**ESS 312 Geochemistry Week 4**

**Trace Element Behavior in Igneous Systems**

Patterns of trace element concentrations in rocks and minerals provide a powerful way to quantify melting and crystallization processes. We can obtain information about the extent of melting and the mineral assembleage of the parent rock. Likewise, we can identify the minerals that crystallized from a melt before eruption, and determine the amounts removed. We will explore general principles of element *partitioning* between co-existing melt and mineral phases; these will turn out to be useful in understanding and modeling geologic processes beyond magmatism and differentiation in igneous systems.

These exercises depend on using Excel spreadsheets to perform calculations. If you haven’t used Excel to do the lab and homework exercises over the past few weeks, be sure to check with an instructor on how to write spreadsheet formulae.

When magmas form or crytallize, the liquids and solids in equilibrium with one another have different compositions. Thus the separation of a *partial melt* from its parent rock changes the composition of the residue, and removal of the solids crystallizing from a magma changes the composition of the remaining magma. Both are important processes of *differentiation*. Two simplified conceptual models are used to understand these processes:

Partial Melting

a) Batch (or equilibrium) melting, in which the liquid is assumed to come to equilibrium with the residual solid minerals in its parent rock as a single batch.

b) Fractional (or Rayleigh) melting, in which successive small batches of liquid are removed from the parent rock sequentially, each in equilibrium with the parent minerals at the time of its formation.

Crystallization

a) Batch (or equilibrium) crystallization, in which a single batch of crystals and melt is assumed to come to equilibrium.

b) Fractional (or Rayleigh) crystallization, in which crystals precipitated in equilibrium with the melt are progressively removed. This changes *both* the composition of the melt, and the next crystals to form, as crystallization proceeds.

The objectives of this lab are to: 1) Model batch melting, 2) Model fractional crystallization, and 3) Apply these models to solve a petrologic problem regarding the origin of granites in the Peninsular Ranges Batholith of southern California.

Throughout the lab, we will use the following definitions:

F = fraction of **melt** in the system (from 1 for entirely liquid to 0 for entirely crystalline)

Di = distribution coefficient for element i

**Di = (concentration *i* in mineral)/(concentration *i* in melt)**

Elements with values of Di > 1 are called *compatible* elements, those with Di < 1 are called *incompatible* elements. Recall Goldschmidt’s rules for substitution of trace elements into crystals as you work with these definitions below.

Ci,L = concentration of element *i* in the liquid

Ci,S = concentration of element *i* in the solid

Ci,0 = concentration of element *i* in the total system (*i.e.* In problems dealing with *melting*, Ci,0 is the concentration in the initial solid. In problems dealing with *crystallization* of a magma, it is the original concentration in the liquid.)

It is important to keep these consistent.

**I. Batch (Equilibrium) Melting**

1) Show the derivation for the batch melting equation: Ci,L/Ci,0 = 1 / (F + Di - FDi)

2) Use the Batch Melting Excel template provided to solve this equation for:

F ranging from 0 to 1 in steps of 0.05

Di values of 0.05, 0.06, 0.1, 0.5, 1, 2 and 10

(Put the F values in the first column, and then solve for each D in the next 7 columns. You can write a single Excel equation that can be copied to all of the other cells in the table. Ask if you're not sure how to write Excel formulae that lock row and column references.)

3) Make two graphs, both plotting Ci,L/Ci,0 versus F. Put curves for all values of Di on each plot. Set the y-axis for one plot to range from 0 to 20, to see the behavior of the incompatible elements. Set the other to range from 0 to 2, to highlight the behavior of the compatible elements.

4) In general, what is the behavior of the incompatible elements as partial melting progresses? What is the general behavior of the compatible elements as partial melting progresses? Explain these behaviors in light of Goldschmidt’s rules. When mantle peridotite melts at moderate depths, the magma forms in equilibrium with olivine, orthopyroxene, clinopyroxene and spinel. Suggest two trace elements that would behave as *compatible* elements when melt forms in the presence of these minerals. Suggest two trace elements that would behave as *incompatible* elements.

5) Assume that two elements, one incompatible with Di = 0.1 and the other compatible with Dj = 2, both had the same C0. On the spreadsheet, add a column that calculates the ratio of the incompatible to compatible element in the melt. Describe how this ratio changes as the melt fraction, F, increases from 0 to 1 (from the first drop of melt formed, to the point where the system is entirely molten).

6) Assume two incompatible elements, one with Di = 0.05 and the other with Dj = 0.06, both had the same C0. Add another column to the spreadsheet that shows how the ratio of these two change as partial melting progresses (place the more incompatible element in the numerator). Describe how this ratio changes as the melt fraction, F, increases from 0 to 1.

7) It seems reasonable to hypothesize that lavas erupted from Hawaiian volcanoes formed by partial melting of the underlying mantle. But without actual samples of the mantle, we must use element concentrations in the erupted basalts (Ci,L, measured in the basalt after it has cooled and solidified) to make inferences about the composition of the mantle source (values of Ci,0). Using our understanding of element partitioning, we can now make some useful estimates of mantle source concentrations and place limits on ratios of different elements.

a) Which elements (ranges of Di) change least as partial melting progresses (consider melt fractions up to 30% (F ≤ 0.3), which is probably the maximum extent of melting in the mantle)?

b) Generally, we don’t know the value of F that produced a particular magma. Nonetheless, we can still estimate the mantle concentrations of some elements. By looking at your graphs, and substituting some trial values for Di if necessary, which range of Di values give magmas whose concentrations are within ±25% of the initial composition of the parent mantle Ci,0. (Again, only consider melting up to 30%; F ≤ 0.3).

c) The ratio of incompatible elements measured in Hawaiian lavas can provide us with information about the ratio of these elements in the mantle source that was melted. In terms of relative Di values, which element ratios in the magma would be very close to those element ratios in the mantle source?

8) Th and Ce have D = 0.002. The last lavas that erupted on Oahu are called the Honolulu Volcanic Series. These rocks have Th concentrations of 2.5 to 12.5 ppm, and Ce concentrations of 40 to 200 ppm. In spite of this range of concentration, each rock has a Ce/Th ratio of 16.

a) Can all of these magmas have come from the same mantle source, or is more than one source required? Why?

b) Which samples represent the greatest degree of partial melting? Which the least? Assume no significant crystal fractionation in a magma chamber before each lava was erupted.

c) Nickel content is very high in all these lavas. Nickel is a very compatible element (DNi ~ 10). How does this relate to our assumption that there was no significant crystal fractionation in a magma chamber?

**II. Fractional Crystallization (Rayleigh Crystallization)**

We will now simulate the partitioning of elements between crytsals and residual melt in a magma chamber that is undergoing cooling and fractional crystallization in the crust. It will help considerably if you have in mind a good physical picture of the process. Fractional (or Rayleigh) crystallization describes the idealized process in which infinitesimal amounts of solid are formed and immediately removed from a magma. As each increment of crystals is removed, the composition of the residual liquid changes, and the composition of the next crystals to form must change also. Whenever a process occurs by small increments, it should be analyzed by differentiation, and the cumulative effects of the process calculated by integration. In this exercise we'll simulate the infinitesimal changes by making a spreadsheet that breaks up the process into small steps. In a simple case like this, we can compare the results to an analytical solution, which is given below.

Remember, that in a fractionally crystallizing magma chamber, F *decreases* from 1 to 0. This is the opposite of the case of melting, in which F increases from 0 to 1 (which we dealt with in Part 1 of this lab). We will build a step-by-step model of the crystallization process. Each time a small amount of crystals form, we will calculate the concentration of some element (i) in that crystal based on its D value. We then remove this solid from the system, and crystallize some more.

There is an exact solution that describes this process. Although a little tricky to derive, you could integrate to obtain an analytical formula for the concentration of i in the crystallizing liquid:

**Ci,L / Ci,0 = F (D-1)**

After setting up the incremental model, we will compare the results to this exact formula.

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1) Work on the second sheet of the Excel template (it is labeled Fractional Crystallization).

2) The variables and their initial values are:

Di value (Ci,S / Ci,L) 0.1

starting concentration in the liquid (Ci,0) 0.01

starting liquid weight 100

amount crystallized each step 1

You will want to write equations that refer to these values (*i.e.* put cell references rather than numerical values into your equations). By doing so you'll be able to change the numbers above to answer questions about the behavior of elements with different Di values and different starting concentrations.

3) The first thing to keep track of is how many grams of liquid are in the system. Do this in column A. In A13 start with the initial liquid weight (D7) and have it decrease by the crystallization increment (D8). (Numbers should extend from row 13 to row 113).

4) In column B keep track of the grams of solid formed and removed at each step (starting with step 2). This is already entered in the template for you. Because our crystallization increment is constant, you have the same number all the way down. We start in the row that has 99 grams of liquid, since there can't be any solid if there is 100 grams liquid.

5) Now we’re ready to start filling in the model calculations. To do so, observe that at each step, we divide the total amount of the element that was present in the liquid at the previous step between newly-formed solid and the new (smaller) amount of liquid. We can connect the two steps by writing an equation for conservation of the element’s mass between the present step (subscripted *n*) and the previous step (subscripted *n-1*):



Re-arrange this by re-writing Ci,S,n in terms of Ci,L,n. Then group terms to get an expression for Ci,L,n, which you can use to fill in line 14, column F of the spreadsheet. Your Excel formula will refer to the constants at the top of the sheet, values on the previous line, and values in columns A and B.

6) In column C keep track of the concentration of i in the solid (Ci,S ). (You have to figure out how to calculate this using the known Di value.)

7) In column D, keep track of the total grams of element i that go into the solid in each step. The column is labeled as "grams element i in solid". (Hint: the total number of grams of the element in the solid is calculated from the total weight of the solid (1 gram in each step) and the element concentration which you are tracking in column C.)

8) In column E, keep track of total grams of element i that remain in the liquid after the solid has formed in each step. The column is labeled as "grams element i in liquid". (As above, you can calculate this from the total weight of the liquid remaining and the element concentration in the liquid (from column F.)

If you’ve written the formulae for cells C, D, E and F with clever cell references, you should now be able to copy them down the spreadsheet to the final line, in which the last gram of liquid crystallizes. Check with a TA or instructor if you need help on this.

You can check whether your equations are correct by adding up the values in column D. The total for this column should equal the starting concentration in the liquid Ci,0 x the initial mass of the liquid. For the initial values of 100 g liquid and Ci,0 = 0.01, the initial amount of element i is 1 g.

Now compare your incremental model to the exact Rayleigh equation. The results should be close until the last few steps, where the incremental model will begin to break down because of the inability of the coarse model steps to handle the large concentration changes.

9) In column G keep track of F, the fraction of liquid in the system. (Remember that F should go from 1 to 0.)

10) In column H, labeled "Exact Rayleigh Eqn Ci,L", enter the Rayleigh formula (Ci,L as a function that refers to Ci,0, Di and F. Be sure to reference cells D5 and D6, so you can change those values later). Remember that the Rayleigh equation is given as Ci,L/Ci,0, so you will have to rearrange it slightly.

Check that the step-by-step calculation and the exact equation agree closely for F values greater than about 0.1 - 0.2. You can tabulate the percentage difference between the two in column I.

11) Now use the exact values in column H to make one last column of Ci,L/Ci,0 values (column J). Use the starting value of Ci,0 in cell D6 as the denominator, so that you'll be able to change this to answer the last few questions. Make a plot of Ci,L/Ci,0 vs F. As you change D from 0.05 to 10, how does Ci,L/Ci,0 vary with F? (Recall that in this case the process starts at F=1 and proceeds to F=0 as the melt crystallizes).

12) In basaltic magma, Ni has a D of about 10. In the Honolulu volcanic rocks the Ni concentration ranges from about 300 to 250 ppm. Assume the sample with the highest concentration is a magma that has undergone no fractional crystallization. What is the range of fractional crystallization required to lower the Ni content to 250 ppm? Does this support or argue against the assumption made in Part I, questions 8b and 8c?

13) In a basaltic magma, the REEs have D-values that change in a regular way from 0.10 for La (the lightest REE) to 0.15 for Lu (the heaviest REE). Consider a basaltic magma chamber that is gradually crystallizing. Describe how you would expect the REE pattern to change in a series of lavas erupted from the chamber as the magma crystallizes. As a starting composition, assume (chondrite normalized values) La = 30 and Lu = 5, and a straight REE pattern. (Use F=1 to F=0.5 in steps of 0.1; Calculate Lu and La at each step. The initial La/Lu ratio = 30/5 = 6. How does this ratio change as the magma crystallizes?

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# III. Origin of granites in the Peninsular Ranges Batholith

In southern California and northern Baja Mexico a long, narrow, northwest trending series of granites are exposed that make up the Peninsular Ranges Batholith. Although the composition of the batholith does not change much as one samples from southeast to northwest along 600 km, there are dramatic changes in composition from west to east over only 100 km. In this problem we will look at the rare-earth element (REE) composition of the western and eastern granites, and try to determine what the implications are for their origins.

In the final sheet of your Excel lab template (labeled Peninsular Ranges Batholith) you have the data you need for this lab: REE concentrations for two granites (#2 and #56; columns B & C), the chondrite concentrations (column D) to use in making the REE chondrite normalized plot, and the distribution coefficients for several minerals (columns A through E, rows 16 through 24).

Although tonalites from the western and eastern parts of the PRB have very different REE patterns (see question 1 below), they have very similar major element compositions. This suggests that they were derived by partial melting of *sources* with similar major element compositions. It is likely that much of the crust at the edge of the continent is made of basalt erupted in older volcanic arcs. We will test the hypothesis that the PRB granites formed by partial melting of older basaltic crust. Use the following as the REE concentration typical of basaltic crust (already divided by chondritic values):

Assumed basaltic crust composition (chondrite normalized; in cells G5 thru G12)

Ce 15.0 Gd 10.5

Nd 13.0 Dy 10.0

Sm 12.0 Er 9.5

Eu 10.6 Yb 9.0

The mineralogy of the basalt that we propose to melt depends on its depth in the crust. At pressures less than 15 kb we expect:

60% clinopyroxene and 40% plagioclase.

At pressures greater than 15 kb the basalt will have a different mineralogy:

60% clinopyroxene + 30% garnet + 10% hornblende

The question we will try to answer is: could western and/or eastern granites have been formed by partial melting of deep or shallow basaltic crust?

1. In cells E5 through F12, calculate the chondrite normalized values for sample #2 and sample #56. Plot the REE pattern for these samples and the model basaltic crust on the same REE plot. *Sample #2 is typical of the western granites and sample #56 is typical of the eastern granites*. Briefly describe the differences in REE patterns between western and eastern granites. (From now on, always use the chondrite normalized values in your calculations – not the ppm values).
2. If you are melting a rock containing more than one mineral (e.g., cpx and plag) provide the general formula for how you would calculate an overall or bulk D value for that rock. Starting in cells G17 and H17, calculate the bulk D for the shallow basalt and the deep basalt, using mineral proportions given above and the distribution coefficients provided in your template.
3. In rows 26 through 48, calculate the REE composition of Batch Equilibrium partial melts of the deep and shallow basaltic crust. You will have to try a variety of values for the degree of partial melting (i.e., for F). Can you produce a reasonable model that yields the observed REE patterns for the western and eastern granites? Show your results on appropriate REE plots.
4. Based on your REE modeling, what can you infer about the depth(s) of the source region(s) for the PRB? Draw a cross section that schematically depicts your model.

*Relate it to a subduction-zone setting; draw the diagram with a depth scale and sketch in features at appropriate depths and thicknesses; consider the Benioff zone depth*