

Partition Coefficients Lab

To instructors

The purpose of this exercise is to introduce students to hand picking as a sample separation technique, HF dissolution of easily dissolved igneous phases, analysis of a variety of trace elements, calculation of partition coefficients, and finally and most importantly construction and evaluation of a mathematical model for the origin of magmas. This exercise was designed specifically for a pair of samples I collected in Iceland: a basalt from the Thingvellir area (phenocrysts of augite, olivine, and plagioclase), and a dacite obsidian from the Landmannalaugar area. I do not pretend that these samples actually have any cogenetic relationship; the object is to test if a genetic relationship is plausible based on evaluation of a specific set of mathematical models. In principal, this exercise can be done without the two samples being related in any way.

The exercise handout

Introduction

To have a basic understanding of the reasons for chemical variations in magmas you must understand something about the chemical compositions of and physical interactions between minerals and the silicate liquids. In this lab we will analyze two rocks: a porphyritic basalt and a glassy dacite from Iceland. Are the two rocks related by simple geological processes? This is a geochemical question that can be answered only in the context of models of how magmas originate. In order to construct reasonable geochemical models, first we must have some idea of the kinds of models that might apply, such as partial melting or crystal fractionation. Second we must have some model constraints: the chemical compositions of the rocks, mineralogy of the rocks, the chemical compositions of the minerals, and the proportions of the minerals involved are all useful constraints. The data we will gather during this exercise will help constrain the models that we will prepare next week.

Sample preparation

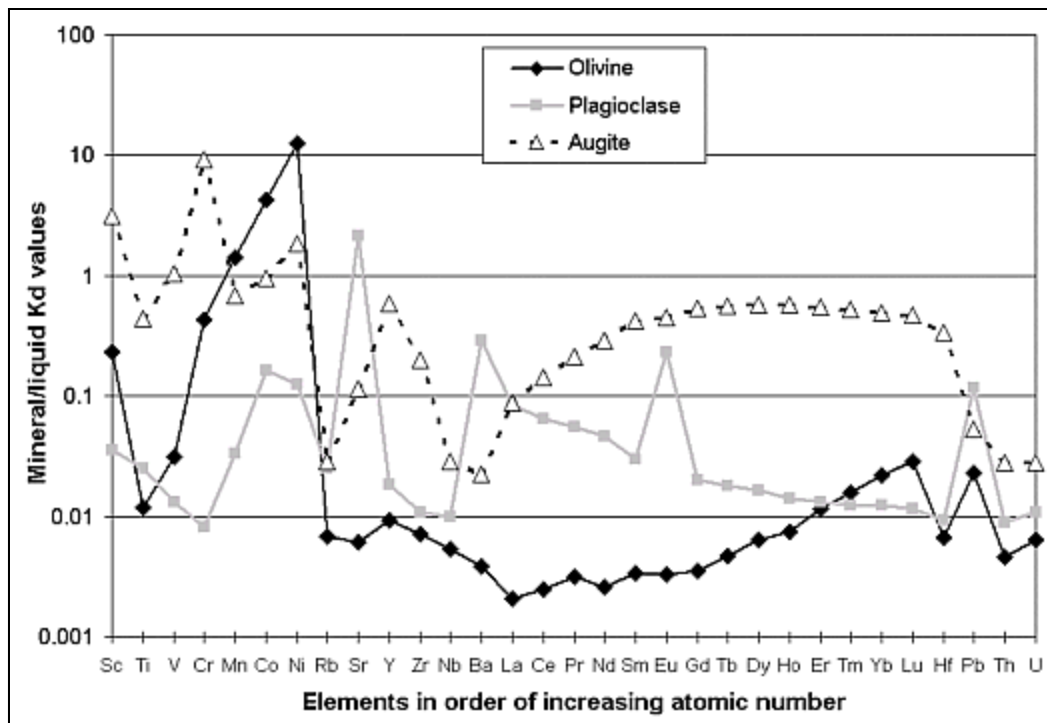
1. The principal sample will be a multiply-saturated Holocene basalt from southern Iceland. There are three phenocryst phases, olivine, augite, and plagioclase, plus the fine-grained matrix representing the liquid that was host to and was precipitating the phenocrysts. A sample of an Icelandic dacite obsidian will also be included (I will prepare the obsidian).
2. Coarsely crush the rock chips with a Plattner mortar. After each tap with the hammer, remove the crushed rock and put it into a sieve stack: 1 mm, 0.25 mm, closed bottom. Collect the sample that is held by the 0.25 mm sieve. Fine-grained material in the bottom can be thrown away; coarse material held by the 1 mm sieve should be kept for recrushing.
3. Put a small amount of your collected sample onto a large glass microscope slide, and spread the grains into a line with a razor blade. Using a binocular microscope and the razor blade, separate pieces of your assigned mineral or matrix. Collect ~0.05 g of your assigned mineral or matrix into a plastic vial. Select clean, inclusion-free grains insofar as possible.
4. If you finish before others, start collecting the material that someone else has not finished to help speed things along.
5. Add some cold 2% HNO_3 to the plastic vial and ultrasonically clean for a few minutes. Afterward, rinse the minerals several times with deionized water, then a few times with acetone.
6. Pour off all excess acetone and let the samples dry.
7. Weigh your sample into a clean, 17 ml Savillex container. Record the weight of the sample and

the number of the container.

8. Dissolve the samples according to the [low-pressure HF dissolution procedure](#) located on the ICP-MS home page.
9. Analyze the samples for a variety of elements, for example: Sc, Ti, V, Cr, Mn, Co, Ni, Rb, Sr, Y, Zr, Nb, Ba, REE, Hf, Pb, Th, U.

Calculations Part 1: All groups

1. The analytical data for all samples are on the Geochemistry web page. Retrieve the spreadsheet containing the data. Elements are in order of increasing atomic number.
2. Subtract the average blank values from all samples, including the blanks.
3. Blanks: For each element, calculate the detection limits as three times the standard deviation of the mean.
4. Standards: For each standard and each element calculate the average, and also the relative deviation of the mean at the 95% confidence limit.
5. Samples: For each element in each of the five sample types (basalt olivine, plagioclase, augite, matrix; dacite obsidian) calculate the average and the relative deviation of the mean at the 95% confidence limit. In your writeup you should comment on the precision for the different elements, particularly if some have worse precision than others. Note that this precision value includes analytical precision AND actual variation from sample to sample. Comment on the precision in the samples as compared to the standards.
6. All of the phenocrysts contain trapped liquid inclusions (now mostly crystallized). Its proportion of the crystal volume is hard to estimate, but it is ~1%. Subtract from each average phenocryst composition a value equal to 0.01 of the average matrix composition.
7. Present your analytical data in a data table. For data like this, you don't need to present the raw data or even the element concentrations in each sample replicate. This table should have the elements analyzed, estimated detection limits, the average and analytical precision of the standards, "accepted" standard concentrations, and sample averages and analytical precision.
8. On a second table show calculated mineral/matrix (matrix = liquid) partition coefficients (K_d 's) for all three phenocrysts and all elements.
9. Plot the partition coefficients on a graph, in order of element atomic number. The Y axis should probably have a log scale.



10. Consider why the high and low Kd elements are different for the three different minerals.
 - A. Review the available cation sites in olivine, pyroxene, and plagioclase.
 - B. Identify the sites into which each element is likely to substitute, based on charge and ionic radius, and if the substitution is simple or coupled.
 - C. Identify the major elements present in each of the sites for each mineral (use forsterite for olivine, diopside for pyroxene, and labradorite for plagioclase).
 - D. The major elements define the site sizes. Also identify the appropriate ionic radii of the sites in the phenocrysts phases.
 - E. In a general way, how do the elements having very different crystal/liquid partition coefficients compare in charge and ionic radius with the elements that usually occupy the sites?
 - F. Comment on each mineral separately. Give some examples
11. In a spreadsheet calculate the chemical composition of the Icelandic basalt whole rock (matrix plus phenocrysts). You have the compositions of the matrix and the three phenocryst phases, and a table giving the weight proportions of the four components. This is a mixing problem.

Weight mode of silicate minerals in the basalt sample			
Component	Phase	Each phase as a proportion of the whole rock	Each phase as a proportion of the component
Phenocrysts only	Olivine	7%	32%
	Plagioclase	8%	36%
	Augite	7%	32%
	Total phenocrysts	22%	100%
	Olivine	4%	5%
	Plagioclase	34%	44%

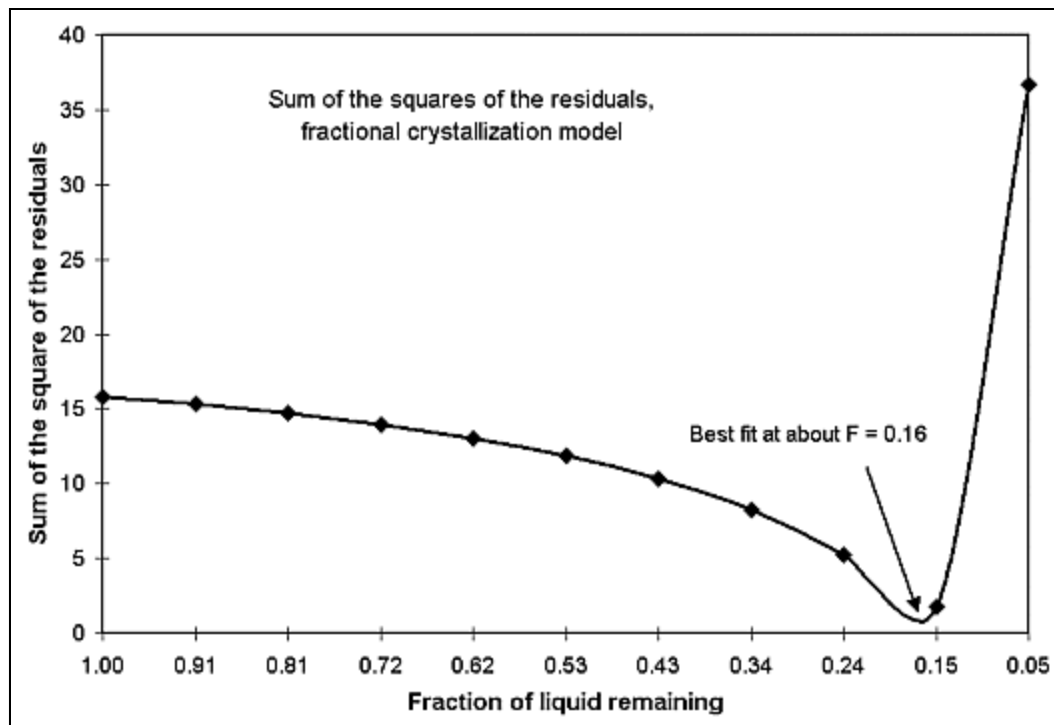
Matrix only	Augite	40%	52%
	Total matrix	78%	100%
Whole rock	Olivine	11%	
	Plagioclase	42%	
	Augite	47%	
	Total rock	100%	

Calculations Part 2: Fractional Crystallization Group only

- Set up a spreadsheet model to derive the dacite by fractional crystallization of the basalt liquid. Use the matrix (liquid) composition as the model parent liquid. Use the phenocrysts in their actual proportions for calculating the bulk partition coefficient for each element. To start, calculate the model in ten increments of 0.1 from F=1.0 to F=0.1. (F is the fraction of liquid remaining).
- Calculate the sums of the squares of the residuals for all elements with respect to the dacite composition (your target).

$$R_i^2 = \left[\frac{(C_m^i - C_d^i)}{C_d^i} \right]^2$$

R_i^2 = The square of the residual (difference) between the model liquid and the actual dacite. C_m^i = The concentration of element i in the model liquid. C_d^i = The concentration of element i in the actual dacite. Note that these are relative residuals, not absolute. Some elements will be very far off, most notably many transition metals. Can they be omitted from the model for a justifiable reason? Regardless of your opinion, omit those elements from the sums of the squares of the residuals that are modeled poorly. Plot the *sums* of the squares of the residuals on a graph. With an arrow, indicate the best model fit composition for the dacite.



- Do all of the elements approach the composition of the dacite with decreasing fraction of liquid remaining (F)? Which elements do not approach the dacite composition at any fraction of liquid remaining from 1.0 to 0.1? Can you explain the reason for the failure of any of these elements to approach the composition of the dacite?
- Calculate chondrite-normalized values for all lanthanides in dacite and the ten model compositions. Once the chondrite-normalized values have been calculated, insert cells between Sm and Nd to include Pm. Pm is not present in significant quantities on Earth, but its inclusion in the rare earth element sequence is essential for smooth chondrite-normalized patterns. Pm is calculated using the equation:

$$Pm_n = \sqrt{Sm_n * Nd_n}$$

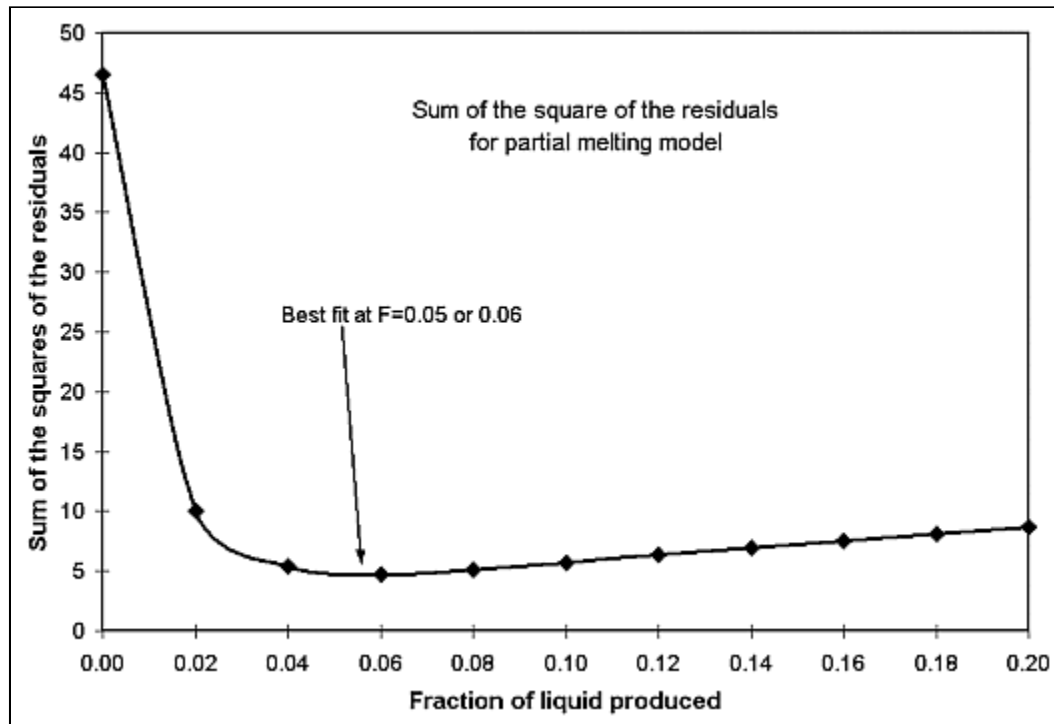
- Once your model is complete, plot a chondrite-normalized rare earth element diagram including the starting rock composition, the dacite and your model liquids.

Calculations Part 2: Batch Melting Group

- Set up a spreadsheet model to derive the dacite by batch melting of the solid basalt, assuming that this basalt makes up the lower Iceland crust. Use the whole rock mineralogy (table above) and the bulk rock composition (derived above) to calculate bulk partition coefficients. To start, calculate the model in ten increments of 0.02 from F=0 to F=0.2. (F is the fraction of liquid produced during melting).
- Calculate the sums of the squares of the residuals for all elements with respect to the dacite composition.

$$R_i^2 = \left[\frac{(C_m^i - C_d^i)}{C_d^i} \right]^2$$

R^2_i = The square of the residual (difference) between the model liquid and the actual dacite. C^i_m = The concentration of element i in the model liquid. C^i_d = The concentration of element i in the actual dacite. Note that these are relative residuals, not absolute. Some elements will be very far off, most notably many transition metals. Can they be omitted from the model for a justifiable reason? Regardless of your opinion, omit those elements from the sums of the squares of the residuals that are modeled poorly. Plot the *sums* of the squares of the residuals on a graph. With an arrow, indicate the best model fit composition for the dacite.



- Do all of the elements approach the composition of the dacite with increasing fraction of liquid produced (F)? Which elements do not approach the dacite composition at any fraction of liquid produced from 0 to 0.2? Can you explain the reason for the failure of any of these elements to approach the composition of the dacite?
- Calculate chondrite-normalized values for all lanthanides in dacite and the ten model compositions. Once the chondrite-normalized values have been calculated, insert cells between Sm and Nd to include Pm. Pm is not present in significant quantities on Earth, but its inclusion in the rare earth element sequence is essential for smooth chondrite-normalized patterns. Pm is calculated using the equation:

$$Pm_n = \sqrt{Sm_n * Nd_n}$$

- Once your model is complete, plot a chondrite-normalized rare earth element diagram including the starting rock composition, the dacite, and your model liquids.

Part 3, All Groups

Your lab writeup must contain at least the following things:

- A table showing standard and sample averages and analytical precision.

2. A table with the crystal/liquid partition coefficients.
3. A figure showing the K_d 's for all three phenocrysts phases, and comment on the crystal chemical reasons for the high and low K_d 's for different elements in the different minerals.
4. A table showing the model values and sums of the squares of the residuals.
5. A figure showing the sums of the squares of the residuals for the elements that you select as fitting the model reasonably well.
6. A figure showing the chondrite-normalized REE patterns for the basalt, dacite, and ten model liquids.
7. Comment on how closely the model liquids fit the dacite composition. Comment on the lanthanides specifically and the other elements generally.
8. Comment on the cause of the fact that some elements in the models miss the dacite target by orders of magnitude.
9. Determine the phase(s) needed for a more complete and accurate model for the dacite. Go to the GERM home page and click on "Partition coefficients". Get the partition coefficients for the phase(s) needed and put them in a table.
10. A substantial discussion: Is your model a plausible way to derive the dacite from the basalt? If yes, then the model is successful though not necessarily perfect (or even correct). If no, then the model fails (it is not a plausible approximation of the actual processes). It may be that geologically reasonable improvements to the model will make the model successful. It may be that the basalt sample is not representative of the magmas or rocks from which the dacites are derived. It may also be that processes other than those in your model are involved (e.g., magma mixing, wall rock assimilation). Success of a model is never proof that it is correct, but failure of a model always proves that it is wrong in at least one important respect. Comment on the fundamental success or failure of the model.

Notes

Things needed for this lab

- Safety equipment (goggles, lab coats, aprons, rubber gloves).
- [Savillex containers](#) cleaned: (6 for standards and blanks) + 2 dacite + (the number of students) = the number of containers needed.
- High-purity HF.
- High-purity HNO_3 .
- Vials for mineral separates; we use 7 ml plastic scintillation vials.
- Autosampler test tubes for ICP-MS.
- Pipettes set up at stations.
- Ultrasonic cleaners.
- 1 mm and 0.25 mm sieves and a bottom pan.
- Rock standards (we use NIST-278 and 688 mostly).
- 1000 ppm internal standard solutions (we typically use Rh, In, Re, and Bi).
- Rock samples.
- Balance for weighing samples.
- Stereo microscopes.
- Large glass slides, razor blades, tweezers.
- Acetone (or a drying oven at 80°C).

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