



# *Petrology of Volcanic Rocks*

**Least-Squares Models of Crystal Fractionation**

## Least-Squares Models of Crystal Fractionation

### Crystal Fractionation

Crystal fractionation, a change in melt or magma composition caused by the crystallization and separation of minerals, comes in two styles. The first shows up as mineral zoning. Each zone in a crystal of variable composition contains material extracted from the melt. The zone and the original melt have different compositions so the melt must change composition in response to the crystallization of the zone. Bowen (1923, p. 23) recognized crystal zoning as one style of fractional crystallization – it is universally present in magmas. [Figure 1](#), with its photomicrographs, shows mineral zoning in pyroxene and plagioclase phenocrysts in an hawaiite from an Itcha Mountain volcano, British Columbia (Stout and Nicholls, 1983). The second style of crystal fractionation, also recognized by Bowen (1923), requires separation of the crystals themselves from the melt – a process we can't observe but must infer from textures and compositions of the rocks and minerals. This style of crystal fractionation produces different rock types. Although the second style of crystal fractionation dominates thinking about magmatic differentiation, mineral zoning can have a significant effect on what the second style of crystal fractionation can accomplish. Crystallization paths controlled by differing sizes of mineral zones will not coincide with each other in compositional space, and melts with different compositions can, after mineral separation, lead to different rock types.

A volume of magma that fractionates changes that volume's composition and its size – crystals must leave the magma for the second style to operate, creating a smaller volume. The original composition no longer exists. The initial magma can only be represented by a sample that split off prior to fractionation and then came to the Earth's surface or by an independently generated magma with essentially the same composition as the original batch that was subsequently modified through fractionation.

Construction of any fractionation model should begin with a critical look at thin sections, followed by an examination of the chemistry of the rocks and minerals involved. For example, the photomicrographs in [Figure 2](#) show images of two picrites from the 1968 eruption of Kilauea. The

# Least-Squares Models of Crystal Fractionation

more magnesian picrite, shown in the upper photomicrographs, has larger phenocrysts of olivine and smaller phenocrysts of augite and plagioclase in a groundmass of glass. This rock presumably represents the initial magma. The second picrite, lower photomicrographs, has phenocrysts of olivine and a few smaller crystals of augite. If only olivine saturates the derivative magma early, then it is likely that the initial magma fractionated olivine before augite and plagioclase saturated the melt later in the crystallization history of the derivative magma.

## Least-Squares Models

The general problem in testing whether or not crystal fractionation happened comes down to the question of whether two rock analyses can be related by adding or subtracting mineral compositions from one or the other rock compositions taken to represent different magmas. Several algorithms for analyzing such problems have appeared in the literature (Bryan, *et al.*, 1969; Wright and Doherty, 1970; Stormer and Nicholls, 1978). All involve a multivariate, least-squares calculation. The models described here result from applying the algorithm developed by Stormer and Nicholls (1978). The algorithm is derived in detail in the section on this web site: *Mass Balance Constraints on Volcanic Processes*.

Extracting logical inferences about how magmas are related from a least-squares analysis can be (and usually is) tricky. Humans are not proficient evaluators of risk, chance, and probabilities. Consequently, conclusions drawn from statistical methods, which include the least-squares methods, should get a critical scrutiny. The connections between the calculated results and observed chemical and textural features of the rocks should receive close attention.

The data that enter a least squares model are two rock analyses and a set of mineral analyses. The rock analyses, we think, represent in some fashion, the composition of two magmas that, we think, may be related by crystal fractionation.

The two analyses in [Table 1](#) come from lava flows erupted at a volcano in eastern Iceland, Thingmuli (Carmichael, 1964). From which magma were the minerals fractionated to form the derivative magma? Petrologists think felsic rocks, if they result from crystal fractionation, are derived from magmas that, if left alone, would crystallize as more mafic rocks. This is, perhaps, one of the few verities from Bowen's reaction series: Given two magmas, then if they are related by crystal fractionation, the derivative magma is expected to

# Least-Squares Models of Crystal Fractionation

crystallize to a more felsic rock than would the initial magma G101 is an olivine tholeiite, which is a more mafic rock than a tholeiite, G99. Our first statement of the model becomes: Can the tholeiite magma, G99, be derived by crystal fractionation from the olivine tholeiite magma, G101?

## Mineral Analyses

But fractionation (removal) of what? Before minerals can be fractionated, they must be present in the initial magma. Consequently, the fractionated phases must be present as phenocrysts in G101; they must be in the set of phenocrysts: olivine, orthopyroxene, clinopyroxene, and plagioclase. Average compositions (Carmichael, 1967) of the phenocrysts in G101 are listed in [Table 2](#).

We are evaluating a model, and models, in general, are simplifications of reality. We simplify by removing extraneous and minor variables. First, FeO often suffers oxidation on and after eruption. To minimize the effect of oxidation on the model,  $\text{Fe}_2\text{O}_3$  is converted to equivalent FeO before running the least squares algorithm. Second, the algorithm was constructed on the assumption that the masses of the oxides in the initial magma sum to 100 mass units. Consequently, the masses of the oxides in the analyses of the several mineral phases and those of the rock analyses have been normalized to 100. Third, minor oxides, those present in concentrations less than one percent,  $\text{P}_2\text{O}_5$  and MnO usually, are left out of the analyses. The mismatches in fitting these oxides are often the size of their concentrations in the rocks and minerals or even larger. Unless a special phase, such as apatite for example, is suspected of being part of the fractionated assemblage, the minor oxides are best left out of the least-squares calculations.

## What Needs to be Modeled?

The chemical variables that the shifting mineral phases need to satisfy are the differences in oxide percentages between the two magmas. In other words, the observed differences in the contents of each oxide between the two magmas are what need to be modeled ([Last column in Table 3](#)). The least-squares model attempts to determine how much of each of the phenocrysts phases must be subtracted from G101 to give the closest approximation possible to these differences.

# Least-Squares Models of Crystal Fractionation

## Model Results and Model Evaluation

The primary results of the least squares model, the amounts of the phenocryst phases, which need to be fractionated from G101 to give the best fit to the model, are displayed in [Table 4, first column](#). One of the first things to notice is that our model as last stated is incorrect; the best fit occurs when olivine, clinopyroxene, and plagioclase are fractionated (subtracted, minus sign) and orthopyroxene is accumulated (added, positive sign).

The calculated amounts of the mineral phases can be compared to the relative amounts of the phenocryst phases in the rocks to evaluate the validity of the model. The original model postulated fractionation of the phenocrysts, not accumulation of one of them. Does a model, revised to accord with these calculations, make sense; a model with phases being accumulated? If orthopyroxene accumulates, what would we expect to see in G99? First, orthopyroxene phenocrysts should be abundant. After all, the model predicts orthopyroxene accumulation. Second, the orthopyroxene compositions that crystallized in G101 should differ from those that crystallize in G99. The orthopyroxene that crystallized early in the G101 magma should be more magnesian than the orthopyroxene that crystallized in the magma at the G99 stage. These accumulated orthopyroxenes should be partly dissolved or protected in the cores of crystals by more iron-rich overgrowths. Do phenocrysts in G99 have overgrowths or overgrowths on dissolution surfaces? Another possibility: the accumulated orthopyroxene could completely dissolve in the G99 magma. If such happened, then the P-T conditions where fractionation took place would have to be conditions where orthopyroxene was not on the saturation surface for a melt with the composition of G99. You can check Carmichael (1964, 1967) to see whether his petrographic notes shed light on the accumulation – fractionation hypotheses.

## Information Derived from the Model

The model compositions of the added and subtracted substances are shown in [Table 5](#). Having calculated the amounts of added and subtracted phases (previous page) it is straight forward to calculate the compositions of the added and subtracted substances ([First two columns in Table 5](#)). We can then calculate a magma composition with the exact composition that would result in the composition of G99 being formed by adding and subtracting the calculated amounts of the phenocrysts found in G101. The composition of this *perfect parent* magma is listed in [Table 5, column 4](#). From there one can calculate the difference between G99 and this hypothetical magma ([Column](#)

# Least-Squares Models of Crystal Fractionation

5 in Table 5). The differences between the observed difference between G101 and G99 and the calculated difference (Column 5 minus Column 3) are listed in the last column of Table 5. These are the residuals we will be talking about shortly, along with the sum of their squares, which is a minimum, hence the name least-squares. The best model has a minimum, least-squares, value of 0.688.

## An Alternative Model

Suppose only olivine, clinopyroxene, and plagioclase fractionated; what would the least-squares algorithm produce? The results are shown in Table 6. First, note that the sum of squares of the residuals has increased to 0.784 from 0.688 in the last model. Part of the increase is due to the difference in the number of mineral phases entered into the two models; four in the first model, three in the second. If the number of mineral phases is increased, the sum of squares will always get smaller – guaranteed. The limit occurs when the number of mineral phases equals the numbers of oxides. At that stage, the sum of squares will be zero. However, such a model hardly merits the name because it tests nothing. The question is: How can we determine whether the first model with four phases is really better than the second model with three phases? An intuitive answer suggests we divide the sum of squares by the difference between the number of oxides and the number of phases ( $M - N$ ). Division by  $(M - N)$  suggests the three-phase model, with a value of 0.157 for  $S/(M - N)$  is better than the four-phase model with  $S/(M - N)$  equal to 0.172. If  $M$  should equal  $N$ , the number of oxides equals the number of phases, then the sum of squares of the residuals divided by  $(M - N)$  will be indeterminate because the denominator is zero; such a model has no probative value.

Like the four-phase model, which suggests accumulation of orthopyroxene, the three-phase model also has implications for orthopyroxene crystallization. Four phenocrysts are found in G101: olivine, clinopyroxene, plagioclase, and orthopyroxene. If G99 forms by fractionation of the first three phases, why wasn't orthopyroxene fractionated as well? It seems unlikely that the three phenocrysts could settle through the melt or be swept away by convection currents while orthopyroxene remained behind. One way out of the dilemma would have fractionation occur before orthopyroxene saturates. Is there a region in P-T-composition space where olivine, clinopyroxene, and plagioclase saturate either an olivine tholeiite magma, like G101, or the perfect parent (Table 5) before orthopyroxene appears? One way to test this suggestion would be through thermodynamic modeling.

# Least-Squares Models of Crystal Fractionation

## Model Fit and Analytical Uncertainty

At this point, we have two models; both require some special circumstances to be viable. There remains the question, however: Do the models adequately agree with the chemical data for either to be considered correct? The answer lies in comparing the fits to the uncertainties expected from analytical uncertainties. The fits between the model and data are given by the differences between the observed and calculated values. Actually, statisticians compare the squares of values to each other in order to remove troubles associated with positive and negative signs. The analytical uncertainties are always positive whereas the residuals can take either sign. The squares of the residuals are listed in the fifth column of [Table 7](#). If the fit were perfect, the residuals and their squares would all be zero. Are the squared values, though non-zero, less than uncertainties expected from analytical uncertainty? And what, exactly, do we mean by expected uncertainty? The uncertainty expected from the sum or difference of two values; each value having the same individual uncertainty is two times the individual uncertainty. Each residual should be smaller than two times the analytical uncertainty for that particular oxide if the models, as stated, are consistent with the data. The squares of the residuals are compared with the squares of the expected analytical uncertainties ( $4 AU^2$ ) in [Table 7, last column](#).

The squares of the residuals for the Thingmuli rocks are too large, when compared to the squared analytical uncertainties, for the rocks to represent magmas from the same original batch that split in two. The squares of the residuals are considerably larger than the squares of the analytical uncertainties. The question now becomes: Can the postulated derivative magma, G99, be derived from an olivine tholeiite magma similar to but not identical to G101, say, a composition close to that of the *perfect parent*?

The answer to the question at least verges on speculation. Is the composition of the *perfect parent* sufficiently close to the composition of G101. How do we decide? What criterion do we use to decide? Discussions with several people suggest that a sum of squares of the residuals divided by  $(M - N)$  less than approximately 0.5 would be an acceptable model. What do you think?

## Magma Splits

How common is it, do you think, that separate splits of a magma batch arrive on the Earth's surface where we can sample them? An appropriate answer might be, "I don't know." The 1968 eruption sequence at Kilauea Volcano produced lava flows with chemical and mineralogical characteristics consistent with eruption of splits from a continuous fractionation sequence.

# Least-Squares Models of Crystal Fractionation

Summaries of fractionation models of the picrite to basalt transition are listed in [Table 8](#).

Large olivine phenocrysts dominate the picrites. The compositions of these phases must satisfy the least-squares models. The phenocrysts have a range in compositions (Nicholls and Stout, 1988) and estimating an average composition of the olivine is difficult. So, the two olivine end member compositions,  $\text{Mg}_2\text{SiO}_4$  and  $\text{Fe}_2\text{SiO}_4$ , were chosen as the as the compositions to fractionate. The amounts returned by the model calculations were combined to give the composition of the olivine and the amount of olivine that best satisfied the fractionation model.

The calculated olivine compositions fall within the zoning ranges found in the picrites for every stage of differentiation for which we have samples. The sum of the squares of the residuals is smaller than the value expected from the analytical uncertainties. Consequently, the chemical data are compatible with the hypothesis that a single batch of magma generated at depth beneath Kilauea split into several parts, and the parts then erupted at the surface, forming lava flows.

The lava flows that formed from the 1968 sequence of eruptions reached the surface at the summit caldera of the volcano and at separate vents along the East Rift Zone (Jackson, *et al.*, 1975). Magma transport vertically to the reservoir beneath the summit and horizontally through conduits along the East Rift provided opportunity for the magmas to split into multiple pockets. This scenario is not inconsistent with geophysical evidence on magma generation and transport beneath Kilauea (Ryan, *et al.*, 1981; Bohron, 2007) nor with other chemical and mineralogical evidence discussed in the *Magmatic Histories* section of the web site.

## References Cited

- Bohron, W. A., 2007, Insight into Subvolcanic Magma Plumbing Systems: *Geology*, v. 35, no. 8, p. 767-768. doi: 10.1130/focus082007.1.
- Bowen, N. L., 1928, *The Evolution of the Igneous Rocks*: Princeton, NJ, Princeton University Press.
- Bryan, W. B., Finger, L. W., and Chayes, F., 1969, Estimating proportions in petrographic mixing equations by least squares approximation: *Science*, v. 163, no. 3870, p. 926-927.
- Carmichael, I. S. E., 1964, The petrology of Thingmulu, a Tertiary volcano in

# Least-Squares Models of Crystal Fractionation

- Eastern Iceland: *Journal of Petrology*, v. 5, p. 435-460.
- Carmichael, I. S. E., 1967, The mineralogy of Thingmuli, a volcano in eastern Iceland: *American Mineralogist*, v. 52, p. 1815-1841.
- Jackson, D. B., Swanson, D. A., Koyanagi, R. Y., and Wright, T. L., 1975, The August and October 1968 East Rift eruptions of Kilauea Volcano, Hawaii: *United States Geological Survey Professional Paper*, v. 890, p. 1-33.
- Nicholls, J., and Stout, M. Z., 1988, Picritic melts in Kilauea - Evidence from the 1967-1968 Halemaumau and Hiiaka eruptions: *Journal of Petrology*, v. 29, p. 1031-1057.
- Ryan, M. P., Koyanagi, R. Y., and Fiske, R. S., 1981, Modeling the three-dimensional structure of macroscopic magma transport systems: Application to Kilauea Volcano, Hawaii: *Journal of Geophysical Research*, v. 86, p. 7111-7129.
- Stormer, J. C., Jr., and Nicholls, J., 1978, XLFRAC: A program for the interactive testing of magmatic differentiation models: *Computers and Geosciences*, v. 4, p. 143-159.
- Stout, M. Z., and Nicholls, J., 1983, Origin of hawaiites from the Itcha Mountain Range, British Columbia: *Canadian Mineralogist*, v. 21, p. 575-581.
- Wright, T. L., and Doherty, P. C., 1970, A linear programming and least squares computer method for solving petrologic mixing problems: *Geological Society of America Bulletin*, v. 81, no. 7, p. 1995-2008.

**Cover Photo:** Hekla volcano, Iceland. A large volcano in the rift zone that crosses the island. The rift zone connects with the MidAtlantic Ridge north and south of Iceland. Diverse rock types erupted from the volcano.