PART 1 Classroom Activities After students have read Part 1 and turned in problems.
Goal: To guide discussion of Part 1 reading assignment and introduce concepts for Parts 2 and 3.

Question 1. What factors affect the oxygen isotope composition of a metamorphic rock?

Assign students into small groups to ponder this question for 5 minutes, or discuss as a class. The answer to which the class should eventually arrive is:

1.) the protolith
2.) the effect of volatile loss
3.) exchange with any infiltrated fluid

(The specific effect of either 2 or 3 would be temperature-dependent)

Question 2. Consider the effects of "decarbonation" in a marble undergoing the metamorphic reaction (assuming the CO_2 is expelled, removing carbon and oxygen from the rock)

dolomite + 2 quartz = diopside + 2 carbon dioxide
$CaMg(CO_3)_2 + 2SiO_2 = CaMgSi_2O_6 + 2CO_2$

What would you need to know to calculate the isotopic effect from this reaction in a real rock? Again, give time either in groups or as a class to discuss and come with as many ideas as possible. This problem is fairly open-ended. Depending on the depth of their answers, this would be an opportunity to introduce the equations for calculating "Batch" and "Rayleigh" volatilization covered in Part 2. Guided discussion, augmented by mini-lectures, might come to the following list of answers:

1. The isotopic effect will be in both $\delta^{18}O$ and $\delta^{13}C$
2. Need to know $10^3\ln\alpha$ or Δ for CO_2-rock for oxygen and for carbon, which means you'll need to know the temperature of reaction (and mineral modes, mini-lecture on Figures 5 & 6).
3. Need to know the mechanism of CO_2 removal. Specifically, the two end-members are batch CO_2 volatilization and Rayleigh CO_2 volatilization (mini-lecture on Fig. 4 and Eqns 11 & 12).
4. The F values for carbon and oxygen will be different, but not independent.
5. Assumptions will have to be made about all phases remaining in isotopic equilibrium during the volatilization process.

NOW: Chromatography Demonstration (materials needed: water soluble markers, strips of filter paper, beakers, water. Permanent markers are fine if you use alcohol as the solvent). If possible, allow groups of students to set up their own demonstrations. It is fun to use single pigment ink (cyan, yellow, or magenta) as well as mixtures that separate on the filter paper.

Question 3. What factors control the movement of ink on the paper? When fluids flow though rocks, what factors control the movement of geochemical "markers" through the rocks? Point out that both the fluid and the marker (ink) move, but the fluid moves farther (faster). Draw a parallel to geochemical fronts or reaction fronts in rocks.

Question 4. Time permitting, present the isotopic data for the Alta contact aureole. How might these data be best explained? Encourage all ideas. Leave unanswered for now. Assign Parts 2 and 3 for reading.

ANSWER KEY: **Part 1** Problems

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.

Approximate solution: $10^3 \ln\alpha = 7.0 \approx \Delta_{Cc\text{-}H_2O}$, $\delta^{18}O_{H_2O} \approx 9.2‰$.

Exact solution: $\alpha = 1.0070 = 1016.2 \div (1000 + \delta^{18}O_{H_2O})$, $\delta^{18}O_{H_2O} = 9.136‰$ (round to 9.14‰ or even 9.1‰)

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

Approximate solution: $10^3 \ln\alpha = 7.0 \approx \Delta_{Cc\text{-}H_2O}$, $\delta^{18}O_{Cc} = 7.0‰$.

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?

Given: $\delta_{Cc} - \delta_{H_2O} = 5.5‰$, and
$(3\ \text{mol} \times \delta_{Cc} + 1\ \text{mol} \times \delta_{H_2O}) \div 4\ \text{mol} = 7.5‰$.
Thus: $\delta_{Cc} - 5.50 = \delta_{H_2O}$ and replacing δ_{H_2O} in the second equation we get,
$(3 \times \delta_{Cc} + 1 \times (\delta_{Cc} - 5.50‰)) \div 4 = 7.50‰$. This rearranges to
$4\delta_{Cc} - 5.50‰ = 4 \times 7.50‰ = 30.0‰$, and thus,
$4\delta_{Cc} = 35.50‰$, so $\boldsymbol{\delta_{Cc} = 8.875‰}$, and
$\boldsymbol{\delta_{H_2O}} = 8.875 - 5.50 = \mathbf{3.375‰}$.

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?

Given: $\delta_{Cc} - \delta_{H_2O} = 5.0‰$, and
$(6\text{mol} \times \delta_{Cc} + 1\text{mol} \times \delta_{H_2O}) \div 7\text{mol} = (6 \times 25 + 1 \times 5) \div 7 = 22.14‰$.
Thus: $\delta_{Cc} - 5.0 = \delta_{H_2O}$ and replacing δ_{H_2O} in the second equation we get,
$(6 \times \delta_{Cc} + 1 \times (\delta_{Cc} - 5.0‰)) \div 7 = 22.14‰$. This rearranges to
$7\delta_{Cc} - 5.0‰ = 7 \times 22.14‰ = 155.0‰$, and thus,
$7\delta_{Cc} = 160.0‰$, so $\boldsymbol{\delta_{Cc} = 22.86‰}$, and
$\boldsymbol{\delta_{H_2O}} = 22.86 - 5.0 = \mathbf{17.86‰}$.

ANSWER KEY: **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.

A value of 1.0035 to 1.0038 would be a good choice. This larger $\alpha_{CO_2\text{-rock}}$ (carbon) would result in "stretching" the curves in Figure 4 downward. That is, there would be a greater decrease in $\delta^{13}C$ at given F value.

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.)
The plot of Figure 4 can be found on sheet 3 of spreadsheet "Alta Data Complete" found at http://www.mtholyoke.edu/courses/sdunn/geol201/index.html and modified to your taste.
This will be very challenging if they have never used Excel (or other software)!

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?

Need to know: $\alpha_{H_2O\text{-rock}}$ (which may require knowledge of temperature and rock mineralogy) and F_{oxygen}. The batch and Rayleigh models will give essentially the same result because the F value will be large.

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.

Water will have a lower $\delta^{18}O$ than quartz and muscovite at 400°C, so dehydration will increase the $\delta^{18}O$ of the rock. The opposite will be true in the second question, because at 500° muscovite + phlogopite will have a lower $\delta^{18}O$ than water.

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 wt.% H_2O is approximately 9 mol% 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).

Either Eqn. 11 or 12 can be used because F_{oxygen} is 0.9.
Equation 11: $\delta_f - \delta_i = -(1-F)10^3\ln\alpha_{H_2O\text{-rock}}$
From Figure 5, $10^3\ln\alpha_{H_2O\text{-muscovite}} \approx 0$, and $10^3\ln\alpha_{H_2O\text{-phlogipite}} \approx 1$, thus $10^3\ln\alpha_{H_2O\text{-rock}} \approx 0.5$
$\delta_f - \delta_i \approx -(0.1)0.5 \approx -0.05‰$ The final rock is slightly "lighter", but not significantly so.

ANSWER KEY: **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.

The T-X_{CO_2} diagrams require very water-rich conditions for periclase + calcite at 600°C

2.) The decrease in $\delta^{18}O$ in the Alta aureole has been attributed to water infiltration outward from the intrusion into the marble, but what about the decrease in $\delta^{13}C$? Is it feasible that the decrease in $\delta^{13}C$ 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 $\delta^{13}C$ of the periclase zone rocks?

The magnitude of the decrease in $\delta^{13}C$ could be achieved by Rayleigh decarbonation, if the F-carbon values in the rocks are low enough. Thus one would need to know the modal mineralogy of the samples and determine F for carbon. The other possibility is if carbon is also present in the infiltrating fluid, and if its isotopic composition is relatively low.

3.) The raw data is provided in a spreadsheet. Make a plot similar to Figure 13, except for the $\delta^{13}C$ values. Spreadsheet → http://www.mtholyoke.edu/courses/sdunn/geol201/index.html "Raw" data gives only $\delta^{13}C$, $\delta^{18}O$, and distance, "Complete" includes all finished plots.

This will be very challenging if they have never used Excel (or other software)!

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

The "front" in carbon is closer to the contact. This would be expected if the concentration of carbon in the fluid were lower than the concentration of oxygen, which we can presume to be true ($X_{CO_2} \leq 0.3$). Thus the carbon data could be the result of isotopic exchange with the infiltrating fluid. Compare figure below with Figure 13.