Bowman, 1994). Peak temperatures were ~450°C between the tremolite-in and the forsterite-in isograds, and 600°C near the contact. Periclase + calcite at ~600°C requires very H_2O-rich fluid (Figure 11). Because the prograde reactions produce more CO_2 than H_2O, the H_2O-rich conditions near the contact require infiltration of externally-derived H_2O, either from the pluton itself, or by hydrothermal circulation driven by the heat of the intrusion.

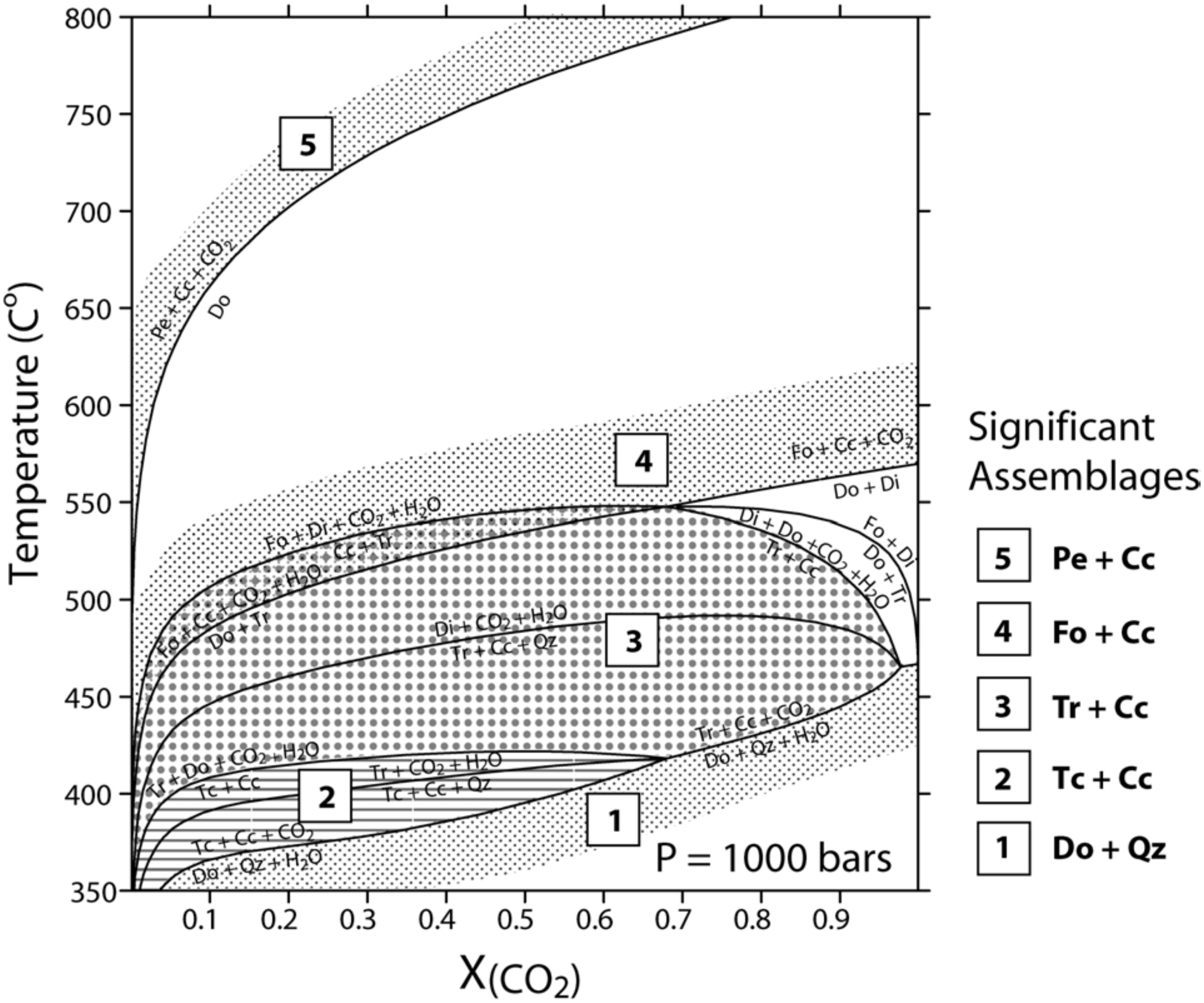

Figure 11. T-X_{CO_2} diagram for selected reactions with significant mineral assemblages highlighted. The sequence of mineral reactions seen approaching the Alta stock contact are consistent with increasing temperature. Geothermometry yields peak temperatures of 600°C in the periclase zone, which requires H_2O-rich fluid conditions.

Stable Isotopes at Alta

Stable isotope analyses show significant variation in $\delta^{18}O$ and $\delta^{13}C$ values in the southern contact aureole of the Alta stock (Bowman et al., 1994). Figure 12 shows the coupled $\delta^{18}O$ - $\delta^{13}C$ trend for carbonates from each of the mineral reaction zones. The lower grade talc and tremolite zone samples have similar "normal" marine carbonate δ values, but the periclase zone and many of the forsterite zone samples have much lower $\delta^{18}O$ and $\delta^{13}C$ values. Figure 12 also shows the Rayleigh CO_2-volatilization trend of Figure 4, emanating from the average of the talc zone samples. Natural variation in the initial $\delta^{18}O$ and $\delta^{13}C$ of sample protoliths allows the volatilization trends to shift around from sample to sample, but clearly the amount of decrease in $\delta^{18}O$ of samples in the highest grade zones closest to the contact cannot result from volatilization alone. Exchange with a low $\delta^{18}O$ fluid is required to explain these data.

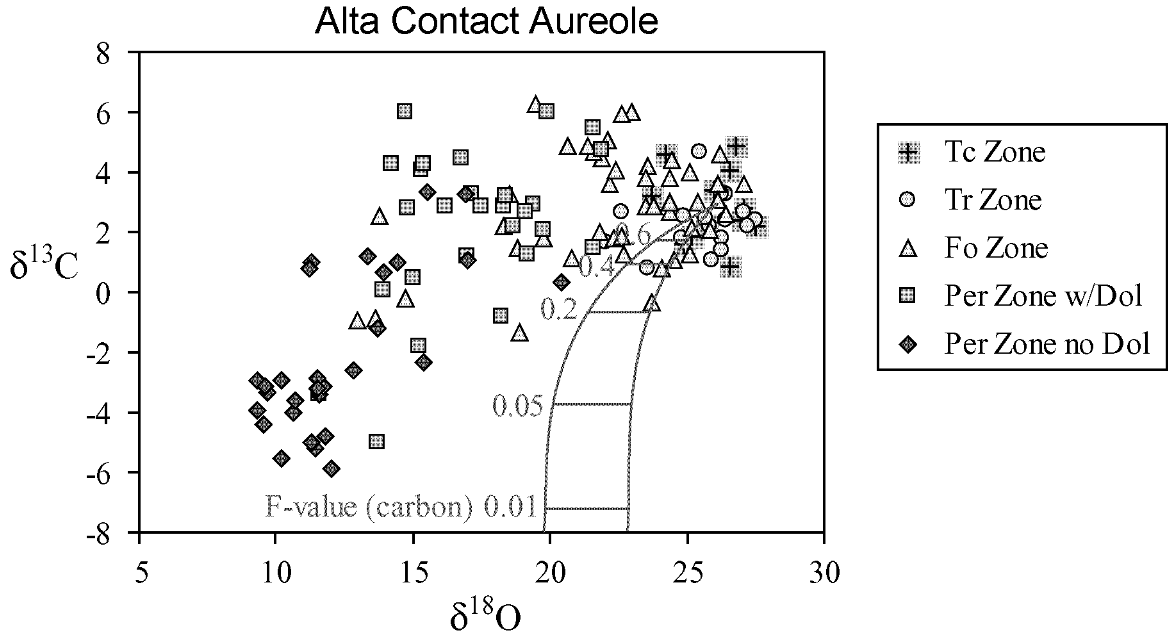

Figure 12. C-O isotopic trend for carbonates from the southern Alta aureole. The Rayleigh volatilization trend starts at the average of the talc zone samples, 26‰ and 3‰, and uses the same fractionation factors as Fig. 4. Data from Bowman et al., 1994, and additional unpublished data from J. R. Bowman.

Figure 13 shows that the $\delta^{18}O$ value of these samples decreases markedly approaching the Alta contact. Dolomite far from the contact has $\delta^{18}O$ values of 23.5 to 27‰ (Bowman et al., 1994). The $\delta^{18}O$ is essentially unchanged within the talc zone and the tremolite zone, and even the beginning of the forsterite zone. But within about 500 m of the contact, and especially within 250 m, stratigraphically equivalent marbles have $\delta^{18}O$ values as low as 9.0‰. These data have been interpreted as evidence for water infiltration into the contact aureole flowing outward from the contact into the marble (Bowman et al., 1994).

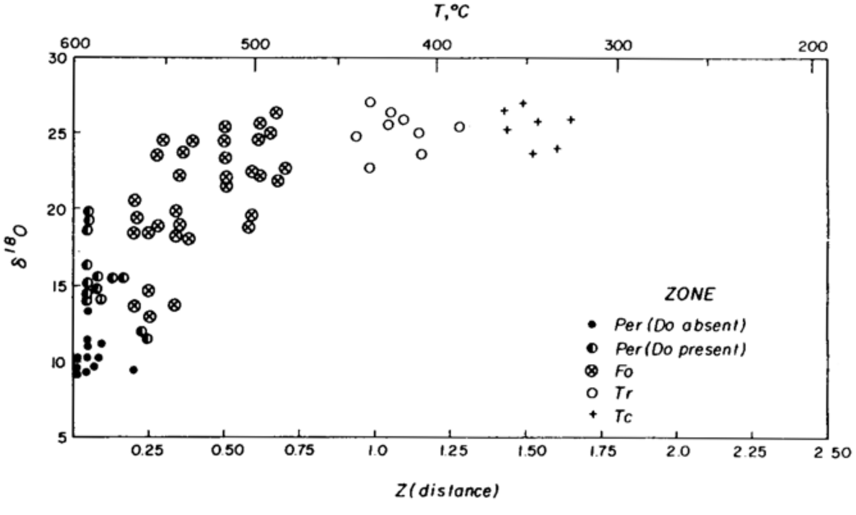

Figure 13. $\delta^{18}O$ versus distance (Z, in kilometers) from the contact of the Alta stock Temperatures are from Cook and Bowman (1994). Taken from Bowman et al. (1994).

One-dimensional fluid flow models have been applied to the Alta data by Bowman et al. (1994). A model result that fits the data fairly well is shown in Figure 14. The curved lines in Figure 14 represent model exchange fronts that change position with time (τ is a dimensionless time variable). The model assumes 8‰ for the infiltrating fluid, which would be in equilibrium with a carbonate rock of 9‰ at 600°C. The dashed curve labeled “final” in Figure 14 represents the $\delta^{18}O$ toward which the rock will tend if flow continues indefinitely and the temperature profile remains as it is. (This particular model assumes that the effects of dispersion during fluid flow is minimal relative to the fluid flow rate. This is reflected in the peclet number, $N_{Pe} = 20$.)

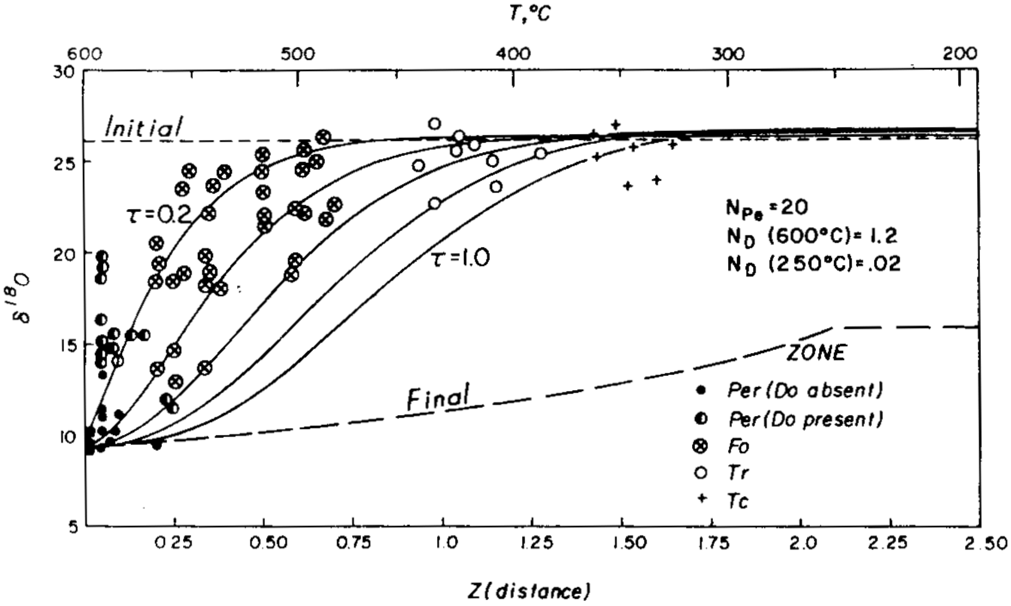

Figure 14. One dimensional fluid flow models superimposed on the Alta $\delta^{18}O$ data (figure taken from Bowman et al., 1994). Model inputs include initial rock at 26‰, fluid input at 8‰, temperature steady-state as indicated. Distance (Z) is in kilometers.

Considerable variation is apparent in the δ^{18}O values at any distance from the contact, due to natural heterogeneity in the rocks to begin with. The amount of variation increases as the δ^{18}O values decrease toward the contact. The increased variation is expected to result from differences in the original permeability structure of the rocks, which may focus or inhibit fluid flow. Some rock layers may act as aquifers while other layers act as aquitards or aquicludes.

The best fit of the Alta oxygen data to the model is for $\tau = 0.2$ to 0.6 (Figure 14). These values relate the fluid flux to the path length and correspond to total fluid fluxes of about 220 to 800 m^3/m^2. This is a considerable quantity of fluid to pass through solid rock! Depending on the duration of the contact metamorphism, fluid fluxes of this magnitude can also result in considerable heat transfer (Bowman et al., 1994).

Summary: Stable Isotopes in Metamorphic Processes

The Alta contact aureole is only one of many igneous intrusions where significant water-rich fluid flow has been documented. The ultimate source of the water in these systems is either igneous (expelled by the crystallizing pluton), or meteoric (heated groundwater, possibly in convecting hydrothermal systems), or both. Stable isotopes are generally just one piece of the puzzle, though in some cases an important piece, but the strength of stable isotope geochemistry is when it is used in conjunction with other petrologic data or constraints. In the Alta study, for example, the petrology indicates that fluid conditions were water-rich at the contact, and this is consistent with the expulsion of magmatic water from the pluton.

Hydrothermal systems associated with numerous shallow igneous intrusions have been well studied using stable isotopes (e.g., Criss and Taylor, 1986). Such hydrothermal systems can produce important deposits of many metals, including copper, lead, zinc, tin, silver, gold, and many others. Similarly, hydrothermal systems associated with mid-ocean ridge spreading centers can also result in significant ore deposits, and stable isotopes are particularly useful in understanding the processes active in this setting (e.g. Shanks, 2001). Large fluid fluxes can transport significant quantities of material, even material that is generally considered to have low solubility, and stable isotopes can be very useful in studying any situation where large quantities of fluid have interacted with rocks.

Part 3 Problems

1.) Aside from the stable isotope data, explain the evidence that the metamorphic fluid was water-rich close to the Alta contact.

2.) The decrease in δ^{18}O in the Alta aureole has been attributed to water infiltration outward from the intrusion into the marble, but what about the decrease in δ^{13}C? Is it feasible that the decrease in δ^{13}C resulted from volatilization? How else might the carbon isotopes be explained? What additional information about the samples would you want to have to know whether or not volatilization caused the decrease in δ^{13}C of the periclase zone rocks?

3.) The raw data is provided in a spreadsheet. Make a plot similar to Figure 13, except for the δ^{13}C values.

4.) Compare your plot of the δ^{13}C values versus distance. How is it similar and how does it differ from the δ^{18}O data? Can the carbon data be explained by a fluid flow exchange front?

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