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89.304 - IGNEOUS & METAMORPHIC PETROLOGY
VARIATION DIAGRAMS

In studying igneous rock series, particularly volcanic rocks, petrologists often make use of variation diagrams to show the changes in rock chemistry with differentiation. These diagrams have two general uses:

1. Descriptive to show and compare the general aspects of chemical variations in and between series.

2. To suggest, from the shape of the curves and their relative trends, the petrogenetic history (evolution) of the rock series.

It is often thought, in fact assumed, that variation diagrams represent the *liquid line-of-descent*, the path of magmatic evolution followed by an evolving liquid. Volcanic rocks, or fine-grained rocks in general, are often considered to represent liquid compositions. Careful work, however, had shown that many rocks believed to represent solidified liquids in fact contain some cumulus minerals. Coarse-grained rocks, particularly of mafic character, most certainly do not represent liquid compositions, although regular chemical variations reflecting changes in the chemistry of the cumulus minerals may be found. In plotting and interpreting variation diagrams it is essential that the petrologist know in detail the mineralogy and texture of the rock samples that were analyzed. The distinction between cumulus and noncumulus rocks is of fundamental importance, and can often best be made on petrographic grounds.

The simplest type of variation diagram is one involving two oxides. The most commonly used diagram of this form is the *Harker diagram* on which the various oxides are plotted versus SiO_2. SiO_2 is used as the *fractionation index* (measure of the evolution of the magma) since it is commonly observed that SiO_2 increases in the successive liquids of fractional crystallization. However, in basaltic rocks SiO_2 may remain relatively constant during the early stages of crystallization if this stage is dominated by the crystallization of pyroxenes and calcic plagioclase which have SiO_2 contents similar to that of basaltic magma. It is usally the onset of crystallization of a SiO_2-phase, such as magnetite, that eventually causes SiO_2 to become enriched in the residual liquid. Once this has happened the continued crystallization of plagioclase and pyroxene will reinforce the SiO_2-enrichment trend. For this reason Harker diagrams tend to be more useful for intermediate to acid rocks.

The *Peacock alkali-lime index* is based on the Harker diagram. For a group of apparently related rocks, Na_2O+K_2O and CaO are plotted versus SiO_2. The index is based on the point, in weight percent SiO_2, at which the Na_2O+K_2O and CaO trends cross.

Group Name	SiO_2 (wt.%)
Calcic	>61
Calcic-alkali	56-61
Alkali-calcic	51-56
Alkalic	<51

Table 1 lists the chemical analyses for a group of volcanic rocks that apparently crystallized from a single magma. Careful petrographic work suggests that these rocks do represent liquid compositions. These data will be used for all the following questions.

Table 1. Chemical analyses for a suite of related volcanic rocks.

wt.%	1	2	3	4	5	6	7	8	9	10
SiO_2	45.51	47.36	48.35	49.00	50.09	52.45	56.17	56.87	61.01	61.22
TiO_2	3.52	3.30	2.82	2.73	2.48	2.29	1.61	1.40	0.68	1.00
Al_2O_3	15.24	16.32	16.01	16.33	16.83	16.09	17.13	16.96	17.14	17.10
Fe_2O_3	3.64	4.64	5.87	2.35	1.65	5.02	2.91	3.88	5.09	2.03
FeO	8.84	6.89	5.37	8.67	8.80	4.19	4.79	3.93	1.21	4.06
Fe_2O_{3t}										
MgO	5.80	4.82	4.30	4.00	3.31	2.67	1.73	1.57	0.76	0.92
CaO	10.40	9.30	9.04	8.70	8.50	7.49	5.20	4.83	3.33	3.28
Na_2O	4.54	4.63	5.32	4.98	5.31	6.11	6.33	6.47	7.07	6.61
K_2O	1.09	1.49	1.14	1.66	1.39	1.64	2.22	2.43	2.87	3.05
P_2O_5	0.20	0.38	0.46	0.54	0.63	0.68	0.73	0.80	0.94	1.00
Norm (%)										
Q	0	0	0	0	0	0	0	0.6	4.1	4.0
Or	6.5	8.9	6.8	9.9	8.3	9.8	13.3	14.5	16.9	18.0
Ab	18.3	26.6	33.3	29.0	33.7	45.9	54.2	55.2	59.8	55.8
Ne	11.1	7.0	6.7	7.4	6.3	3.5	0	0	0	0
ppm										
Rb	10	18	24	28	31	33	37	41	46	50
Sr	500	490	460	460	410	400	360	350	240	200
Ba	200	230	230	250	270	280	270	300	350	320
Ni	250	120	100	50	50	70	70	70	80	90
Sc	25	20	12	12	11	8	7	5	6	5
mg#										
DI										

1. Plot Na_2O+K_2O and CaO versus SiO_2. Draw best-fit straight lines through the two sets of data points. At what SiO_2 concentration do these two trends cross? What is the Peacock alkali-lime index for this group of rocks?

2. Plot MgO and total iron as Fe_2O_{3t} (Fe_2O_3 + FeO/0.9) versus SiO_2. Draw smooth curves through the data points. From the plots of Na_2O+K_2O, CaO, MgO, and Fe_2O_{3t} versus SiO_2, what can you conclude about the magmatic evolution of this group of rocks?

Indices based on the *magnesium-iron (Mg/Fe) ratio* have been widely used and take several different forms. The two most commonly used are $MgO/(MgO+FeO+Fe_2O_3)$ and $Mg^{2+}/(Mg^{2+}+Fe^{2+})$. The latter ratio is referred to as the *magnesium number (mg#)*. Note that these are molecular or atomic ratios. The Mg/Fe index is unaffected by the crystallization of plagioclase and it is useful for the study of cumulate rock sequences affected by crystal sorting. In many basaltic liquids the Mg/Fe ratio falls steadily during the early stages of crystallization because the common ferromagnesian silicate minerals always have higher Mg/Fe ratios than the liquids from which they crystallize.

The Mg/Fe ratio has drawbacks simply because it is a ratio. It is also, like the other indices discussed, fallible in certain circumstances, particulary when the crystallization of ferromagnesian silicates is accompanied by magnetite. When this happens the index either falls much more slowly as crystallization proceeds (and thus becomes and insensitive index of crystallization) or its behavior may be slightly reversed.

3. Calculate the mg# for the various samples. There is space in the data table for your answers. Note that Fe^{2+} in this calculation is total iron expressed as Fe^{2+} (i.e., FeO = $FeO+0.9Fe_2O_3$). Plot TiO_2 and MgO versus mg#. How does the plot for MgO compare to the one you made in Question 2?

In view of the limitations to the previous differentiation indices, attempts have been made to devise more complex indices intended to have a more comprehensive use. Two of these in particular are widely used: the *Solidification Index (DI)* of Kuno and the *Differentiation Index (DI)* of Thornton and Tuttle.

The *Solidification Index* is expressed as

$$SI = \frac{100MgO}{MgO+FeO+Fe_2O_3+Na_2O+K_2O}$$

which, for basaltic rocks rich in MgO and FeO and relatively poor in alkalis, acts much like other forms of the Mg/Fe index. In most magmatic series, however, the residual liquids are enriched in alkalis. The inclusion of Na_2O and K_2O in the index helps offset the potentially poor performance of a solely Mg/Fe index in intermediate and acid suites, particularly when there is little or no iron enrichment relative to magnesium.

The *Differentiation Index* is expressed as

$$DI = normative\ (Q + Or + Ab + Ne + Ks + Lc)$$

This index is based on the simple petrogenetic idea that during differentiation the constituents of *petrogeny's residua system* will become concentrated in the residual liquid since these are the minerals that begin to crystallize, in general, only at low magmatic temperatures. For silica-saturated rocks only Q, Or, and Ab will appear in the norm, whereas the norm for silica-undersaturated rocks may contain any of the normative minerals except Q (quartz).

4. Calculate the DI for the various samples. There is space in the data table for your answers. Plot TiO_2 and MgO versus DI. How do these data plots compare with those from Question 3?

5. Based on the diagrams you have plotted, does any particular index appear to yield superior results? Which index would you routinely use? Defend your selection(s).

Triangular Diagrams. Diagrams showing the simultaneous relative variation of three chemical parameters are widely used and usefully employed in comparative studies of rock suites. Commonly selected parameters are MgO, FeO (FeO+0.9Fe$_2$O$_3$), and Na$_2$O+K$_2$O or Na$_2$O, K$_2$O, and CaO. The values of the three selected parameters are summed, recalculated to total 100, and the results plotted on triangular graph paper.

Triangular diagrams have the disadvantage that they do not show absolute values of the parameters. They are, however, very useful in the illustration of certain features. For example, changes in inter-element ratios, which do not necessarily show up clearly on two-oxide plots, are shown clearly on triangular diagrams. The magnesium-iron-alkali plot (the so-called *AFM diagram*) is, for example, particularly useful in discriminating between tholeiitic and calc-alkaline suites. This is because there is a strong increase in Fe relative to Mg, as alkalis increase, for the tholeiitic suite while a similar trend is only weakly developed in the case of the calc-alkaline suite.

6. If you have access to *PetMin* plot your data on an AFM diagram. Is the resulting trend tholeiitic or calc-alkaline? Representative AFM diagrams for the two suites are found in the textbook.

Indices based on the so-called *incompatible* elements are of considerable theoretical interest and have been used successfully on a number of occasions. An incompatible element is one which is essentially excluded from the crystal structure of the minerals crystallizing from a magma. The elements concentration increases in the magma in a manner simply related to the amount of the original liquid that has crystallized. In the ideal case where the (concentration of element in solid/concentration of element in liquid) approaches zero

$$C = C_o \frac{1}{F}$$

where C_o is the concentration of the element in the original liquid, F is the amount of liquid remaining (expressed as a fraction of 1), and C is the concentration of the element in the remaining liquid. The amount of the liquid that has crystallized at any given time is

$$F = \frac{C_o}{C}$$

To use an incompatible element index we must make two assumptions:

1. All of the rocks that we are investigating have descended from a single definable parent.

2. A mineral has not begun to crystallize that concentrates the incompatible element (i.e., the element is now behaving as a compatible element). For example, as long as apatite is not crystallizing P behaves as an incompatible element and can be used an incompatible element index.

On the variation diagrams, the concentration of P or another incompatible element is plotted on the abscissa. If more than one magma is involved in our rock suite, incompatible element variation diagrams may

be useful in defining separate elemental trends representing the different magmas.

7. Make a plot of Rb (ordinate) versus P_2O_5 (abscissa) for your rock suite. Assume that apatite was not fractionated from the magma so P behaves as an incompatible element. What can you conclude about the behavior of Rb?

Certain trace elements are favored by particular minerals. For example, if olivine, augite, plagioclase, and alkali feldspar were the only minerals that crystallized during the fractionation of a magma, we might expect the following:

1. Removal of olivine leads to Ni depletion because this mineral strongly concentrates Ni.

2. Removal of augite leads to Sc depletion because this mineral concentrates Sc.

3. Removal of plagioclase leads to Sr depletion because this mineral concentrates Sr.

4. Removal of alkali feldspar leads to Ba depletion because this mineral concentrates Ba.

5. With respect to these four minerals, P and Rb behave as incompatible elements.

8. For your rock suite plot Sr, Ba, Ni, and Sc versus P_2O_5. What can you conclude about the crystallization of olivine, augite, plagioclase, and alkali feldspar from the magma which gave rise to this suite of rocks? Be as quantitative as possible in your answers, that is, assuming that P behaves as a perfectly incompatible element estimate the degree of solidification at each point where a mineral starts or stops crystallizing. Sample #1 represents the most primitive magma composition for your suite of rocks.