

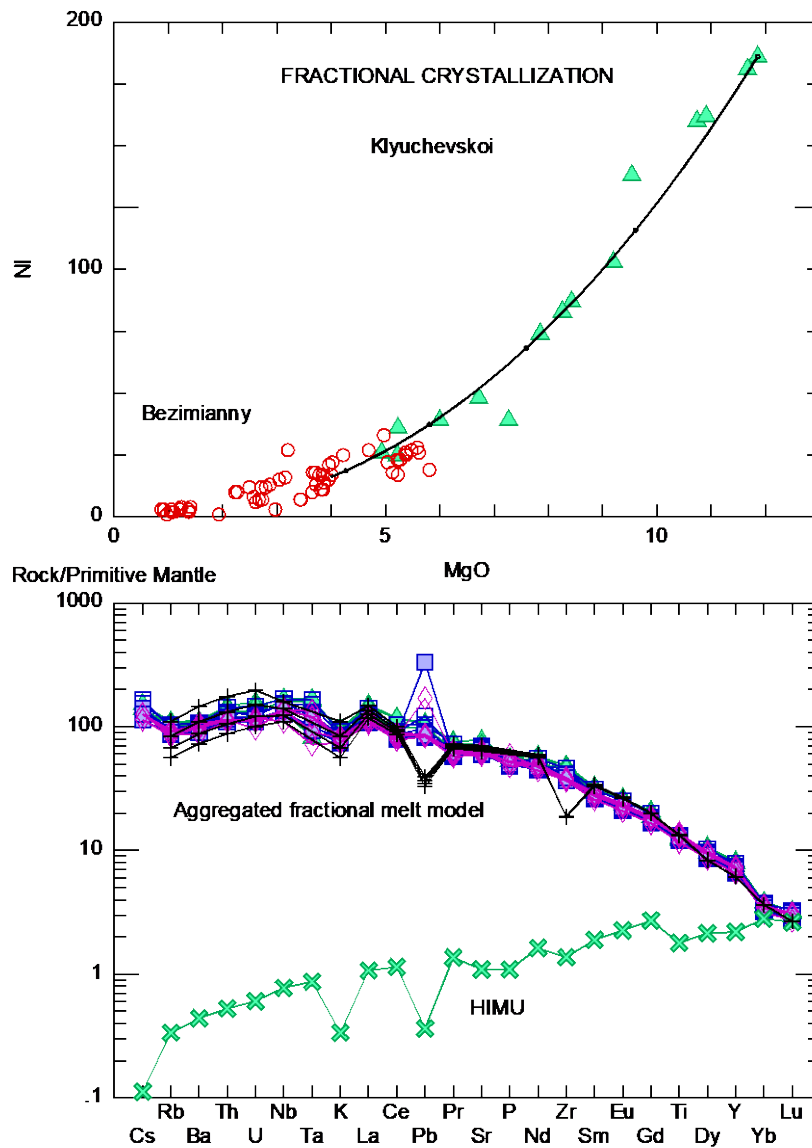
# Igpet Workbook

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**Igpet Workbook**  
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## **Introduction and suggestions for use**

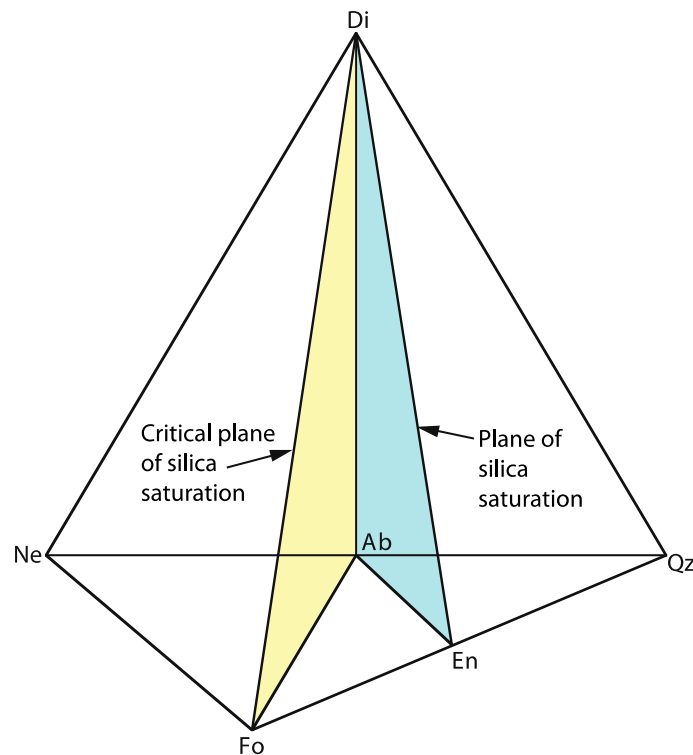
Igneous Petrology includes many processes that can be described in mathematical terms that allow quantitative testing. However, igneous systems are open, very large in scale and not easily replicable in experiments. The open nature of the natural systems allows forward modeling but restricts more powerful inverse models to a few simple systems. A further difficulty is that we primarily observe the results of natural experiments that are only partly exposed. Although quantitative testing is compromised by complexity and by gaps in observations, much insight can be gained by testing models that span a wide range of experimental and theoretical development and then focusing on the few that are compatible with actual sample suites. For the problems considered here, we create models consistent with the data but do not arrive at unique solutions. This is the nature of forward models. Furthermore, any possible geochemical explanation will still will require geologic interpretation.

Most of the data sets used here come from research done by the authors. Familiarity with the complete research process from field to lab to analysis allowed us to define problems that we understand more deeply than similar and equally good problems or data sets in the literature. Literature reports final interpretations and not the false leads, miss-fits, pit-falls and flat out errors that preceded a reasonable solution. Furthermore, literature tends to not have field, hand sample and thin section observations that set the stage for data obtained from million dollar instruments. Therefore, please use this workbook as a set of ideas of what can be done. The exercises are starting points. By modification and emulation you can provide better problems for your students using your own research results. Our experience has been that students especially like to see the actual rocks or at least the field context that gave rise to a problem.

The first 5 problems should be suitable for undergraduates. The next 5 are intermediate and the last 2 are graduate level.

## Problem 1. Uses of the CIPW Norm

Petrology texts commonly have a section on calculating a CIPW Norm, a procedure that is over 100 years old. It is a complicated rule following an arithmetic exercise that can teach a fundamental principle, especially through multiple calculations of the Norm. That principle is the divergence of evolving basalt lavas depending on whether hypersthene or nepheline is in equilibrium with the initial magma. With hypersthene initially present evolved magmas head toward quartz; while with nepheline present magmas evolve towards nepheline-rich compositions. Yoder and Tilley (1962) made this divergence the foundation of their experimentally derived classification of basalts. They created a tetrahedron of normative minerals with a base of Nepheline (Ne), Forsterite (Fo), and Quartz (Qz). The upper apex is Diopside (Di). The presence of Albite (Ab) and Enstatite (En) on the base plane allow the construction of two planes that divide the tetrahedron onto 3 fields, basanite or alkaline basalt group to the left (Ne in the Norm), olivine tholeiite group in the center (Ol and Hy in the Norm) and tholeiite group to the right (Qz and Hy in the Norm).



*Figure 1.1 Basalt tetrahedron (after Yoder and Tilley, 1962). The two internal planes do not represent surfaces where two minerals co-precipitate; e.g. they have compositional meaning but no thermodynamic significance.*

**The critical plane separates alkaline basalts from subalkaline basalts.** The plane of silica saturation further divides the subalkaline basalts into two tholeiite groups. During fractional crystallization, magma follows a path determined by what minerals are crystallizing and being removed. Two distinct magma series follow divergent paths. Paths starting on the right of the critical plane stay to the right and head toward Qz,

defining a **subalkaline** magma series. Paths starting to the left stay to the left and head for the Ne apex defining an **alkaline** magma series. Consider two very similar parental basalts, close to each other on opposite sides of the critical plane. Both crystallize Ol (olivine), Di (cpx) and Ab (plag) and move away from the critical plane. One magma has a tiny amount of Hy in the norm and evolves toward Qz and the other, with a tiny amount of Ne, evolves toward Ne. Radically different evolved magmas are the result, especially at the end stages of crystallization. The phrase ‘hypersthene in the norm’ means **subalkaline** (tholeiitic) and ‘nepheline in the norm’ means **alkalic**. At low pressures the critical plane is a thermal divide that magmas cannot cross because their temperatures do not increase during crystallization.

The plane of silica ( $\text{SiO}_2$ ) saturation is less fundamental during crystallization because it is not a thermal divide. The volume in which Ol is the first mineral to crystallize extends over the plane of silica saturation at the low pressures where most crystallization occurs. Cooling magmas evolve through the silica saturation plane crystallizing Ol or Ol and Hy. On ternary phase diagrams (e.g. Ol-Di-Qz) there is a change in direction when Ol is no longer stable and no longer contributing to the instantaneous crystal growth.

The importance of the plane of silica ( $\text{SiO}_2$ ) saturation is in melting. Consider melting in the mantle or lower crust and imagine two very similar compositions on either side of the plane of silica saturation. Melting occurs when the phases present, Ol-Hy-Di-Ab to the left and Qz-Hy-Di-Ab to the right, coexist with a melt. The phase boundaries are not shown in the tetrahedron but the initial melt with Qz present is rhyolite or dacite, whereas the first melt with olivine present is basalt. In many areas of extensional tectonics there are basalt-rhyolite associations of identical age.

### *Igpet exercise*

Start Igpet and go to **File**, select **Open** and then choose the file called CIPW\_Exercise.txt. Click **File** then **Add CIPW**. Answer the three options that appear with **Yes, Cation Norm, Yes**. This allows you to use the Irvine and Baragar (1971) rock classification scheme. Now select **Plot** then **Diagrams** then IrvineBaragar. Find the Diagram option that is analogous to the base of the basalt tetrahedron.

Once you have the base of the basalt tetrahedron on the screen, click the **ID ON** button and then click on samples very close to the critical plane and write down a few (3) sample names on a scrap of paper.

Now open the Igpet folder and click on the CIPW program (app or exe extension). Click **File** then **Open** and select the CIPW\_Exercise.txt file again. There are 114 analyses in the file and you can calculate a CIPW Norm on any of them by double-clicking the sample name in the multi-line text box, then selecting a few options (ignore all the options except the one dealing with Fe oxides) and then clicking the **Calculate CIPW** button.

Select sample HON-YO7, near the end of the list, by double clicking. This will populate the calculator with data from the sample. Notice, however that no value was imported for Fe<sub>2</sub>O<sub>3</sub>. This indicates that Fe<sub>2</sub>O<sub>3</sub> was not determined for this sample. For rocks measured by X-Ray Fluorescence (XRF) Fe<sub>2</sub>O<sub>3</sub> is usually reported and FeO is zero. With other techniques the reverse is commonly the case with all the Fe expressed as FeO. The reporting of only one Fe-oxide is common in modern analyses because the wet chemical techniques for determining the Fe<sup>2+</sup> and Fe<sup>3+</sup> oxides are tedious and hazardous and more modern techniques like  $\mu$ -Xanes are in the development stage. More importantly, many rocks are altered to some degree and one of the first changes from alteration is oxidation of FeO to Fe<sub>2</sub>O<sub>3</sub> (hematite) thereby creating a reddish color. So, failure to measure one of the Fe oxides and oxidation (either by chemical weathering or during cooling of a lava) are problems for the Fe oxides.

The degree of oxidation has a significant effect on the calculation of the CIPW norm. Different amounts of oxidation can flip a basalt from the alkaline group to the subalkaline group.

For HON-YO7 calculate a CIPW Norm with all Fe as FeO (the way it is in the data file), then click the lower left check box (If FeO=0 or Fe<sub>2</sub>O<sub>3</sub>=0 or Fe<sub>2</sub>O<sub>3</sub> > TiO<sub>2</sub> +1.5) that follows the Irvine and Baragar rule for adjusting the Fe oxides and then calculate a Norm. How do ne and hy change? Double click on the sample name again (HON-YO7) and set all the Fe to Fe<sub>2</sub>O<sub>3</sub> and set FeO to zero. Do this manually; Fe<sub>2</sub>O<sub>3</sub> is about 1.1\* FeO. Again, how do ne and Q change? Try this with the 3 samples you picked to see if the same movement occurs.

**1A.** *Make a table of your 3 results with column headers: sample name, FeO, Fe<sub>2</sub>O<sub>3</sub>, ne and hy. Hand in the table along with your answer to the question below.*

**1B.** *What is the effect of increasing oxidation? More precisely, does increased oxidation move the Norm toward Ne or toward Qz?*

## Problem 2. Rock Nomenclature and Tectonic Discrimination

### *Rock Nomenclature*

Geoscientists need a reliable method for determining names for the rocks they sample. The presence or absence of particular minerals, or mineral paragenesis is key. For volcanic rocks this is difficult because many are too fine grained to determine the minerals present. However, a phenocryst or two usually can be identified and a thus a rough name can be assigned in the field. For example a rock with olivine phenocrysts could be named “olivine basalt” whereas one with pyroxene or amphibole might be called “andesite.” Beware of using color because that characteristic is more commonly deceiving than illuminating. Thus, general names, based on phenocrysts, are useful for the field but appropriate names are required to communicate correctly.

Fortunately, there is an international commission on rock nomenclature established by the International Union of Geological Sciences (IUGS) to set the rules for how igneous rocks should be named (Le Maitre et al., 2002 and 2010). The IUGS commission specifies two diagrams based on modal analysis, QAPF plutonic and QAPF volcanic for the majority of igneous rocks. QAPF stands for quartz, alkali feldspar, plagioclase feldspar and feldspathoids. These diagrams are based on the percentages of minerals in the rock as determined by thin section analysis, either by point counting or by image analysis. This approach is more suitable for intrusive rocks, which are commonly completely crystalline yielding minerals large enough to easily count. For volcanic rocks, an alternate method is to obtain the chemical analysis and use a TAS diagram, total alkalis ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) versus silica ( $\text{SiO}_2$ ) (Figure 2.1). Igpet is primarily aimed at chemical petrology so the most useful IUGS diagram in Igpet is the TAS diagram (file IUGS2002Chemical, in the Diagrams folder). The digital version (2010) of the IUGS classification is available at most research libraries. There are many, many details, so do not rely on Igpet alone for rock nomenclature. A complete study should also include petrographic descriptions and mineral compositions.

The IUGS classification was designed to not include genetic ideas about magma evolution. The preference for defining rocks by their mineralogy not their chemistry is consistent with this approach and with history. Mineralogy and modal analyses were the original ways of naming rocks and thousands of names were generated. Most of the names refer to a type locality. Thus, a tholeiite was named for an outcrop in Tholey, Germany. The igneous body is a Permian sill, exposed in Shaumberg. The basalts of the ocean floor, the most abundant igneous rock on the planet, were commonly called tholeiites or tholeiitic basalts. How such an old and obscure outcrop in Germany’s Saar basin became the type locality for the planet’s most common igneous rock is a bit crazy. The historical development of nomenclature has created some odd results and petrology would be more logical if the term tholeiite were replaced by subalkaline. The term tholeiite is less used now and most papers on ocean floor lavas describe them as mid-ocean ridge basalts (MORB). However, tholeiite has not disappeared and has taken on a genetic meaning. Genetic aspects of rock names are common and should be understood.

The genetic nomenclature briefly discussed below is for basalts. Granite nomenclature includes adjectives that refer to the source rock (peraluminous implies a source rich in mud) and tectonic setting (A-type for anorogenic). Perhaps the next version of this workbook will be improved by adding more granite discrimination diagrams.

Problem 1 identified two evolutionary series for basalt magmas, subalkaline and alkaline. The subalkaline group can be further subdivided into calc-alkaline and tholeiitic. Kuno (1962) proposed a high-Al series as well. These three subalkaline magma series have reasonable tectonic associations and some genetic implications. Tholeiites are the most common including; the MORB, the subalkaline ocean island basalts (subalkaline OIB), and most continental flood basalts. The defining concept for the tholeiite series is that Fe initially increases during fractional crystallization. Calc-alkaline comes from a paper by Peacock (1931) and, regardless of Peacock's original observation, is now almost synonymous with andesites of convergent margins. In contrast to tholeiites, the calc-alkaline series does not have Fe increasing with fractional crystallization. The high-Al basalt group is a bit suspect because some very high (>19%)  $\text{Al}_2\text{O}_3$  contents occur by accumulation of plagioclase. However aphyric lavas with 18% or so  $\text{Al}_2\text{O}_3$  exist, primarily at convergent margins (arcs). The high-Al content suggests that plagioclase stability was suppressed, most likely by high water content. Kuno also suggested that convergent margins had tholeiitic basalts close to the trench, high-Al basalts a bit further back, and alkaline basalts well behind the main chain of arc volcanoes.

To better understand the 'genetic' terms, **start Igpet** and click **File, Open** and select TholeiSchaumberg.txt. These data are wet chemical analyses from Jung (1958). There may be newer analyses of this sill but we did not find them in a brief search. Given that this is the type locality for Tholeiite, use the rock identification diagrams to determine whether or not these are consistent with the modern use of this name. Start with Irvine and Baragar, so click **File, Add CIPW** and answer, **Yes, Cation, Yes**. Next, click **Plot, Diagrams** and select IrvineBaragar.txt. The diagrams are in a specific logical order. The first two diagrams allow discrimination between the alkaline and subalkaline series. Try them. The answer is clearly subalkaline for the Schaumberg data. Four subsequent diagrams further define the subalkaline rocks and the final diagrams allow subdivision of the alkaline rocks. The next two diagrams allow discrimination between the tholeiite and calc-alkaline series. Try them. That did not go well, the type locality for tholeiite fails the tholeiite discrimination test. However, there is Fe enrichment in the Schaumberg sill so this inconsistency arises from failure of the discrimination diagrams. Now click **Plot, Diagrams** and select RockType.txt. In the middle of the list are two diagrams by Miyashiro (1974). The first is his preferred plot for separating tholeiitic from calc-alkaline variation. In this diagram the type Tholeiites are tholeiitic. The lines in the next diagram are not discrimination boundaries but typical magma evolution paths. Amagi is a calc-alkaline volcano and it has a path of  $\text{TiO}_2$  decreasing with fractionation. For arc volcanoes,  $\text{FeO}^*/\text{MgO}$  ( $\text{FeO}^* = \text{FeO}^{\text{total}}$ ) is an index of magmatic evolution/differentiation that increases with fractional crystallization (FC).  $\text{SiO}_2$  also increases with FC and MgO decreases with FC. Against any of these indices, the original Tholeiites have  $\text{FeO}^*$  and  $\text{TiO}_2$  increasing and are consistent with being called a 'tholeiitic' magma series. The slope of the evolutionary path is more important than its



absolute position on any of the diagrams. Thus the failure of the Tholeiites in the AFM diagram is only a partial failure because the initial slope is towards the  $\text{FeO}^*$  apex.

### *Tectonic setting*

Igneous rocks record information about tectonic setting in their chemical composition and in the evolutionary path of the magma from a primary composition. The tectonic settings of most active volcanoes are clear and we know how a volcano is related to a plate margin or an intraplate setting. However, volcanic rocks in the deeper geologic record are separated from their original tectonic context and have been subjected to weathering, burial, reheating, faulting, metamorphism and even metasomatism.

Therefore, many proxies have been developed to try to elucidate the original context of altered and metamorphosed rocks of igneous origin. Tectonic discrimination diagrams are a good starting point because they identify possible suspects. More robust interpretations require stratigraphic and geologic context, as well as any preserved textures from hand specimens or thin sections.

Many elements readily move about during the various processes that change igneous rocks from their original shapes and compositions. Mobile elements include Na, K, Rb, Ba, Cs. Tectonic discrimination diagrams ignore these and focus instead on elements that are resistant to change, such as the high field strength elements (HFSE); Zr, Hf, Nb, Ta, Ti, Th. Many rare earth elements (REE) are also preserved through geologic time.

However there are occasional instances where a phosphate mineral that forms during weathering in a hot wet climate grossly distorts the REE by enriching the heavy REE and losing Ce, which takes on a different oxidation state. Overall, tectonic discrimination depends heavily on the HFSE and REE groups of elements.

Attempts to identify the tectono-magmatic setting of ancient igneous rocks started in earnest with the work of Pearce and Cann (1971, 1973) using trace elements that are immobile and well analysed on X-ray fluorescence machines. The file, DiscrimBasalts.txt in the Diagrams file has 26 discrimination diagrams. Over time the quality of analytical instrumentation has increased broadening the scope of well-determined elements. There are some relatively new diagrams but old problems remain. What are the tectono-magmatic entities that should be identified? What statistical approach should be taken? For what range of  $\text{SiO}_2$  values is a diagram valid? Verma et al. (2006) uses major elements and Aggarwal et al. (2008) use trace elements to define fields for MORB, OIB, IAT and CRB (continental rift basalts). They use a sophisticated statistical approach to define discriminant functions using modern analyses as training and test data. Although this new approach is superior, it is hard to dislodge the existing methods that have been applied for several decades.

### *Igpet exercise*

The Santa Elena peninsula in western Costa Rica has a remarkable variety of igneous rocks in a small area. Read Santa\_Elena.txt into Igpet. First **add a CIPW Norm** using the **File Menu**. Click **Yes, Cation, Yes**. Then click **Plot** and then **Diagram**. Start with Irvine and Baragar and use the plots designed to determine if the rocks are tholeiitic

(subalkaline) or alkaline. For just the tholeiitic (subalkaline) groups use other diagrams to discriminate between tholeiitic and calc-alkaline. Once again click **Plot** then **Diagram**. Select IUGS2002Chemical to define internationally recognized rock names using the TAS diagram.

**2A.** *For each of the four symbol groups, define appropriate rock names. Include the adjectives determined from the Irvine and Baragar plots. The blue squares require a small range of names. The two golden crosses are not adequately named by the TAS diagram, so examine the secondary diagrams designed for high MgO. The **SubSelect** button opens a window that lets you set ranges for elements. The **Value** button is useful because it allows you to write a value, such as MgO content, right onto the diagram.*

Another useful Diagram file is called, RockType.txt. So, click **Plot** and then **Diagrams** and select RockType.txt and then browse through the different diagrams.

The diagrams mentioned above should give you a reasonable idea of what type of rocks you have. However the tectonic identification is much more difficult to pin down. Vagueness, inconsistent names and overlap make tectonic identification confusing. In other words you will have to evaluate conflicting evidence. Have pencil and paper handy to take notes as you explore the tectonic discrimination diagrams. Pay attention to the limits of the diagrams. Almost all are only for basalts so click **SubSelect**, then click **SiO<sub>2</sub>** and enter 41 for the minimum value and a very generous 57 for the maximum value. Note that the first several diagrams have a limit of  $12 < \text{MgO} + \text{CaO} < 20$ . To set this you create a new parameter by clicking **File**, then **Make a new parameter**, then click the **A+B** button and click on **MgO** and then **CaO** and then finally on the new **MgO+CaO** button. Now click **SubSelect** again and set limits of 12 and 20 for the new parameter, **MgO+CaO**.

Click **Plot** then **Diagrams** and select DiscrimBasalts.txt. Determine a tectonic setting for each of the symbol types. For the purple diamonds use DiscrimGranites.txt. Pay attention to any comments on the top of the diagram. If some diagrams turn out blank, you found a bug. Restart Igpet, read the file and click **Plot**, **Diagrams** and select DiscrimBasalts. The numbers in the first column are the figures in Rollinson (1993). His chapter 5 is one of the best summaries of tectono-magmatic discrimination diagrams available.

**2B.** *Hand in a short essay: for each of the four rock suites provide a tectonic setting and your reasoning.*

Some abbreviations used in tectono-magmatic discrimination diagrams

MORB	mid-ocean ridge basalt (spreading margins)
E-MORB	enriched MORB (it is more complicated than just E and N varieties)
N-MORB	normal MORB
OIB	ocean island basalt (Hawaii=tholeiitic OIT, Tahiti=alkaline OIA)
IAT	island arc tholeiite (convergent margins)
CAB	calc-alkaline basalt (very similar to IAT)
WPB	within plate basalt (Hot spots in the oceans and continents)
VAT	volcanic arc tholeiites (might include CAB as well as IAT)

Plate margin basalt - unfortunately includes IAT, CAB and MORB!  
 Continental arc - most of the plate convergence zones  
 Oceanic arc - Izu-Bonin-Marianas, Kuriles, Aleutians, Tonga-Kermadec etc  
 VAB volcanic arc basalt=IAT+CAB  
 CFB continental flood basalt (e.g. Columbia River basalts)  
 BABB back-arc basin basalt (e.g. Mariana Trough basalts)  
 Sho short for shoshonite

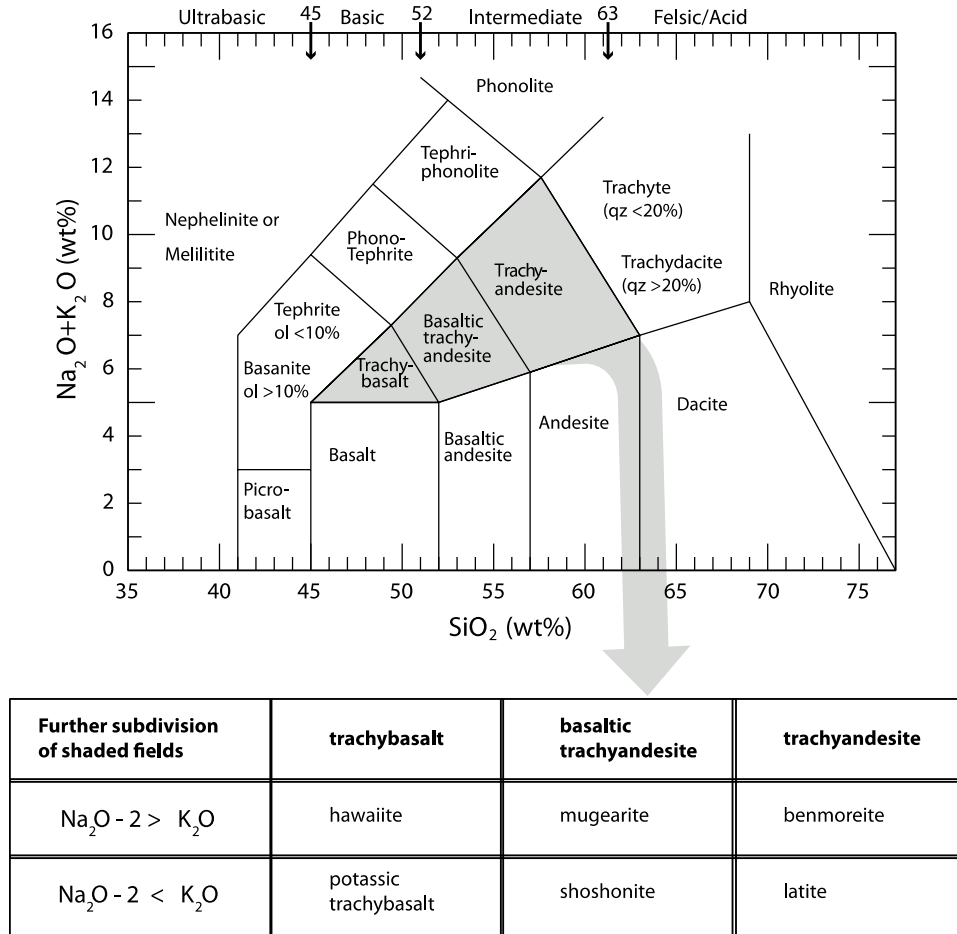


Figure 2.1 Geochemical classification diagram of silica versus total alkalis (TAS). The line between foidite (nephelinite/melilite) and basanite-tephrite is provisional because additional criteria are necessary to separate these rocks. Abbreviations ol=normative olivine, qz=normative  $100 \cdot Qz / (Qz + or + ab + an)$

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### Problem 3. Least Squares approach to petrologic mixing problems

Magma chambers are reservoirs of generally unknown geometry where different magmas can mix or become un-mixed as crystals separate. If magma mixing occurs just prior to eruption, disequilibrium textures and bimodal populations of phenocrysts are likely to be preserved. With time, such evidence will be lost as crystals re-equilibrate or are removed. Un-mixing is a term used in the literature for crystallization differentiation by growth and removal of crystals. This process is also called fractional crystallization.

Petrologists once used graphical tools to argue for or against mixing and fractional crystallization. This practice was superseded by mathematical analysis soon after computers became available (e.g, Bryan et al., 1969) making the modeling of this process straightforward today.

Magma mixing can be defined as: Hybrid magma =  $c_1 \cdot \text{Magma}_A + c_2 \cdot \text{Magma}_B$ .

One needs to solve for the coefficients,  $c_1$  and  $c_2$ , but there are more than two equations so the problem is oversubscribed (more equations than unknowns). The three magmas can be represented as vectors with 9 members, the oxides of Si, Ti, Al, Fe, Mg, Ca, Na, K, P. The Fe is assumed to be all FeO and Mn is ignored because of its low content. So there are 9 equations (for the oxides) for 2 unknowns (the coefficients).

$$H = c \cdot M$$

Using linear algebra, H is a column vector (9), c is a row vector (2) and M is a 2 by 9 matrix. This problem can be solved by least squares where the quantity minimized is the sum over all 9 oxides of (estimated  $H_{\text{ox}}$ -actual  $H_{\text{ox}}$ )<sup>2</sup>.

For fractional crystallization the equation given a typical basalt is:

$$\text{Parent}_{\text{lava}} = c_1 \cdot \text{Daughter}_{\text{lava}} + c_2 \cdot \text{olivine} + c_3 \cdot \text{cpx} + c_4 \cdot \text{plag} + c_5 \cdot \text{magnetite}$$

$$\text{or} \quad P = c \cdot M$$

This is just like magma mixing except that there are several more components and therefore several more coefficients to solve for. Given that there are just 9 oxide equations it is best to keep the number of minerals to a minimum. The appropriate minerals are those present as phenocrysts in the rock, not necessarily the ones in the equation above. Do not select two minerals of the same type, such as both albite and anorthite.

Mixing (.app or .exe), a program in the Igpert folder, calculates major element least squares models. The solution is based on major elements only. The logic makes the simplifying assumption that mineral compositions are constant during crystallization. This is reasonable for small steps along a fractional crystallization path. Trace elements are calculated using the Raleigh equation for fractional crystallization  $C_1 = C_0 F^{(1-D)}$  but do

not contribute to the solution. This modeling requires the geochemist to check the models for the reasonableness of the solution.

### *Igpet exercise*

Double click on the Mixing (.app or .exe) program in the Igpet folder. Click on **Part.Coeff.file**. Select Gill1981.PC.txt. Next, select a weighting function for oxides file by clicking on **Weights files**. Select default.wt.txt and click **Okay**. Click the **View PCs** button to view the partition coefficients selected and note that there is 0 weight for  $\text{Fe}_2\text{O}_3$ . This is a reminder that Mixing puts all the Fe into FeO and normalizes the remaining oxides to 100%. The abundant oxides,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , are given weights less than one to reduce their dominant effect on the solution. Now click on the **Mineral Files** button and select CerroNegro.Minerals.txt. Then click the **Rock files** button and select CerroNegroGeochem.txt. Next click the Fractional Crystallization button (**Fract. Xtl.**). Now you need to pick minerals. Start with the most magnesian ol (highest Fo) and cpx (highest En), a Ti-rich magnetite and the most calcic plagioclase (highest An). Note that magnetite samples end in -mt, plagioclase samples end in -pl, clinopyroxene samples end in -cpx and olivine samples end in -ol. Next click **Ok**. You will now be prompted to select a daughter lava. Choose NIC-CN1 then click **Ok**. Finally you will be prompted to select a parent lava. Choose NIC-CN12 then click **Ok**.

The result appears as soon as you finish your selections. It is a “successful” model with a sum of squares of residuals of less than 0.05. If you wish, you can select a few different minerals to try to improve the model (i.e. get a lower sum of squares of residuals).

**3A.** Output goes first to the screen, but you can send a copy to a text file. For this exercise send the successful model to a txt file after deciding on your preferred set of minerals. Click **to:text file button** and click **save** to save the file in a preferred location. Then click **Close** which takes you back to the main screen with the inputs still selected. *Print the file you made with TextEdit or Notepad and hand it in with the answers to 3B.*

**3B.** Keeping NIC-CN12 as the parent, try the rest of the Cerro Negro lavas as daughters by clicking the New Daughter button and sequentially selecting CN2, CN3 etc. Keep the minerals the same. *Make a list of those that succeed and those that fail. Write down the sum of squares of residuals as well.* Failure is up to you in cases where the trace elements get calculated. That is, you can set a limit to the maximum size of the sum of squares or you can decide that the error in some oxides is just too large. Note that  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$  can be difficult. In many cases the result is obviously flawed because minerals are being both added in and subtracted out. That is just wrong in petrology even though the math doesn't care. *Hand in your complete list of successes and failures.*

The purpose of the assignment is to familiarize you with this simple type of modeling.

#### **Problem 4. Cerro Negro: CMAS projections for fractional crystallization**

Cerro Negro had its first eruption in 1850 and most recent eruption in 1999. It is now a nascent composite cone. Young volcanoes may provide insight into the magmatic processes that are obscured in large magma chambers present beneath larger well-established volcanoes.

Overall, Cerro Negro's geochemistry is typical of arc volcanism where fluids from a descending slab generate magma in the overlying mantle wedge by lowering the melting temperature. Such magmas have high H<sub>2</sub>O contents, making them notably explosive. In Central America and most other convergent margins (arc systems) the crust is thick and most magmas reaching the surface are more evolved than those found at mid ocean ridges. They have changed their initial picritic to basaltic chemistry by losing considerable mass by fractional crystallization (FC) of mafic minerals and gaining some mass via assimilation of crust. Assimilation occurs when bits of the crust are broken off, enter the magma body and melt.

One way magma composition can change rapidly is by adding a rising primitive basalt into a crustal chamber that contains evolved magma such as basaltic andesite or andesite. Common signatures of mixing are dual populations of phenocrysts, plagioclase crystals with rotted looking resorption zones and reverse zoning (from sodic to calcic rather than the expected calcic to sodic). A useful acronym for crustal magma evolution is MASH for the processes of mixing, assimilation, storage and homogenization (Hildreth and Moorbath, 1988). Fractional crystallization accompanies these processes but did not fit into the acronym. MASH can increase the concentrations of incompatible elements (elements that do not fit into the minerals that first crystallize, typically elements with large ionic radius such as Ba, K, Rb, REEs). Cerro Negro's magma may have undergone less crustal evolution than magmas at other Nicaraguan volcanoes because Cerro Negro's incompatible element contents are the lowest. Alternatively, the low contents of K, Ba et al. at Cerro Negro may be due to a higher degree of melting in the mantle.

Melts (the liquid component of magmas) evolving in mid or lower crustal chambers evolve following the laws of thermodynamics, that is, they define a string of compositions that follow the liquid line of descent on a phase diagram. Magma replenishment and incomplete removal of crystallizing minerals can complicate matters. In the real multi-dimensional world of basalts, each common mineral has a volume of phase space where it is stable and is the only mineral stable. This is a primary phase volume. In a four-component system, two volumes intersect in a plane where two minerals are stable and three mineral volumes intersect in a line, where three minerals are stable and co-precipitating. In a quaternary phase diagram the co-precipitation line (also called a cotectic) is a liquid line of descent where the primary phase volumes of the three minerals intersect. Visualize the line as the intersection of three soap bubbles.

Magmas that rise from the vicinity of the subducted slab (> 100 km depth in Nicaragua) formed at high pressure where the primary phase volume of olivine is substantially reduced from the volume it occupies at 1 atmosphere. Pausing within the crust after a

rapid rise from the mantle, the magma composition will now be inside a much expanded olivine field and will crystallize olivine until the remaining liquid is modified enough to reach the stability field of the next mineral, typically clinopyroxene or plagioclase. With two minerals now crystallizing and being removed, the liquid will change composition rapidly and soon reach multiple saturation with co-crystallization of olivine, clinopyroxene and plagioclase. Spinel, first chrome spinel and then magnetite, often accompanies olivine crystallization. Many lava suites in Central America define arrays parallel to the multi-saturated cotectics defined from experiments on basaltic compositions at a pressure of 1 atmosphere. The arrays defined by the active Central American volcanoes do not overlie the liquid line of descent defined by experiments because the experiments were at a pressure of 1 atm, a much lower pressure than that estimated for most arc magma chambers. Furthermore, at 1 atm, no H<sub>2</sub>O is retained but H<sub>2</sub>O is abundant in arc magmas.

Pseudo-quaternary phase diagrams are used to depict magma evolution in real world composition space. Most basalt chemistry is a mix of C+M+A+S or CMAS, where the letters are shorthand for CaO, MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. In primitive basalts, these 4 oxides can make up 80-85% of the total. It is not obvious how the other 7 oxides (TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeO, MnO, Na<sub>2</sub>O, K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>) should be treated, although including FeO and MnO into M is straightforward. P<sub>2</sub>O<sub>5</sub> can be assigned to apatite, thus reducing C by 3.333\*P<sub>2</sub>O<sub>5</sub>. TiO<sub>2</sub> can be assigned to ilmenite, thus reducing M by the amount of TiO<sub>2</sub>. Fe<sub>2</sub>O<sub>3</sub> is commonly added to A. The alkali oxides that make alkali feldspar affect C, A and S. There is no perfect way to assign the 11 major oxides to the 4 CMAS end members. The figures below use the projection of Sack et al. (1987) where TiO<sub>2</sub> is ignored and thus the mineral rutile is effectively projected from.

It is convenient to look at a sub-tetrahedron within CMAS space, one that has the common minerals in basalts at its apices, S (or SIL) is quartz, M2S or OL is olivine, CAS2 or PLAG is plagioclase and CMS2 or DI is diopside. The equations for these pseudo-minerals are:

OL= 0.5Al<sub>2</sub>O<sub>3</sub>-0.5Fe<sub>2</sub>O<sub>3</sub>+0.5FeO+0.5MnO+0.5MgO-0.5CaO-0.5Na<sub>2</sub>O-0.5K<sub>2</sub>O

DI= CaO+Na<sub>2</sub>O+K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>

SIL= -SiO<sub>2</sub>+0.5Al<sub>2</sub>O<sub>3</sub>+0.5Fe<sub>2</sub>O<sub>3</sub>-0.5FeO-0.5MnO-0.5MgO-1.5CaO-5.5Na<sub>2</sub>O-5.5K<sub>2</sub>O

PLAG= Al<sub>2</sub>O<sub>3</sub>+Na<sub>2</sub>O+K<sub>2</sub>O

To envision a plagioclase projection, assume you are at the plagioclase apex on top of the mineral tetrahedron, looking down at the base defined by the other three minerals. Your lava is hanging somewhere within the tetrahedron or possibly just below it. To plot your lava on the base plane, you add or subtract the projecting mineral (plagioclase) until you intersect the plane.

For an experiment to define a valid point on a liquid line of descent the run products must include a glass (the quenched liquid or melt found at the end of the experiment) and the three minerals, ol, di, plag. Evidence for equilibrium is also required. The point on the cotectic (or co-precipitation line or liquid line of descent) is the composition of the glass. The experimental charge is mostly glass at high temperature and mostly minerals at low

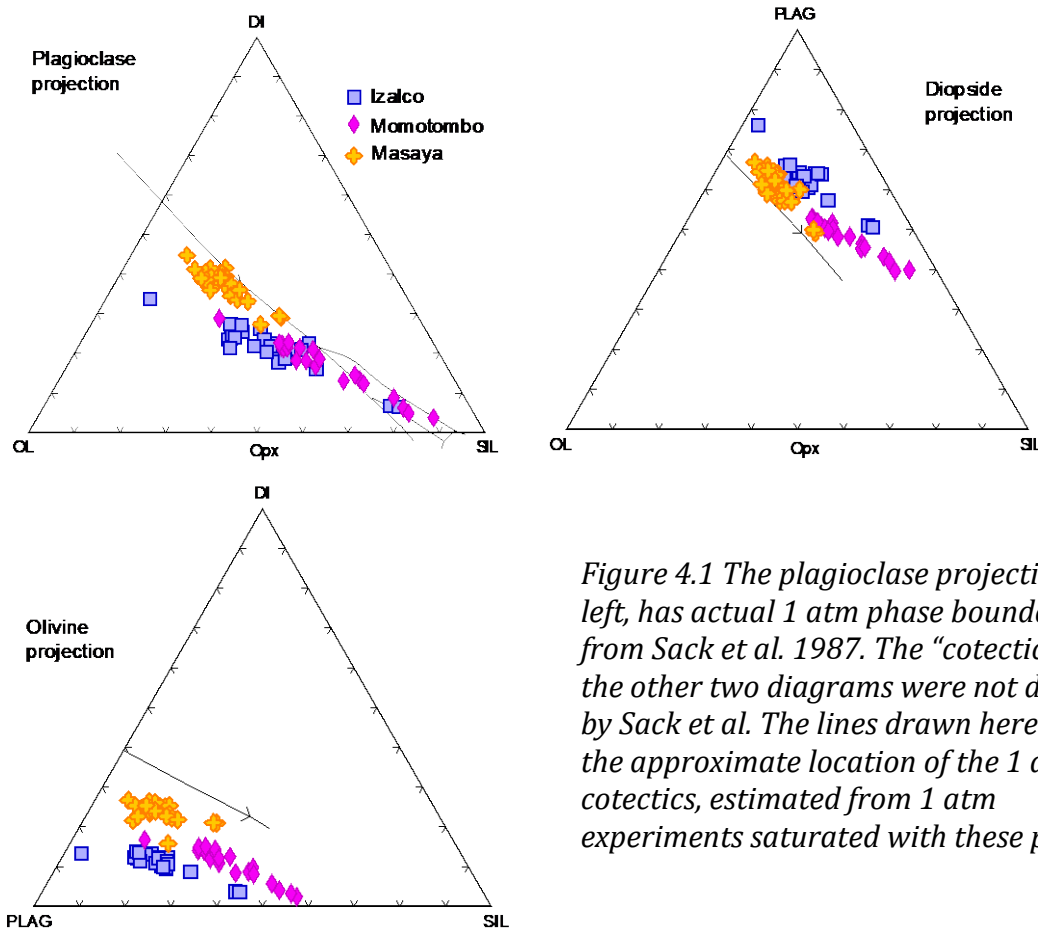


temperatures. Attempting to use lavas to define liquid lines of descent is dangerous because many lavas are too full of phenocrysts to serve as indicators of liquid line of descent. The most common case in arc magmas is accumulation of plagioclase because plagioclase is only slightly more dense than basalt liquids that have a few wt.% of water. An accumulation of plagioclase should be expected for any lava composition with 19 wt.% or more of  $\text{Al}_2\text{O}_3$ . This is especially true at higher pressures because melts are much more compressible than minerals.

Ideally, you would have an aphyric lava that you knew (from some magic trick) had just risen from a magma chamber growing ol, di and plag on its walls. Alternatively, you can have a magma with few phenocrysts and you can assert that these few crystals don't substantially change your bulk composition. The real situation is that most arc lavas have substantial amounts of small phenocrysts. You hope (assert) that the crystallization happened on the rise from the magma chamber and the crystals did not have time to separate, thus your bulk lava composition has the composition of a "glass" (i.e. a composition on the liquid line of descent.) Given these serious difficulties, it is surprising that CMAS systematics are common in arc basalts, though certainly not universal.

Phase diagrams, including pseudo-quaternary ones, are important because the cotectics (places where multiple minerals are crystallizing) shift with changes in pressure and changes in volatile content. Two major shifts of the cotectics are important for arc magmatism. First, higher pressure (e.g. magma chambers near the base of the crust) causes shrinkage in the stability field of olivine, so the liquid line of descent (LLD) shifts toward the olivine apex. Second, water shrinks the stability field of plagioclase, causing the LLD to move toward the plagioclase apex. We expect well-behaved arc lava suites to define apparent cotectics that are parallel to the LLD defined by experiments at 1 atm but shifted toward olivine and toward plagioclase. The LLD is a line in 3D created by the intersection of the primary phase volumes of the minerals co-precipitating. Once again, visualize the intersection of three soap bubbles. Another feature of the LLD is that the direction the magma evolves must be directly away from the cumulate (or mass of crystals that are fractionating out) that is forming. Thus, a tangent to the LLD, projected back to the outside of the tetrahedron gives the relative proportions of the instantaneously co-precipitating minerals.

The diagrams below depict apparent cotectics defined by lava suites from Izalco (blue squares), Momotombo (magenta diamonds) and Masaya (yellow crosses). The crust is thicker beneath Izalco in El Salvador, than beneath the two Nicaraguan volcanoes, Momotombo and Masaya. Masaya commonly has a visible lava lake (glowing at night and sometimes with a glow visible in daylight). Clearly the upper part of its plumbing includes a shallow magma chamber perhaps similar to magma chambers at mid-ocean rifts. Therefore, the shifts in pressure sensitive cotectics are expected to be greatest at Izalco and least at Masaya.

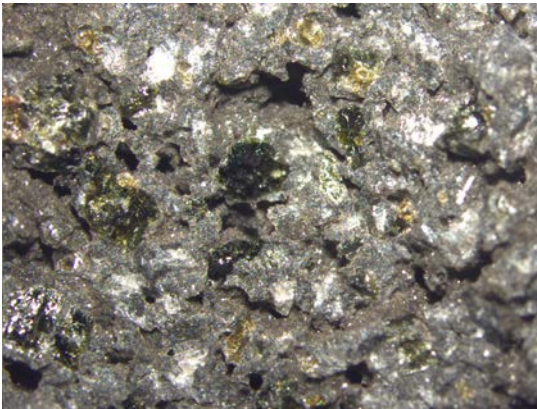


*Figure 4.1 The plagioclase projection, top left, has actual 1 atm phase boundaries from Sack et al. 1987. The “cotectics” in the other two diagrams were not defined by Sack et al. The lines drawn here show the approximate location of the 1 atm cotectics, estimated from 1 atm experiments saturated with these phases.*

The three volcanoes, presented here, have arrays that roughly parallel the 1 atm lines defined by experiments. In the plagioclase projection (top left), Masaya plots nearly on the 1 atm cotectic, indicating minimal shrinkage of the olivine field and magma evolution at shallow depth. Momotombo and Izalco have clearly reduced olivine fields indicating magma evolution within or at the base of the crust. In the diopside projection (top right) the three apparent cotectics shift towards plagioclase rather than toward olivine. This suggests that the presence of water has shrunk the plagioclase field more than the added pressure has shrunk the olivine field. Finally, the substantial shrinkage of the plagioclase field is obvious in the olivine projection (bottom right).

This introduction to CMAS was necessary to interpret an interesting aspect of Cerro Negro’s chemistry. Before assessing geochemistry it is always best to look at the actual rocks. The images below are hand specimens of Cerro Negro lavas. Many of Cerro Negro’s lavas are unusually beautiful because of abundant dark green pyroxenes and light brown olivines. However, high abundances of beautiful large phenocrysts should always lead one to question whether or not the lava represents a magma on the liquid line of descent. Picture a magma rising in a dike. Rising into progressively cooler surroundings causes crystallization. Gravity causes the minerals to sink because their density is greater

than that of the liquid. The lower pressure during magma rise leads to release of gas into small bubbles that may adhere to the minerals. The very light gas bubbles adhering to plagioclase may cause plagioclase to float. Fluid mechanics will decide the type of flow and the extent of mineral sorting caused by density and grain size variations (Stokes Law etc.). During a rise of 5 to 10 km a magma body can become zoned with liquid at the top, then a plagioclase enriched zone, and then a zone enriched in cpx and ol.



*Figure 4.2 Images of hand specimens from the 1960s eruptions.*

*Top Left image is CN5. Top Right image is CN4. Dark green mineral is cpx, yellow-brown mineral is olivine, white mineral is plagioclase.*

*Left image is CN6. White mineral is plagioclase.*

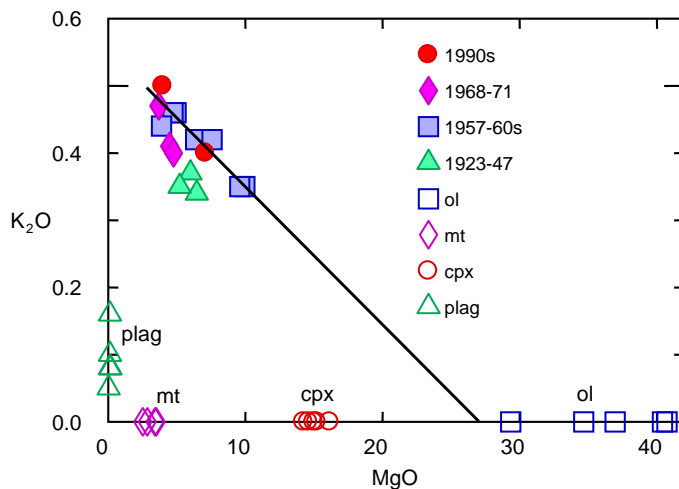
#### *Igpet exercise*

**4A.** Open Igpet and click **File** then **Open** and select CerroNegroGeochem.txt. Now click **Plot** then select **CMAS** and select SackWalkCarmichael87.txt. The window for adjusting Fe opens. The bottom has options for using the Kress and Carmichael method for adjusting Fe. Select the QFM buffer. Enter 1 into the box for P (Gpa) and enter 1 into the box labeled “plus/minus”. These are the settings used for Figure 4.1. Now look at the top three projections in the list that appears. Use **Next diag** to scroll through them. *How does the data array for Cerro Negro differ from the arrays defined by three volcanoes in Figure 4.1?* For the diopside and olivine projections click **ID ON** and **Pick** or **Next** to locate NIC-CN4, 5 and 6, the samples in the images above. *What might be causing the orientation of the Cerro Negro data array in the diopside and olivine projections?*

**4B.** Now add mineral analyses by clicking **File - File Operations - Add a file**, click **OK** when warned that you are appending a file. Select CerroNegroMinerals.txt, then click **quit**. Next, click **Plot - XY** and select MgO and K<sub>2</sub>O for the axes. Plagioclases plot near the y-axis but other minerals are hidden because their K<sub>2</sub>O contents are zero. Make them visible by clicking the **zeros in** button on the left hand side of the screen. Now click the **Symbol** button and then click the **Lcode** radio button in the upper left and finally the **OK** button. The Cerro Negro lavas now have symbols coded by age. The blue squares mark lavas from 1957-60 that have abundant mafic phenocrysts. Identify the minerals along the x-axis by clicking the **ID ON** button and then clicking near one of the symbols.

Now click the **Symbol** button again. Note the 1957-60 symbol is the blue box, number 4. Click the **Deselect all** button, then click the check box that has the **x4** label. Now just the blue box should be visible. Click **OK**. Now click **Regress** and select **linear**. Now click **Symbol**, then **Refresh**, then **OK**. The result should be similar to Figure 4.4 below.

*Where does the regression line intersect the x-axis? If adding or subtracting minerals is causing the major element variations at Cerro Negro, what does the X intercept ( $Y=0$  or  $K_2O = 0$ ) define for the 1957-60 samples?*



*Figure 4.4 MgO versus K<sub>2</sub>O with a least squares fit to the 1957-1960 data. Samples normalized to 100%.*

Most of this brief description is after Walker and Carr (1986). The only difference is a change in the age of CN5 from 1923 to 1960. CN5 was taken from a flow mapped as unknown age by Viramonte and Di Scala (1970) and attributed to 1923 by Walker and Carr (1986). Chemically, it is nearly identical to the nearby samples CN3 and CN4, which are from the 1960 eruptions, so 1960 is a better choice for the age of CN5.

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## Problem 5. Graphical modeling of fractional crystallization

In Problem 3 fractional crystallization was modeled as simple sorting using linear algebra. The logic makes the simplifying assumption that the elemental concentrations in the minerals are unchanged. That assumption is incorrect. For example, in Figure 5.1 the first crystallizing olivines form at a higher temperature and will have higher MgO content. As MgO is preferentially removed compared to FeO, the liquid changes but so does the olivine that crystallizes. Both become more Fe-rich.

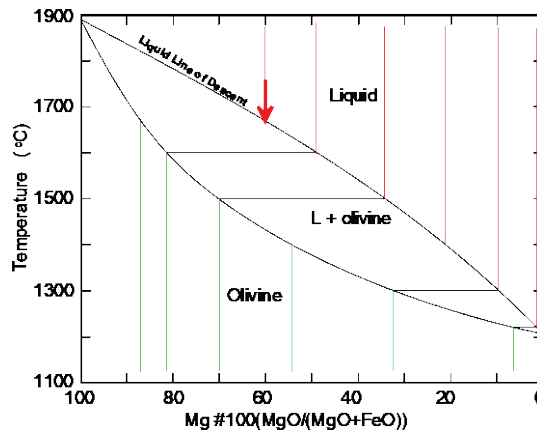


Figure 5.1. Phase diagram describing the fractional crystallization of olivine

For trace elements the changes in composition along the path of magma evolution can be quite large. The equation for modeling these changes is the Raleigh equation,  $C_l = C_o F^{(1-D)}$ .

$C_o$  initial concentration

$F$  amount of liquid remaining (from 1 to 0)

$D$  distribution coefficient, concentration of  $z$  in minerals/concentration of  $z$  in liquid

$C_l$  liquid concentration as a function of  $F$

$D$  requires a better explanation. Modeling trace element behavior begins with  $K_d$ s (Nernst distribution coefficients) or, more generally, partition coefficients.

$K_d$  = concentration in mineral / concentration in melt

The bulk partition coefficient,  $D$ , is the weighted sum of the contributions of all the minerals in equilibrium with the melt.

$D = \sum x_i K_{di}$  for  $i=1$  to  $n$  minerals. The  $x_i$  values are the mineral proportions (they must sum to 1).

The simple graphical modeling tool in Igpet's X-Y plots does not require knowledge of  $K_d$ s. The weakness of this simple tool is that  $K_d$ s are not used. The strength of the tool is that it easily demonstrates what happens as  $D$  values are varied, so it is helpful for learning.

To understand what happens as D values are varied you will make X-Y models using data from the Klyuchevskoi complex, one of the largest arc volcanic centers on the planet and one of the most active. It is unique and interesting in many ways. For an introduction to this volcano see Almeev et al. (2013) and Levin et al. (2014).

#### *Igpet exercise*

**5A.** Start Igpet and click **File** and then **Open** Klyuch-Bezy.txt. Click **Plot** then **XY** and select **MgO** and then **K<sub>2</sub>O**. Now click the **Symbol** button and deselect the red circles (data from Bezimianny) by clicking on the button on the right labeled “7”. Adjust the **Axes** to let the data fill more of the figure. Click the **ID ON** button and identify the sample with the highest MgO content. This will be the Parent for the models. Now click the **Model** button and select **FC**. Now select as parent the high-MgO sample you just identified. You are now asked to enter the D values for MgO and K<sub>2</sub>O. Assume that K<sub>2</sub>O is highly incompatible with a very low D value like 0.001. *What D value for MgO provides the best fit to the base of the data distribution?* MgO is a compatible element and its D is greater than 1. Start by entering 1.5 for the D for MgO, then click **OK**. Click **OK** when asked about ranges for F. Then click the **Add this to plot** button. You will now see a line plotted on the diagram with ticks representing the proportion of liquid remaining. In order to change the D for MgO click on the button **New D F R's** in the window on the left. After determining a D for MgO, now change the Y variable to a different element or oxide by clicking the **New Y** button. Use the **Model** tool to estimate the D values for other elements and oxides. Leave MgO as the X variable and keep entering the optimum D value you determined for MgO. Then try different Ds for the Y variable. Repeat the procedure for several elements and oxides listed below. The incompatible elements, Nb, Y, Zr and La, should all have low D values. Ni is important because it is a compatible element. TiO<sub>2</sub> is also interesting.

**5B.** *Make a table listing the D values of the 8 elements (including MgO and K<sub>2</sub>O (which was given to you)) listed above and two more of your own choosing. Identify any element with D>1 as compatible (C). Identify any element with D<1 as incompatible (I). Identify any element with D<0.01 as Highly incompatible (HI).*

This is an educational **exercise**, not a procedure for an experienced geologist.

**REMEMBER** that Ds are important and the D<1, D=1 and D>1 cases cause very different element variation paths.

#### References

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## Problem 6. Introduction to open-system processes: AFC

Igneous rocks are the result of many processes including fractional crystallization, assimilation, and mixing. Most of these processes are open, where open means that magmatic components can be added or subtracted. During fractional crystallization (FC), minerals grow to a size large enough to be easily separated from the liquid. Assimilation occurs as magma incorporates material from its surroundings. Lavas commonly have clear signs that some crust or mantle has been assimilated into evolving magma. The most obvious evidence is incomplete digestion of foreign inclusions. Magma mixing processes include mixing between quite different magmas and replenishment, which is where a similar parental magma intrudes into an evolved magma derived from the same parent. Open system processes are minimized by rapid rise through the uppermost mantle and crust, coupled with high eruption rates. Nevertheless, some degree of complexity can be expected and can be determined only by careful sampling and analysis.

DePaolo (1981) provides an excellent introduction to the complexities of open system processes by deriving the assimilation-fractional crystallization (AFC) model. This paper is a particularly clear example of applying calculus to petrology. The cartoon below (Figure 6.1) expresses several processes in a magma chamber as functions of time. The change in mass of an element as a function of time is the assimilation rate minus the fractional crystallization rate. This equation is then integrated to derive equations governing the behavior of elements and isotopic ratios as fractional crystallization and assimilation proceed.

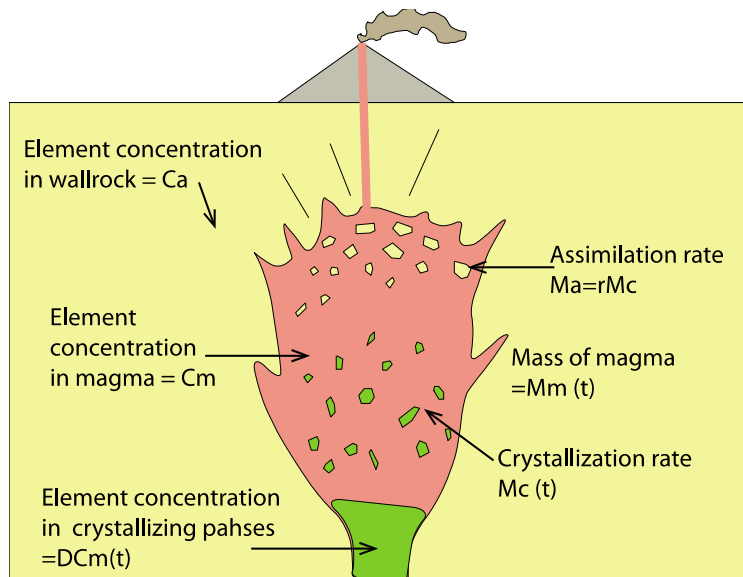


Figure 6.1. AFC conceptual model from DePaolo (1981)

The parameter  $r$  shown in Figure 6.1, is the ratio of the rate of assimilation divided by the rate of fractional crystallization ( $Ma/Mc$ ). Magma evolution divides into three cases,  $r=1$  (constant magma mass),  $r>1$  magma mass increases (because rate of assimilation is larger than rate of fractional crystallization) and  $r<1$  magma mass decreases (because rate of



fractional crystallization is larger than rate of assimilation). The later case is more likely unless the assimilant has a strongly exothermic reaction with the magma.

The AFC model includes FC and Mixing as special cases and is obviously more complicated than either of the two simpler models. However, reality is even more complex and so advanced models add other processes or constraints. RAFC adds replenishment to AFC (DePaolo, 1985). EC-RAFC and EC-AFC, where EC means Energy-constrained, add energy constraints (Spera and Bohrsen, 2001).

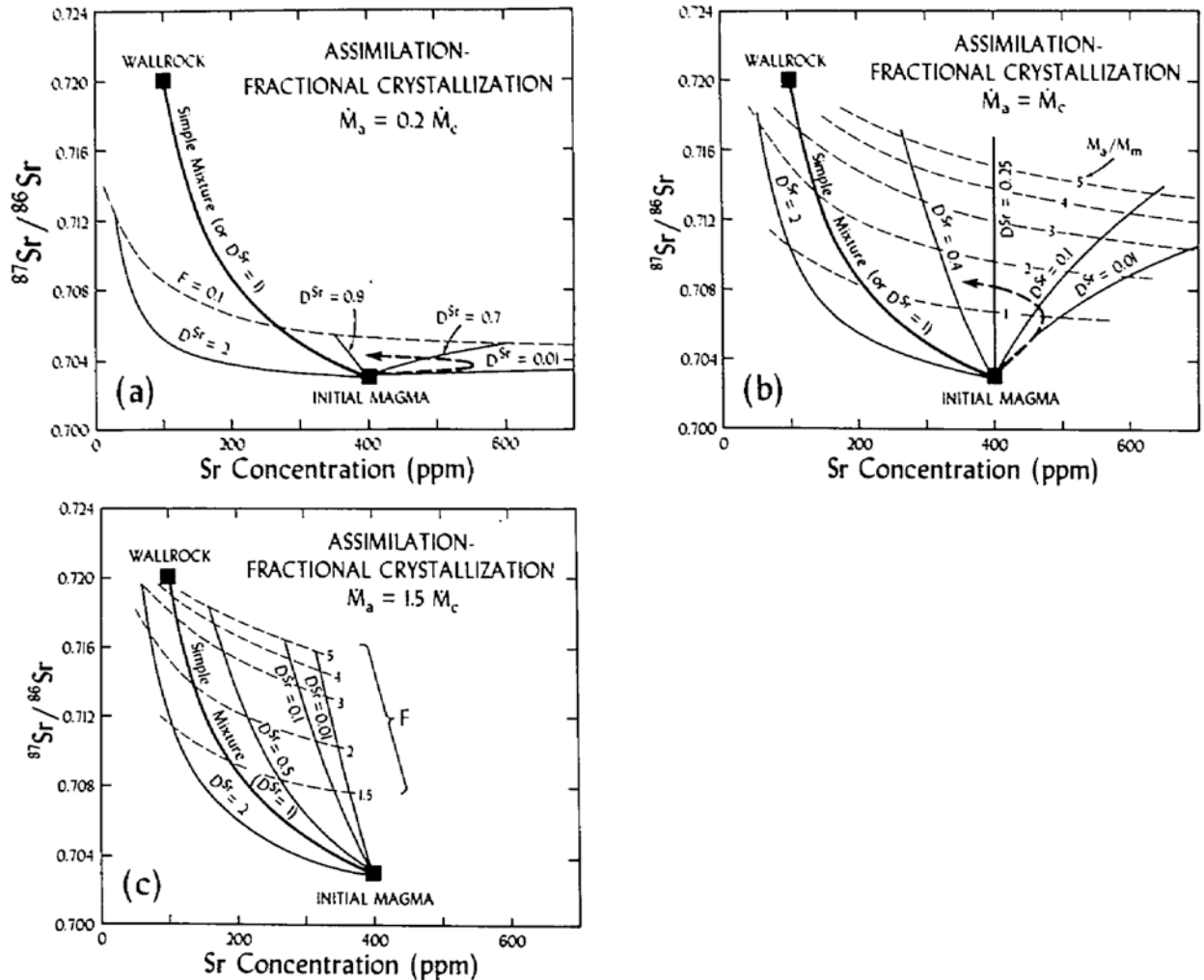


Figure 6.2. AFC models from DePaolo (1981)

#### Igpet exercise

**6A.** Read DePaolo (1981) to better understand the three different cases of  $r$ . Figure 6.2 demonstrates these three cases (note that the equation is written as  $M_a = rM_c$ ). In Figure 6.2a  $r < 1$ , in Figure 6.2b  $r = 1$ , and in Figure 6.2c  $r > 1$ . Each case has a different formulation for the variable that expresses an increment of change. In case (a) the variable being varied is  $F$ , the amount of liquid remaining. The dashed lines in the three Figures connect

steps of equal change on paths of different  $D$ s. *Explain what  $F$  or  $M_a/M_m$  are in the three cases a, b and c.*

**6B.** Start Igpet and go to **File** then **Open** and select the file; Depaolo.txt. Click **Plot** and select **XY** and then select Sr and then  $^{87}\text{Sr}/^{86}\text{Sr}$ . Click the **Name** button to identify the data points. Adjust the **Axes** to be like Figure 6.2b by clicking the **Axes** button. Then click the **Aspect** button and then click the **Aspect ratio** button and finally select **Box** and Click **Symbol** and then click on the button labeled “4” on the right to deselect the blue boxes. Now click **Model** and then **AFC**. Then select init Sr Rb as the parent and wall Sr Rb as the assimilant. Now read off the different  $D$ s on the model paths on Figure 6.2 and in order to *reproduce DePaolo’s case (b) in the figure above*. After inputting a  $D$ , click **OK** and then click **OK** again and then click **Add this to plot**. To input another  $D$  to make a different model click **New D F R’s**.

**6C.** Igpet made the reproduction of the diagram quite easy but it is likely that your understanding of what is going on remains limited so try answering these questions:

- i. Why is the path for  $D=0.25$  vertical?*
- ii. Identify the mixing lines ( $D=1$ ). For all three cases, does the evolutionary path for  $D=1$  move closer to the assimilant in both Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$ ?*
- iii. What happens to the evolutionary paths for  $D$  greater than and less than 1?*
- iv. Fractional crystallization has no effect on isotopic ratios, so how does AFC differ from mixing ( $D=1$ ) and why?*

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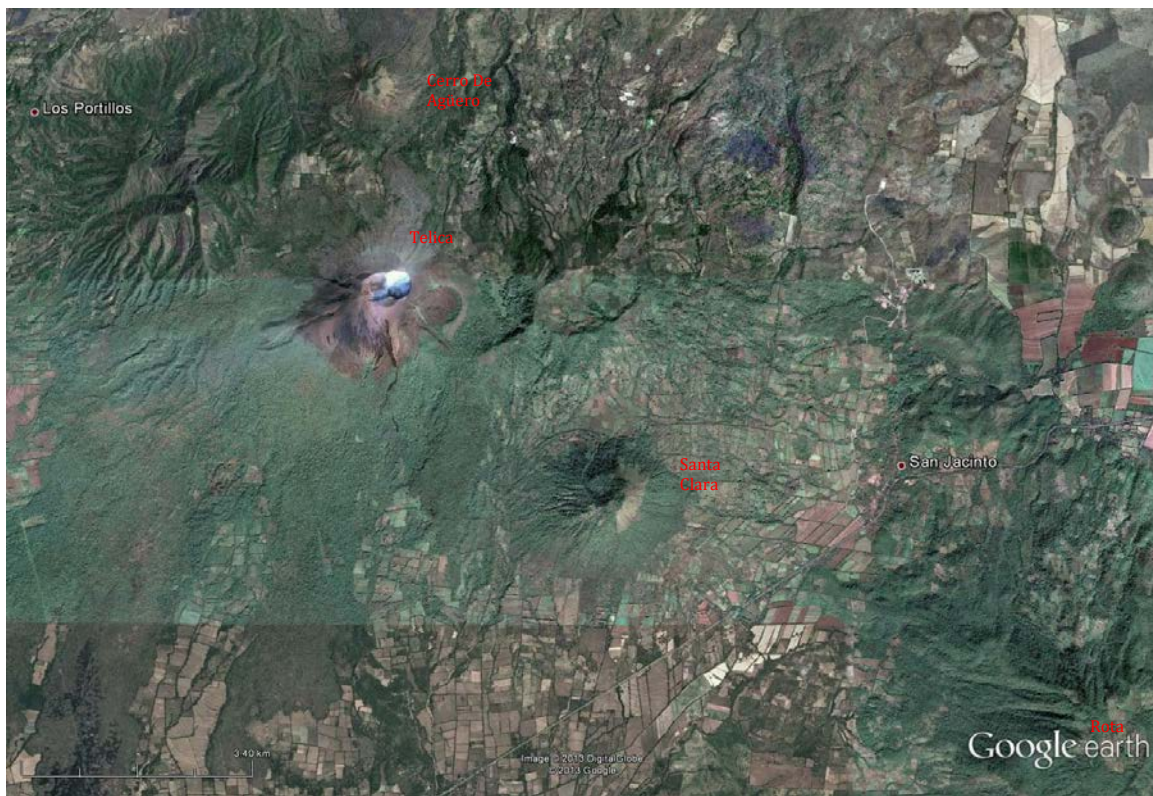
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### Problem 7. Telica: Complex geochemistry

The Telica volcanic center in western Nicaragua is an example of the complexity found at an arc volcanic center. The active vent at Telica differs from Cerro Negro (Problem 4) by being substantially older, at least 330 Ka, and by having mostly moderate sized eruptions, whereas Cerro Negro's eruptions are typically moderately large. They also differ in color. Cerro Negro (translates to "black hill") has pervasive alteration around fumaroles in the crater. Therefore climbing the volcano to get a sample is not a good idea. Telica's summit is red because the flux of volcanic gas has been substantial over at least the last four decades. However, the gas rises from the steeply walled and inaccessible active crater. The red color is a thin coat of hematite caused by acid rain. The coating is not deep and recent bombs near the crater rim have fresh interiors.



*Figure 7.1 Telica complex in Google Earth.*

Although it is a relatively small volcanic center, Telica has a variety of magma types that record the complex tapping of diverse sources. A first interpretation is that Telica lacks a large crustal chamber that intersects all rising magmas and mixes them into a relatively homogeneous magma body. An unusual feature of Telica is the presence of a group of lavas with Nb contents that are much higher than those normally found in arc volcanics. Severe Nb depletion is a prime characteristic of arc magmas and therefore Nb and its near twin, Ta, are prominent in tectonic discrimination diagrams.

Spider diagrams, like the one below, display the elements that are incompatible in the early forming minerals in basalt magmas. The more incompatible elements are on the left and the less incompatible elements are to the right. The order of elements is appropriate for a mid-ocean ridge (MOR) lava and so a typical MOR lava defines a smooth curve, either a flat line or one with lower values for the more incompatible elements on the left hand side. Arc magmas are spiky, with peaks and troughs rather than smooth curves.

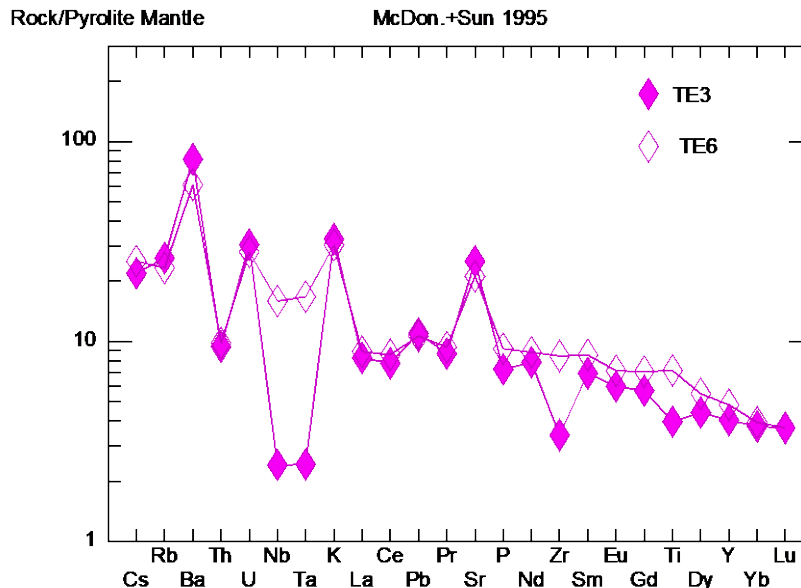


Figure 7.2. TE3 (filled diamond) erupted in the 1970s and TE6 (open diamond) erupted within the last few hundred years. Both came out of the same vent but they are quite distinct. Note: the Y-axis is a log scale, so the Nb and Ta differences are a factor of 10!

The up and down pattern of TE3 is typical of arc magmas. Th and the rare earth elements (REE: La, Ce, Pr, Nd, Sm, Eu, Dy, Yb and Lu) define a relatively smooth curve. Positive spikes occur in Cs, Rb, Ba, U, K and Sr, all of which are readily transported by hydrous fluids derived from subducted sediments and altered MOR lavas at the top of the subducting Cocos Plate. Negative spikes occur for Nb, Ta, Zr and Ti. The negative spikes all occur in what are called high field strength elements (HFSE).

NIC-TE6 is similar to NIC-TE3 except that there are no depletions in the HFSE elements. This is quite odd for an arc magma.

### Stratigraphy

The Telica sample set is comprised of 5 geographic and temporal groups. The first five samples (NIC-TE1- NIC-TE5, green triangles in Figures 7.3 and 7.4) are from the summit region: a flow and several bombs from lava blocks to scoria, all assumed to be quite recent. One sample, NIC-TE2, has inclusions of baked mud and is a sketchy sample although our analysis revealed nothing odd. Of course we avoided all the obvious bits of baked sediment during sample preparation. A recent scoria from a road cut, NIC-TE115,

is geochemically the same as the summit samples. NIC-TE122 is an aphyric lava that is stratigraphically older. However, it has chemistry similar to the Summit group and is therefore included. Most of these Summit group lavas have low phenocryst contents although NIC-TE3 has large clear plagioclases.

The next oldest group is remarkable for its HFS contents. NIC-TE6 is a thin pahoehoe flow present in some of the gullies on the NW side of the summit cone. Although very dark, the sample had few olivines. Instead, there are a few large clear plagioclase phenocrysts. This flow and four other recent flows on the south side of the complex all have the same large plagioclase phenocrysts. These are NIC-TE7, NIC-TE8, NIC-TE123 and NIC-TE124. The latter sample had a giant plagioclase 1 cm square. NIC-TE123 has the highest proportion of these phenocrysts. Members of the HFS group are slightly older than the Summit group, but the flows are still fresh and have sparse vegetation. There is overlap in the eruptions of the Summit group and the HFS group because the oldest lava of the Summit group, NIC-TE122, is below NIC-TE123 and, if the relative amount of vegetation has age significance, it is older than all the HFS group lavas.

Un-eroded cones comprise the next group. The two cones are Santa Clara (NIC-TE125, NIC-TE126), south of Telica and El Agüero (NIC-TE116 to NIC-TE119) north of Telica. Large clear plagioclases are present in most of this group.

The NE Sector group (Purple crosses) is a clear geographic cluster from the NE sector. Three are geochemically similar, NIC-TE121, NIC-TE127 and NIC-TE128 but NIC-TE120 has chemistry somewhat like the Summit group. NIC-TE128 has large clear plagioclases but the others have few phenocrysts. NIC-TE120 is aphyric.

Los Portillos (Blue X) is the oldest group with dates of 170 Ka and 330 Ka. All came from the substantially eroded volcano, Cerro Los Portillos, on the NW side of the center. All have small cloudy plagioclases. Their incompatible element signature is odd and looks very similar to that expected from fluid derived from carbonate sediment, consistent with the lower half of the Cocos Plate sediment pile. The rest of Telica, especially the youngest samples, have an incompatible element signature consistent with addition of a fluid derived from the upper sediment section on the Cocos Plate, a hemipelagic mud.

The division of the sample set into groups is a nit-picking approach to geochemistry-petrology. An opposite approach is to just lump everything together and call it all Telica and give it one symbol. If you have access to Google Earth, **put the file, Telica.kml on the desktop and double click it. Google Earth will start and display the Telica samples on an image. Now you can make your own decision about whether the groups are justified or not.** Also note that the locations were pre GPS and rounded to the nearest 100 m. At least one sample, NIC-TE 120, looks like it came from the middle of a corn field. It did not, it was from the adjacent mound of lava about 100 m North. Using Google Earth is an excellent way to think about volcanoes.

The most remarkable characteristic of the HFS group at Telica is the lack or reduced size of Nb depletion. Very low Nb contents are characteristic of typical arc magmas. NIC-TE6 has normal Nb content, not depleted at all. The other 4 samples in this group have lower Nb contents and the Nb content of NIC-TE8 is almost the same as the “normal” Telica lavas. Nb is a highly incompatible element and it should increase as SiO<sub>2</sub> increases. What mechanism would allow Nb to decrease with SiO<sub>2</sub> as is seen in Figure 7.3 for the HFS group, the open magenta diamonds?

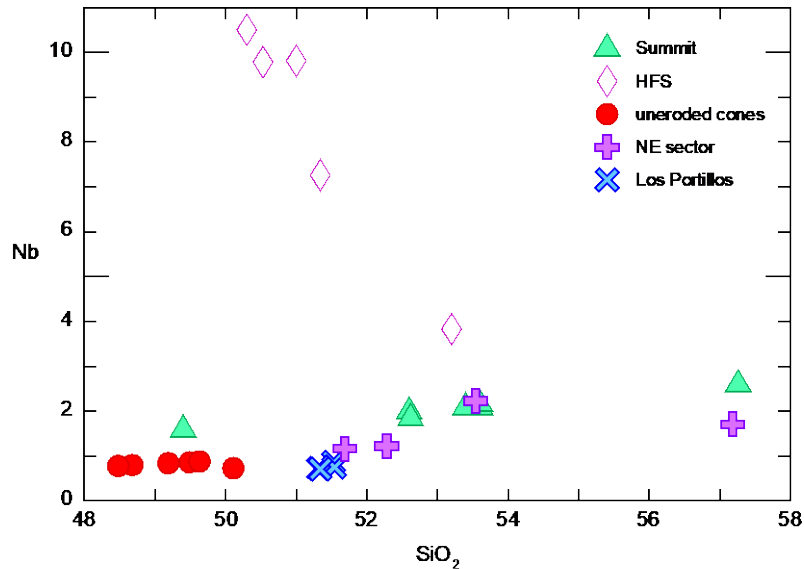


Figure 7.3 Variation of Niobium versus Silica at Telica volcano. Symbol key is in stratigraphic order with Los Portillos the oldest.

A parameter called Stratigraphic order was added to the data set, young samples have low numbers and old samples have high numbers. The numbers are relative, and based on the expectation that the age distribution is log normal because of burial of older lavas. The reason for establishing the order of the lavas is that age can provide useful insight. One of the first things to ask about a volcano from a petrological perspective is whether or not there are changes in lava composition with time.

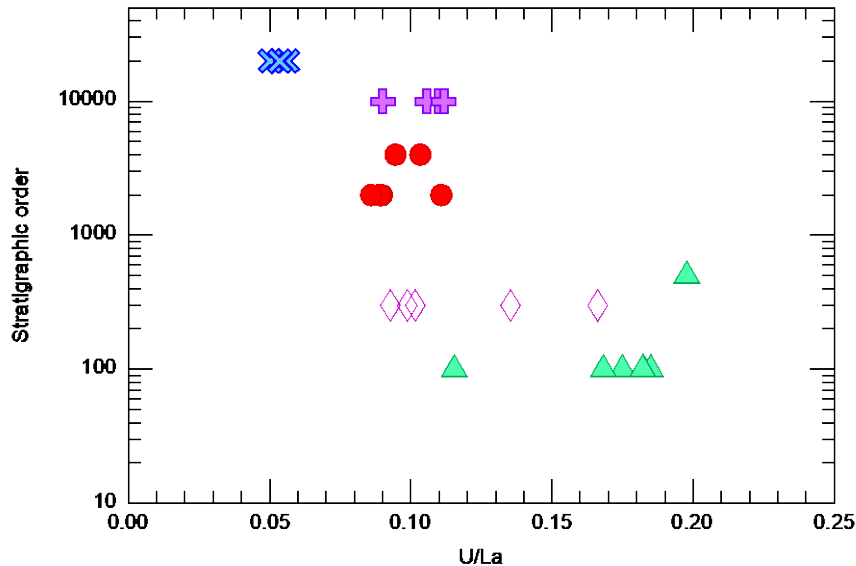


Figure 7.4 Change in U/La with stratigraphy. Symbols as in Figure 7.3

In the diagram above there is a crude decrease in U/La as one goes back in time. However, there is a wide range for the two youngest groups suggesting a fair amount of mixing of contemporaneous magmas with 0.18 U/La, the Summit group (green triangles) and 0.10 U/La, the HFS group (cluster of open magenta diamonds). From this perspective there have been three steps, from an initial 0.05 U/La, to 0.10 U/La and, most recently, 0.18. There are some possible causes for this variation but the arguments are complicated and not resolved. The point of this diagram is to show that real differences occur in the history of a volcanic center. One should not expect simplicity. There are magma batches and they can be identified with very good chemical analyses and attention to stratigraphic sampling.

#### *Igpet exercise*

**7A.** Load the Telica.kml file into Google Earth and reexamine the division of the samples suite into groups, unless you have already done so as suggested above. *List any changes you would make.* The point is to think about stratigraphic sequence as an important factor in petrology/geochemistry!



**7B.** Nb is a highly incompatible element and it should increase as SiO<sub>2</sub> increases. *What mechanism would allow Nb to decrease with increasing SiO<sub>2</sub> as is seen in Figure 3 for group 2, the open magenta diamonds?*

**7C.** It is useful to determine magma batches and trace magma evolution within a batch. *Open Igpert and then click **File** then **Open** and select Telica.txt. Given that Al and Sr are strongly partitioned into plagioclase, make plots of SiO<sub>2</sub> vs Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> vs Sr by clicking on **Plot** and then **XY** and then selecting your X and Y-axis variables. What is going on with the different batches or groups? How do they differ? Assume SiO<sub>2</sub> increases with increasing fractional crystallization.*

**7D.** *What other elements behave like Nb in the Nb versus SiO<sub>2</sub> plot shown earlier? Make plots in Igpert using the file: Telica.txt.*

**7E.** *In the tedious storytelling above about Telica, there is a MacGuffin. First, what is a MacGuffin? Second, what is it in this case?*

#### Reference

Patino, L. C., M. J. Carr and M. D. Feigenson (2000), Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input, *Contrib. Mineral. Petrol.*, 138, 265-283.



## Problem 8. Partition Coefficients

Depending on starting compositions and the T, P, fO<sub>2</sub> conditions of different experiments, there are substantial ranges for published K<sub>d</sub> (partition coefficient) values. The file PlotPCs.txt in the Data Files folder allows one to examine a variety of K<sub>d</sub> values. Open Igpet and then click **Open** and then **File** and select PlotPCs.txt. Then click **Plot** and then **Spider**. Select **REEs set to 1**. Select all the samples and you will get a real mess. Adjust the **Y-scale** to Log values of 0.00001 and 200 to get a better view of the confusion. However, considerable order appears if you look at only at one mineral at a time. Use **Repick** to reduce the clutter by selecting only the olivines (ol). Use **Repick** multiple times to separately examine the other minerals; orthopyroxenes (opx), garnets (gt), clinopyroxenes (cpx) and a few trace minerals. Note the range for each mineral and the fact that the Y-scale is a Log<sub>10</sub> scale. For each mineral the overall shape of the REE pattern is similar but there is considerable range in the actual values of the K<sub>d</sub>s among the different publications. This comparison should cause you to develop a large degree of caution when using PCs.

### *Igpet exercise*

**8A.** Make separate REE spider diagrams of the K<sub>d</sub>s of the minerals (ol, opx, cpx, gt, sp). Print the diagrams after making sure all have the same y-axis scale. Print a blank diagram for use in **8B**. Use **Repick** and **Clear** to make a blank diagram.

The extended REE diagram, which includes many large ion lithophile (LIL) elements and high field strength (HFS) elements, is called **PM set to 1**. Click **New Spi** and select **PM set to 1** and change the Y-axis scale (0.00001 to 200) to again to look at the wide ranges of K<sub>d</sub>s determined for the incompatible elements outside the well-behaved REE group. Although the extended spider diagrams with LILEs (large ionic radius lithophiles K, Rb, Cs, Sr, Ba, Pb and Eu<sup>+2</sup>) and HFSEs (high field strength; Ti, Nb, Ta, Zr, Hf, Th, U, P, Ce<sup>+4</sup>) allow examination of a wider range of trace element behavior, the partition coefficient data are considerably more scattered.

Although the large K<sub>d</sub> variations are discouraging, there are some reference points worth knowing, especially if your interest is the partitioning of trace elements during melting in the mantle. In this case, the minerals are olivine, orthopyroxene, clinopyroxene, garnet or spinel and possibly a few accessory minerals. First, K<sub>d</sub>s below 0.01 are not all that different in their effects on melting if the % melt is 5% or more. Furthermore, an abundant mineral with a moderate level of incompatibility (e.g. cpx) will have a dominant effect on the D value and prevent D from being extremely low. Finally, regardless of the data source, ol, opx, cpx, and gt have similar patterns (roughly parallel slopes). This is most obvious for the REE, especially for garnet which has K<sub>d</sub>s >1 for the heavy REE and therefore a pattern that inclines steeply up to the right. Clinopyroxene has a bow shaped pattern with a maximum in the middle REEs that gets close to 1 but remains below it. Olivine and orthopyroxene are low and flat. Spinel is low and flat except for Nb and Ta. The minerals present in the residue of partial melting impart their signature on the melts. Assuming an initial flat pattern in the mantle prior to melting,

melts inherit a trace element signature that is inverse to the shape of weighted sum of the residual minerals.

**8B.** Make two hand drawn spider diagrams, one for REEs and one for the PM group. Draw the approximate ranges of the  $K_d$ s of ol, opx, cpx, gt all on the same sheet. Use colors. If your department no longer has a light table, tape the individual spider diagrams to a window and overlay a blank one to consolidate the patterns for easy comparison. Simplify as appropriate by ignoring outliers. Hand in a Xerox copy and keep the colored one for your reference.

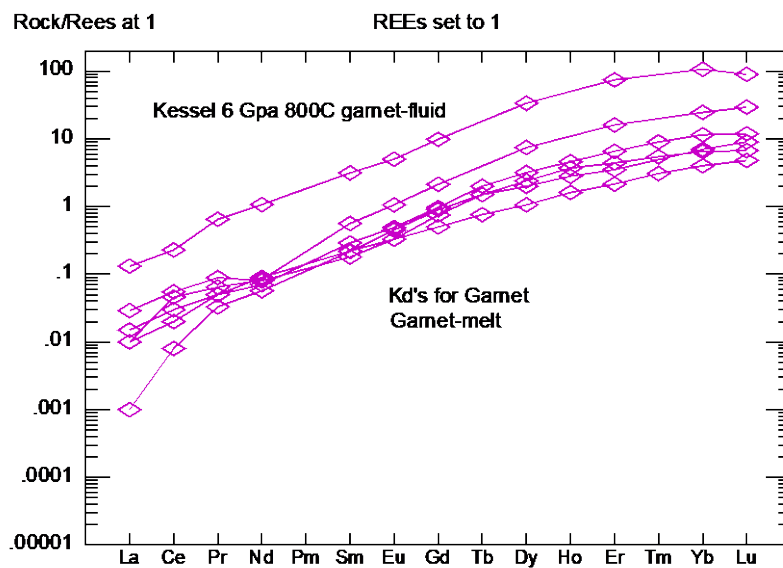


Figure 8.1 REE partition coefficients for garnet-melt. Top one from Kessel is garnet-fluid.

#### Reference

Kessel, R, MW Schmidt, P Ulmer and T Pettke (2005). Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth. *Nature* 437, 724–727.

### Problem 9. Trace element mixing in XY plots: Central American example

The following exercise uses tools for examining the mixing process. Mixing occurs on many scales in igneous rocks so it is a legitimate and verifiable process. Pure mixing, the process examined here, may be less common than mixing accompanied by fractional crystallization. In answering the questions below, consider allowing common sense to trump mathematical wizardry.

Open Igpert and click **File**, then **Open** and select CAVF.txt, a data file with a comprehensive set of trace elements and isotope ratios for Central America. Use it to explore ratio/ratio plots and make models of magma mixing by clicking **Plot**, then **XY** and then selecting the X and Y-axis variables. To use a ratio as one of the variables, first click the **A/B** button and then select the numerator and then the denominator. Your selections will create a new button in the lower left, click this to select it as your variable. Ba/La versus La/Yb is an example of regional data that are nominally compatible with mixing between very dissimilar end members. Plot Ba/La versus La/Yb and note the shape. Now make a new plot using Distance (kilometers from the NW end of the Central American volcanic front) as the X variable and Ba/La as the Y variable. This is a very large regional variation and Ba/La is just one example of several ratios that follow the same regional pattern (Carr et al. 1990; Patino et al. 2000, Saginor et al., 2013). Click **New Y** button on the left and change the Y-axis variable to La/Yb. La/Yb varies in an opposite sense to Ba/La. Now click the **Symbol** button and click the button **Deselect all**. Then click the buttons labeled **x6** (corresponding to the magenta diamond = western Nicaragua) and **x14** (purple cross = central Costa Rica). Exit the window by clicking **OK** and you will find a plot that is much simpler. Note that the two symbols represent regions separated by about 300 Km. Now make the Ba/La versus La/Yb plot again. Click the **Mix** button. First use **Two Endpoints** (e.g. NIC-TE116 and CR-IZ-02-19). Select **e-n\*20%** as your tick scheme. Set the bounds of mixing line at **endpoints**. Finally click **Add this to plot**. A hyperbola is calculated and plotted. Now click **Mix** again and select **Least Squares fit** and then **OK**. A different hyperbola appears, one based on all the points not just two.

#### *Igpert exercise*

**9A.** *Hand in the Ba/La versus La/Yb diagram with the two mixing hyperbolas. Which hyperbola fits the data most closely? Is the closer fit more meaningful given the geographic reality? Is simple mixing the likely explanation for the geochemical variation along the Central American volcanic front?*

#### References

Carr, M.J., Feigenson, M.D. and Bennett, E.A., 1990. Incompatible element and isotopic evidence for tectonic control of source mixing and melt extraction along the Central American arc. *Contribs. Mineral. Petrol.*, 105:369-380.

Patino, L.C., Carr, M.J. and Feigenson, M.D., 2000. Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input. *Contrib. Mineral. Petrol.*, 138:265-283.

Saginer, I., E. Gazel, C. Condie, M. J. Carr, 2013. Evolution of geochemical variations along the Central American volcanic front. *Geochemistry, Geophysics, Geosystems (G<sup>3</sup>)*, doi:10.1002/ggge.20259

### Problem 10. Multi-element fractional crystallization modeling at Klyuchevskoi

In this exercise we will improve the fractional crystallization model introduced in Problem 5. The excellent data from Klyuchevskoi volcano allows realistic modeling of the fractional crystallization process that appears to dominate the evolution of this remarkable volcano. Klyuchevskoi appears to be the most active arc volcano on the planet. It is unique and interesting in many ways. For an introduction to this volcano see Almeev et al. (2013) and Levin et al. (2014). Almeev et al. (2013) describe the earliest crystallization as being dominated by the mineral, clinopyroxene.

Fractional crystallization generally causes melt evolution paths to be curves in element versus element plots. Often the fractional crystallization process is blurred by sporadic introduction of new magma that mixes with evolved magma in the plumbing of the volcano, a process called recharge, a type of magma mixing. Mixing of two magmas causes linear arrays on element versus element plots. For incompatible elements (e.g. SiO<sub>2</sub> at arcs) and highly incompatible elements (K<sub>2</sub>O) the magma evolution path for fractional crystallization can be roughly linear in an element-element plot and indistinguishable from the process of two magmas mixing which is exactly linear. Compatible elements vary more with fractional crystallization and so the shape of the magma evolution path in element versus element plots tend to have more curvature and are therefore distinctly different from the linear array of magma mixing. Curved paths on element-element plots are an indication of fractional crystallization and compatible elements are more sensitive to this than incompatible elements.

Open Igpet and then flick **File**, then **Open** and select the file Klyuch-Bezy.txt. Click **Plot** then **XY** and select **MgO** and then **K<sub>2</sub>O** as the X and Y-axis variables. Now click the **Symbol** button and click the small button labeled **7** to deselect the red circles, data from Bezimianny. Click **Ok** to close the window. Click **ID ON** and then use **Next** and **Prev.** or click **Name** to identify the sample with the highest MgO and write down the sample name because you will use it as the “parent” for this exercise.

Next, click **Plot** then **Spider** and select: *Laubier\_FC Traces+Majors*. When asked to select samples click **All** and then **Done**. Then click **Y-scale** and select **Log Scale** and have the scale go from **0.01** to **100**.

Next click **Model** and select: **ray frac xtal**.

In the model window make selections:

**Read PCs file:** select Laubier2014QFM.PC.txt by double clicking (QFM signifies that partition coefficients were determined at the QFM buffer, where quartz, fayalite and magnetite coexist and thereby determine the oxygen pressure).

**Select Source:** enter the parent you picked earlier by double clicking.

**Min. Mode-D:** here you enter the percentages of minerals in the cumulate. Note that the most mafic lavas in this rock suite have just cpx phenocrysts. Enter **100** for cpx. Click **OK**.

Click **Normal** and then **Make Calculations**. A small window displays the d's and p's. Check if the d for Mg is close to the D you estimated for MgO in problem 5. Note which elements are modeled then Click **OK** to close the window and then **Finish/Close**.

In the resulting spider-diagram, do the models (black) completely cover the data (green)? Maybe you have a successful model but be wary because the Y-scale is a Log<sub>10</sub> scale!

To test the model, make X-Y plots. Click **Plot** and then **XY** and select MgO and K<sub>2</sub>O as your X and Y-axis variables. If the black line goes through the data, then the model is quasi-successful. To be completely successful the black line should run through the data for the full range of elements modeled. The elements are those present in the partition coefficient (PC) file.

Some elements or oxides fail. Failure could be caused by many factors:

- Mixing may cause several samples to fall within the curve of the FC model line  
*with compatible oxide MgO as the x-axis, FC on incompatible elements creates a bow-shape line increasing as MgO decreases. Subsequent mixing can fill in the bow area (e.g. K<sub>2</sub>O).*
- The parent was not perfect for some elements.  
*model is displaced from most of the data but has the same slope so it is a "good" fit.*
- The partition coefficients may not be completely appropriate.  
*Laubier PCs came from experiments on MOR basalt and Medicine Lake basaltic andesite*
- The cumulate has other minerals, not just pure cpx.  
*Ol, opx and pl may help. Magnetite (mt) occurs in arc volcanoes but no PCs for mt in this file*

*Igpet exercise*

**10A.** Is there a more appropriate cumulate than 100% cpx? Investigate what occurs as you add ol, opx and plag to the cumulate. Start with two phase cumulates such as 10% ol and 90% cpx. You will need to replot the data as a spiderdiagram first. Then make a series of models before returning to the XY plots. In order to identify the models on your XY plots click **ID ON** and then use the **Prev.** and **Next** buttons to scroll through the samples and models.

*Make a grid on a sheet of paper with the elements/oxides as columns and cumulates as rows. Mark fits as E (excellent) G (good) or F (fails). Ideally one would check everything but instead check 4 incompatible elements, K<sub>2</sub>O, TiO<sub>2</sub>, Zr, Ce, (a LIL, two HFS and a REE), and the compatible elements Ni and Ca.*

Start with 100cpx

Then olivine 10ol 90cpx If this model is worse, move on to opx. If better, try 20ol and continue incrementing ol until the overall fits turns worse. Decide which ol cpx model is best and move on to opx and repeat the process.

The tedious grid creation can be fairly fast if you add models in a sequence such as: 100cpx, 10ol90cpx, 20ol80cpx. Use the **ID On** and **Pick** buttons to keep track of which model is which.

*Hand in the grid and identify your preferred cumulate.*

Considering all the uncertainties, the 100% cpx model is remarkably good. There is room for improvement and you will likely find a somewhat better model. Perfection is probably not possible in this case but that is true in most geological models given the open nature of our systems and the high level of complexity. The initial 100% cpx model fits the high MgO samples so well that one can feel confident in the high quality of the analytical data for Klyuchevskoi and the appropriateness of the partition coefficients.

### *References*

Laubier, M., Grove, T.L. and Langmuir, C.H., 2014. Trace element mineral/melt partitioning for basaltic and basaltic andesitic melts: An experimental and laser ICP-MS study with application to the oxidation state of mantle source regions. *Earth Planet. Sci. Lett.* 392:265–278.

### Problem 11. Make a multi-element melting model

There are several different types of melting models used in igneous geochemistry, including batch melting, aggregated fractional melting and fractional melting. Aggregated fractional melting is likely the most realistic physical model of melting. It is worthwhile to compare the results of agg fract melt and the computationally simpler batch melting and fractional melting.

In fractional melting each increment of melt is immediately separated from the source, depleting it. At very low values of  $F$ , the melts are similar to melts from the aggregated fractional melting model but at modestly higher values the more incompatible elements (left side of plot) are already effectively removed so the melt values plunge for the elements on the left side of the plot. At small degrees of melting fractional melting produces nearly complete elimination of the most highly incompatible elements.

In aggregated fractional melting each increment of melt is immediately separated from the source rock and then pooled in a body with minimal contact with the source, perhaps a sill or dike. So this is a series of fractional melts that are averaged. This magma is sampled when the mass of the magma times its buoyancy generates sufficient force to break open a crack or initiate a diapir.

In batch melting each increment of melt remains in contact with the source rock until some event (earthquake) or threshold (total % melt > magic%) is reached, then all the melt is separated and the process is over. For batch melting one therefore uses the equilibrium melt equation (see below).

After opening Igpet click **File**, then **Open** and select **Mantle\_traces.txt**. This file has several mantle models, two non-depleted (flat) patterns, two depleted choices and three ocean island basalt (OIB) models; enriched mantle one (EMI), enriched mantle two (EMII), and high mantle Uranium (HIMU). Click **Plot** and then **Spider** and pick **McDon.+Sun 1995** and select all the mantle estimates in the file by clicking the **All** and then **Done** buttons. Adjust the **axis** by clicking the **Y-scale** button and select **Log Scale** and have the scale go from **0.01** to **10**. Click the **ID ON** button and use **Prev.** and **Next** to see which is which. Use **Repick** to select a particular mantle source. Now press the **Model** button and select **batch melt** or **agg fract melt**. Ignore the other options.

Melting involves two mineral assemblages. The first, the percentages of minerals in the mantle, determine  $D$  values. The second, the percentages of minerals that are actually melting, determine  $P$  values. Including both assemblages is called non-modal melting. A simplification that uses only the mantle mineral percentages is called modal melting. For non-modal melting you need to provide two mineral assemblages, one for  $D$ s, another for  $P$ s. The  $d$  values in the following equations represent the weighted sum of the partition coefficients of the minerals present in the mantle. The  $p$  values represent the weighted sum of the partition coefficients of the minerals that are actually melting.



Batch melting equation: derived from mass balance constraint (Shaw, 1971)

$$C_l = C_o / [d + f * (1 - p)]$$

Aggregated fractional melting equation: See Albarede (1995) for derivation.

$$C_l = C_o * [1 - (1 - f * p / d) ^ (1 / p)] / f_i$$

*Note: the term  $(1 - f * p / d)$  can be negative for a  $p$  much larger than  $d$ . If this term is negative, Igpet inserts a blank for  $C_l$ . There are similar checks for illegal function calls in several of the spider models. If some of your spider models mysteriously lack an element or two at some  $F$  value, this is the likely reason.*

Fractional melting equation: See Albarede (1995) for derivation.

$$C_l = (C_o / d_o) * (1 - p * f_i / d_o) ^ [(1 / p) - 1]$$

#### *Igpet exercise*

In order to compare batch and aggregated fractional melting click **Model** then **agg fract melt** and the **Non Modal** option. Click **Read PCS file** and select **StalterStracke3GPA.PC.txt**. Click Select Source and select DMM\_Salters and Stracke. In the % liquid's ( $F$ 's) text box enter values of **1, 5, 10**. Click **Min. Mode-D**, enter **55** for ol, **25** for opx, **20** for cpx and **0** for ga then click **OK**. Click **Melt. Mode-P**, enter **15** for ol, **25** for opx, **60** for cpx and **0** for ga then click **OK**.

Then click **Make Calculations**. Exit the modeling window and then make a second set of models keeping everything the same but selecting batch melting instead. Use the same  $F$  values, 1, 5, 10.

*How different are the two sets of models?* Having compared the models on the spider diagram, now click **Plot XY** and compare La/Yb versus Ba/Nb. The XY plots show the differences more clearly.

**11A.** *Hand in a spider diagram with the two sets of models (agg frac melt and batch melt) and a brief discussion of the difference between the batch melting and aggregated fractional melting models.*

Now consider fractional melting. Use the same parameters as the previous question, changing only the melt model. Make a set of models using the fractional melt model. Many highly incompatible elements plunge. Reduce the values of  $F$  until you get some results that are not severely depleted for most of the highly incompatible elements. You can use the **remove all models** button to eliminate failures.

**11B.** *Hand in a spider diagram for fractional melting and mark the melt percentages ( $F$ ).*

Return to the model in 11A for agg frac melt. After recreating the non-modal agg frac melt models, click the Model button again but this time specify modal melting.

**11C.** *How do the modal and non-modal melting models differ? Which end of the spider-diagram is most affected?*

To summarize, the melt modeling process for trace elements is:

1. select a starting composition (Igpert has a file called Mantle\_traces.txt for this purpose)
2. select a model e.g. batch melting, fractional melting, aggregated fractional melting.
3. select a file of partition coefficients appropriate for the composition, temperature, pressure,  $fO_2$  etc. of the system you desire to model.
- 4a. determine the mineral mode: proportions of minerals in the mantle.
- 4b. determine the melt mode: proportions of minerals entering the melt.
5. calculate  $D_s$  and  $P_s$  for each element of interest from the data in steps 3 and 4.
6. for a range of  $F$  values, usually % melts, use the selected model's equation to determine the values of each element at each value of  $F$ .

References

Albarede, F., 1995. Introduction to Geochemical Modeling, Cambridge Univ. Press, New York, 543 pp.

Shaw, D. M., 1970. Trace element fractionation during anatexis, *Geochim. Cosmochim. Acta*, 34:237 – 243, doi:10.1016/0016-7037(70)90009-8

Additional thoughts on creating successful melt models

Because finding a successful forward model is difficult, a modeling strategy is useful. One can start at the top and work down toward a mantle composition or start with an ideal mantle composition and work forward to a lava.

Starting at the top, the first objective is to determine a primary magma. Ideally, an aphyric lava with high MgO exists and has the necessary characteristics of a primary magma but this is rare. Less ideal but still useful is to start from the most mafic lava available. A primary magma can be approximated from the most mafic lava by using the fractional crystallization model and choosing the inverse option. It is best if one only has to add olivine.

The mantle source composition can be estimated from a primary magma by applying the aggregated fractional melting option (or other melting model) and choosing the inverse option once again. Different partition coefficients are appropriate for the fractional crystallization process in the crust and the melting process in the mantle. Selecting the appropriate  $F$  values for these two inverse steps is difficult, especially for alkaline lavas for which  $F$  is likely to be quite small. However, the goal is to create a plausible model not perfection. The local mantle 'created' is more convincing if it has the same general spider diagram shape as a more generic global mantle type such as DMM (depleted MORB mantle) or one of the OIB (ocean island basalt) mantle flavors. Creating a local

source composition allows local trace element variations to be incorporated at the beginning of the modeling process. The trouble with the top down approach is that circular reasoning is involved!

The second approach, perhaps especially appropriate for a batch of lavas from an oceanic island, is to start at the bottom by creating a blended mantle as a mix of two or more of the mantle flavors. Willbold and Strake (2006) created models of the main OIB flavors, HIMU, EM1 and EM2 by mixing primary earth reservoirs, including DMM, continental crust and altered oceanic crust. For specific cases these strongly flavored OIB end-members can be diluted with shallow asthenospheric mantle (DMM). Under continents one can also mix in some lithospheric mantle.

Isotopic data provide powerful constraints. If a lava suite has a large range of incompatible element contents for a small range of MgO, then it may be a collection of melts from the same mantle that formed by different degrees of melting. Alternatively, a lava suite may sample many small volumes of mantle that were enriched/depleted to varying degrees. The latter case should have strong isotopic variations whereas the former case will have no isotopic variation. Two distinct mantles (one a predominant composition, the other a set of veins in the predominant composition) is another possibility. Unfortunately, the possibilities or hypotheses keep expanding unless the lava suite is well behaved and high quality isotopic and trace element data are available. Excellent data often reveal that some favored hypotheses are inadequate.

Willbold, M., and A. Stracke, 2006. Trace element composition of mantle end-members: Implications for recycling of oceanic and upper and lower continental crust, *Geochem. Geophys. Geosyst.*, 7, Q04004, doi:10.1029/2005GC001005.

## Problem 12. Multi-element forward models

Forward modeling in igneous geochemistry is both complex and non-unique. The complexity arises from the interplay of several variables that have opposing effects, thus limiting interpretation to describing a volume in multidimensional space that yields results consistent with the actual data. The simplest example of opposing effects is that decreasing the degree of melting can be countered by decreasing the incompatible element concentration of the source. Despite the problem of non-uniqueness, some useful bounds may be found. Furthermore, to argue for a model, your choices should result in a calculated trace element profile that agrees with the data.

To arbitrarily find an excellent modern dataset, the *Bulletin of Volcanology* was searched backward in time from the September 2015 issue until the first geochemical paper with a comprehensive data set. An interesting paper by Jordan et al. (2015) fit the criteria of this search. JJC will refer to this paper in the rest of this problem. A PDF of this work can be downloaded from the *Bulletin of Volcanology*. Having this paper at hand will make the problem more meaningful.

JJC interpret temporal variations in Pleistocene maar deposits at Lake Purrumbete in southeastern Australia. This is an admirable contribution with excellent data and well thought-out and balanced interpretations. The modeling is a mix of qualitative description (arrows) and a quantitative model of fractional crystallization. This is a prudent mix. Late stage fractional crystallization models the Ni, Zr and Rb variation by 10% to 30% removal of a cumulate that is primarily olivine. The cumulate is based on observed phenocrysts and major element variations. The partition coefficients are a set of published values.

Qualitative models are presented for deeper processes. One is the possibility of cryptic clinopyroxene fractionation deep in the magma system. There are no clinopyroxenes to analyze because cryptic means unseen (not present in the eruptives) and thus inferred only from geochemical variations. The initial partial melting process is also qualitatively described. For this process, there are many unknowns, including: the source composition, appropriate partition coefficients, and the melting model. One immediate lesson from this paper is that realistic inferences can be drawn from data without including elaborate calculations especially in cases where the geochemical variations mimic known patterns. However, the specificity of their interpretations make it clear that the authors carried out numerous modeling calculations but decided not to include that work.

Although the extent of modeling needed to demonstrate the viability of a hypothesis can vary and can be a stylistic or editorial choice, one should always test hypotheses with numerical models as JJC clearly did. With appropriate software, scores of models can be made in an afternoon. One of the biggest problems is keeping track of poor, fair, good and, finally, excellent models. A lab notebook is an indispensable companion during a session in intensive modeling. Taking the time to write things down and make comparisons allows the brain to catch up with the computer.

*Igpet exercise: Late stage fractional crystallization*

Start Igpet, click **File** and then **Open** and select the file **AussieAlk.txt**. Click **Plot** and then **XY** and select Zr and Ni as your X and Y-axis variables in order to reproduce the right hand side of JJC's Figure 6 (copied below). Close study of the plot reveals that the analyses were recalculated to 100% water-free. To do this in Igpet, click **File**, then **Norm. to 100%** and answer **Yes** twice and click **Done**. Now replot the Zr versus Ni diagram. Zr is incompatible in most minerals crystallizing in basalt magma residing within the crust but Ni is strongly partitioned into several minerals, most notably olivine. There is a very wide range of published partition coefficients for Ni into olivine from roughly 4 to 60, so there is lots of room for fitting one's model.

Identify the sample with lowest Zr to use as the parental or initial concentration ( $C_0$ ) by clicking **ID ON** and using the **Prev.** and **Next** buttons or by clicking on the sample. Press the **Model** button, select **FC** (Raleigh fractional crystallization). Select the  $C_0$  (parent) you identified, set the D for Zr to 0.01. Adjust the D for Ni until you get a fit. Click **OK** for ranges of F. If you don't like the model click **Delete this line** and then click **New D F R's** to change the D for Ni. If you like the model click **Add this to the plot** then click **quit**.

**12A.** *What value of D for Ni is the best fit to most of the data?*

Now make a multi-element fractional crystallization model using a mineral mode for the cumulate and a selected partition coefficient file. JJC used partition coefficients from Rollinson (1993) and a mineral mode of 70% olivine, 20% spinel, 5% clinopyroxene and 5% plagioclase. Click **Plot**, then **Spider** and select **Sun +McDon. 1989 Primitive Mantle**. When asked to selected samples click the **All** button and hit **Done**. Now press the **Model** button and select **ray frac xtal**. Click **Read PCS file** and choose the file **RollinsonBasalt.PC.txt**. Click **Select Source** and select the parent you've been using as your  $C_0$ . Click **Min. Mode-D** and enter ol: **70**, cpx: **5**, pl: **5**, sp: **20** and then click **OK**. In the % liquid's (F's) text box enter **100,90,80,70**. Click **Make Calculations**.

Pause and examine the D values calculated from the mineral mode and Rollinson's PCs. Is the D for Ni higher than the one you estimated earlier? Note that there are no D values for Cs, Pb and P so these elements should not show up on models in the spider diagram. Note that the D for Ti is less than 1. This is wrong because the spinel in Rollinson's table is sphene (aka titanite) but there is no partition coefficient listed for Ti.

Click **OK** and then click the **Finish/Close** button and examine the spider-diagram. Ni is not plotted but this is not a concern because the elements modeled are the ones in the PC file, not the ones in the spider-diagram. Notice the contrary behavior of Nb and Ta in the plot. Their D's are very large because the sp in the RollinsonBasalt.PC.txt file is sphene, which has very strong affinity for Nb and Ta. The crystallization and removal of sphene is plausible because some basanites have abundant sphene. Because the actual tephra have only olivine, orthopyroxene and plagioclase (see Petrography section of JJC) sphene

and clinopyroxene are cryptic constituents of the cumulate (see below).

Now click **Plot** then **XY** and select Zr and Ni as your X and Y-axis variables. Your plot should closely reproduce the JJC figure below. The small box at 30% crystallization is about 600 Zr and 45 Ni.

**Fig. 6** Diagram showing variations in the trace element compositions versus Zr. Modelled trends of fractional crystallisation are indicated by the dashed line, and associated numbers indicate the percentages of crystallized material

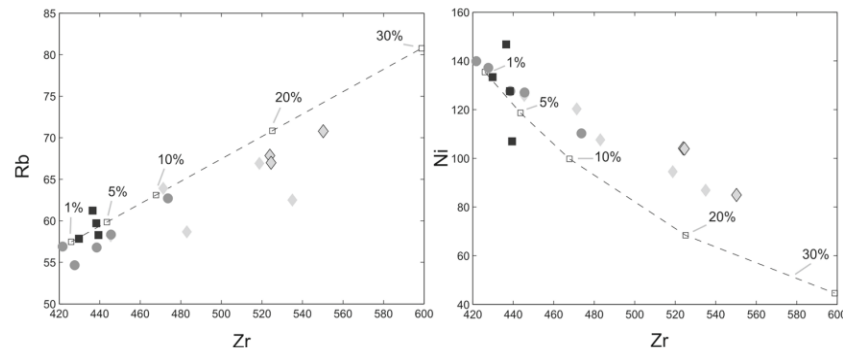


Figure 12.1 Copy of Figure 6 of Jordan et al. (2015)

Now plot several other elements against Zr.

**12B.** What elements have modeled lines that do not roughly coincide with the data? What elements fit quite well? (list 3)

(Roughly coincide is a deliberately vague term to encourage you to exercise choice or judgment.)

Now, once again, click **Plot**, then **Spider**. Follow the same steps as before but this time chose Laubier2014QFM.PC.txt as the PC file. This experimental work focuses on magma evolution in arcs and it has a substantially higher partition coefficient for Ni. It also includes a different mix of elements, including MgO. There are no data for any spinel so take the 20% that went to spinel before and add it to plagioclase.

**12C.** What elements have modeled lines that do not roughly coincide with the data? List three elements that fit quite well?

**12D.** If you assume that the Laubier2014 partition coefficients are superior to the Rollinson 1993 partition coefficients, how would you describe the case for late stage fractional crystallization of a cumulate dominated by olivine? Is that a valid model or a poor one?

Further introduction: Partial melting and the origin of the magmatism

JJC propose that these alkaline tephros are the result of a small degree of partial melting of an enriched source: “Variations in rare earth element ratios indicate that these melts were formed by dynamic melting of garnet lherzolite mantle material, consistent with other volcanic centres within the basaltic cones subprovince of the Newer Volcanics

Province.” Specifically, they cite “Melting of an enriched region of the mantle within the garnet peridotite stability field is also supported by trace element modeling of Lake Purumbete samples that indicates formation of these melts by extremely low degrees of partial melting (0.005–0.01%) of a garnet lherzolite mantle composition that contained 65 % olivine, 18 % orthopyroxene, 10 % garnet and 7 % clinopyroxene.”

To test this model, a mantle composition and a set of partition coefficients need to be selected. These important model constituents were not specified by JJC and so the model arrived at using Igpet is unlikely to be the same as theirs.

*First additional assumption: enriched mantle source compositions*

Enriched mantle trace element compositions are not readily available in convenient published tables. Enriched mantle is a broad term that includes the sources of most oceanic islands formed by ongoing volcanism above hot spots or other mantle perturbations. The lavas formed are called ocean island basalts (OIB). Their trace element concentrations are quite variable but their radiogenic isotope compositions define broad groups, the most prominent of which are: HIMU, EMI and EMII. Because these magmas have higher Sr and Pb isotopic ratios and lower Nd isotopic ratios than mid-ocean ridge basalts (MORB), there are defined as ‘enriched’ and MORB is defined as ‘depleted.’

Willbold and Stracke (2006) characterized the trace element profiles of the three major OIB groups. Parts of their observations about the OIB basalts follow:

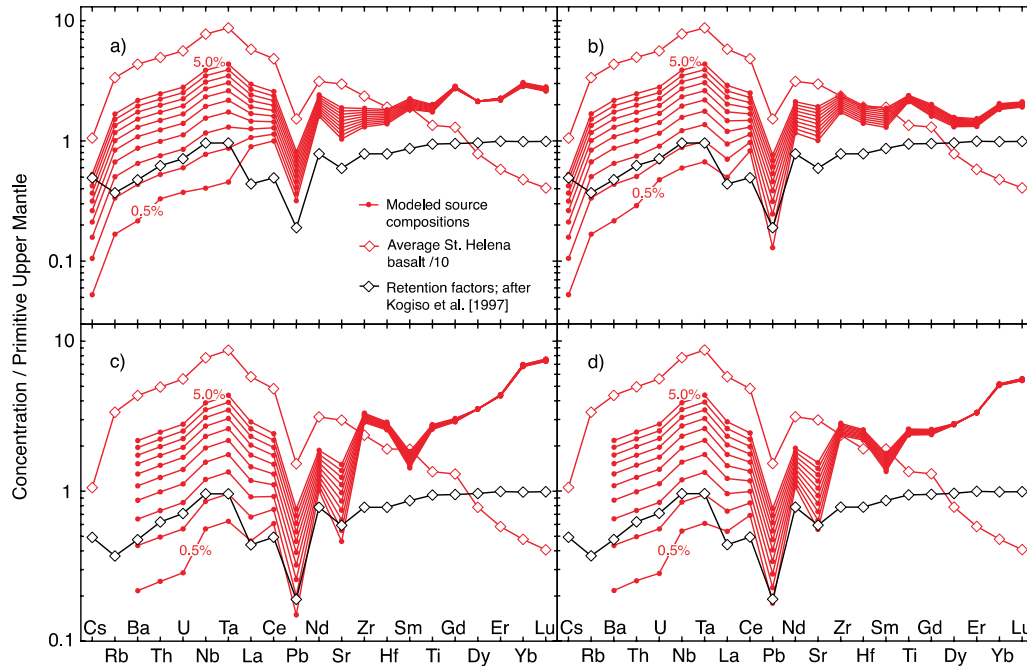
On p. 6: “All OIB investigated in this study have sub-parallel rare earth element (REE) patterns showing enrichment in light REE (LREE) relative to average CI chondrite and primitive upper mantle (PUM). All samples are depleted in heavy REE (HREE) relative to middle REE and LREE concentrations suggesting that melting occurred mainly in the garnet stability field. The ratios between the alkali and alkaline earth elements (e.g., Rb/K, Ba/K) and the La/Th and Sr/Nd ratios are similar in all OIB,”

p. 7: “...HIMU basalts from different localities have remarkably similar trace element compositions. All HIMU basalts are enriched in Nb and Ta relative to Ba and Rb and are overall depleted in Pb, Rb and Ba relative to EM basalts....The decrease in normalized concentrations from Nb to Cs is a unique feature of HIMU basalts that distinguishes them from all EM basalts.....”

p. 12: “.... EM basalts have common trace element characteristics that distinguish them from HIMU, but each suite of EM basalts has its own unique very incompatible trace element signature that is different from those of any other suite of EM basalts and is ultimately related to a unique source composition.”

The characteristics of the OIB basalts propagate down to the mantle source regions so the OIB have multiple local sources although HIMU should be less variable. To obtain sources for OIB, the EM-1 and EM-2 models in Willbold and Strake’s Figure 17 were digitized. For HIMU the model for St Helena with 1% melting in their Figure 9a (copied below) was digitized. For the HIMU model, the 1% melt was selected because that is the

same % melt as the EM-1 and EM-2 models. Willbold and Strake create their models by mixing components rather than inverting an average basalt composition. For example, EM-2 is 90% DMM + 9.8% oceanic crust + 0.2% upper continental crust. EM-1 is 90% DMM + 9% oceanic crust + 1% upper continental crust which results in a less smooth spider-diagram.



**Figure 9.** Calculated PUM-normalized trace element patterns of the St. Helena source assuming accumulated nonmodal fractional melting [Shaw, 1970] of a garnet-peridotite source for a range of different degrees of partial melting and bulk partition coefficients from (a) *Stracke et al.* [2003a], source mode Ol:Opx:Cpx:Grt = 0.55:0.25:0.12:0.08, melting mode Ol:Opx:Cpx:Grt = 0.05:0.05:0.45:0.45; (b) *Salters and Stracke* [2004], source mode = 0.53:0.08:0.34:0.05, melting mode = -0.05:0.49:-1.31:-0.13; (c) *Kelemen et al.* [1992, 2003], source mode = 0.54:0.17:0.09:0.20, melting mode = 0.10:0.18:0.30:0.42; and (d) *Workman et al.* [2004], assuming same partition coefficients and garnet-peridotite modal compositions as *Kelemen et al.* [2003] but weighted to 72% garnet peridotite and 28% spinel peridotite (source mode Ol:Opx:Cpx:Sp = 0.46:0.28:0.18:0.08, melting mode Ol:Opx:Cpx:Sp = 0.45:0.55:0.67:0.22). Arrays of curves show different degrees of melting ( $F = 0.5$  to 5% using increments of 0.5%). The normalized concentrations of average St. Helena basalt have been divided by 10. Also shown are the mobility coefficients in a fluid-rock system [Kogiso et al., 1997]. Note that the plotted coefficients are converted to “retention” factors ( $=1$ -mobility coefficient) and reflect the fraction retained in the source. Although the modal compositions and the absolute values for the bulk partition coefficients differ, the depletion in very incompatible elements and light REE relative to heavy REE, the enrichment of Nb and Ta relative to U and La, and the depletions in Pb relative to Nd are common to all modeled source compositions and are difficult to reconcile with partial melting processes alone. Comparison with rock-fluid alteration factors suggests that the HIMU source must have experienced fluid-rock interaction during its evolution.

Figure 12.2 Copy of Figure 9 from Willbold and Strake (2006)

*Second additional assumption: select partition coefficients*

Partition coefficients will affect the model just as much as the choice of enriched source. Kelemen2003Peridotite.PC.txt is a comprehensive partition coefficient file that was



assembled to analyze arc lavas. This file was modified by adding Rb with partition coefficients identical to K. Furthermore, the partition coefficient for Y was re-estimated to be similar to Ho rather than identical to Yb. Other PC files can also be used but, for an exercise it is not worthwhile to have too many degrees of freedom. For research, care needs to be taken to identify the most suitable partition coefficients.

### **12E. Multi-element melt modeling**

Start Igpet, Click **File** and then **Open** and select the file **AussieAlk\_mantles.txt** and click **Plot**, then **Spider** and select **Sun +McDon. 1989 Primitive Mantle**. Select **All**, then **Done** to see the narrow range of the Purumbete samples and the wide range of possible mantle source compositions. Click **Repick** and then **Clear** to deselect everything. Double-click on A17 and An22, which represent the range of Purumbete samples. Also select HIMU and then click **Done**.

After the plot is completed, click **Model**, then select **agg frac melt**. Next select **Modal**. Fill the Modeling Parameters window as follows:

Read PCS file            Kelemen2003Peridotite  
Select Source            HIMU  
Min. Mode-D 65Ol 18Opx 7Cpx 10Ga (should sum to 100)  
% liquid's            0.3,0.4,0.5

Click **Make Calculations**

Click **Skip calculation of residues**

Click **Finish/Close**

Click **OK**

Click **Dash** (to expose the elements lacking partition coefficients and ignored)

Considering all the elements, none of the three models calculated fit within the brackets defined by A17 and An22. For Pb and Zr there is no hope for a fit, most likely because the St Helena source is not quite right for these continental alkaline basalts. Adding a reasonable Kd for Cs will not create a fit because the Cs in the samples is altogether too high for a HIMU source. The same is true of Pb. Therefore ignore, Cs, Pb and Zr.

To improve the fit, the crystal-liquid partition coefficients (Kds) are key. On the left side no mineral has a Kd high enough to control the models and so the elements from Rb to U are controlled by the degree of melting (F) and 0.3% to 0.5% bracket these elements. Elements in the middle are moved most by cpx and the elements on the right side are controlled by ga (garnet). To lower the elements from La to Sm, increase the % cpx in the mantle mode. To lower the heavy REEs, increase the garnet (ga) in the melt mode.

Note that the % melts that bracket Rb-U (0.3% to 0.5%) are substantially higher than those proposed by JJC, indicating that the selected HIMU source is too enriched or that the melt model is different. Dynamic melting can be either, fractional, aggregated fractional or continuous. Of these, the aggregated fractional melt model is both simple and not prone to blowing up. Fractional melting can provide fits at much lower % melts but is prone to failing by using up the most incompatible elements at low degrees of

melting.

**12E.** *Adjust the percentages of cpx and ga in the mantle mode to optimize the fit. Use  $F$ 's of 0.3, 0.4, 0.5 for each trial. When you have a preferred fit click Label and add a description. Click Repick and remove all the failed models, then print the diagram and hand it in. Note: change cpx or ga in steps and compensate by adding or subtracting opx. It is clearest to keep ga fixed and vary cpx, then fix cpx and vary ga.*

*By using  $F$ 's of 0.3, 0.4, 0.5 for each trial, you will make a grid in La/Sm vs Gd/Yb space, which roughly represents % melt versus % garnet in the source. It is more difficult to fit the data in linear plots, so validate your models using La/Sm vs Gd/Yb plots, but don't be a perfectionist. Ideally, you will bracket the cluster of Purumbete samples. In reality, you may succeed in only bracketing a corner of the data.*

**12F.** *Print a La/Sm vs Gd/Yb diagram that includes your most successful models and some labels.*

If you enjoy this, there are many more options,

Select EM-2 as the source and repeat this exercise.

Use fractional melting rather than aggregated fractional melting.

Use Salters and Strake 6GPa partition coefficients.

Etc.

**12G.** *The JJC model includes the following: "Melting of an enriched region of the mantle within the garnet peridotite stability field is also supported by trace element modeling of Lake Purumbete samples that indicates formation of these melts by extremely low degrees of partial melting (0.005–0.01%) of a garnet lherzolite mantle composition that contained 65 % olivine, 18 % orthopyroxene, 10 % garnet and 7 % clinopyroxene." Do you agree? State your reasons.*

### *References*

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