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Analysis of petrologic hypotheses with Pearce element ratios

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Abstract. Pearce element ratios can test whether the members of a rock suite are comagmatic and can illustrate the causes of chemical diversity in comagmatic suites. Comagmatic rocks have constant ratios for elements conserved in the system during changes that led to the chemical diversity. In basaltic systems, the incompatible elements, Ti, K, and P, are often conserved. The slope of the trend on a Pearce element ratio diagram is sensitive to the stoichiometry of the crystallizing and segregating phases. A judicious choice of ratios as axes for the diagram provides a signature for the phases involved and estimates of their compositions. In basaltic rocks, diagrams with Ti/K vs P/K can provide a test of the comagmatic hypothesis. Diagrams with 0.5 [Mg+Fe]/K vs Si/K have trends that are distinct for each comagmatic suite and different mineral assemblage. Different suites are distinguished by the intercepts in diagrams, whereas mineral assemblages are recognized by the slopes of the trends. For example, if olivine is the sole crystallizing and segregating phase, the trend will have a slope of 1. Diagrams with [2Ca+Na]/K vs Al/K distinguish plagioclase from augite assemblages and, in conjunction with 0.5 [Mg+Fe]/K diagrams, unravel the crystallization sequences of suites that have suffered three phase crystallization and segregation. Analyses from the Uwekahuna laccolith, Kilauea, the 1955 and 1967–68 eruptions of Kilauea, Diamond Craters Volcanic Field, Oregon, and experimental data on MORB glasses provide illustrations of the interpretations that can be obtained from Pearce element ratios.

Introduction

The chemical differentiation of most magmas results from processes operating in the subsurface. Because the processes cannot be observed, both their existence and nature are inferred by analysing cogenetic eruption products. The chemical variations between comagmatic lavas can usually be translated into differences in magmatic origin and process. In particular, the variations in rock chemistry can be used to discriminate between differentiation processes such as crystallization, assimilation, and magma mixing or to ascertain the specific mineral phases and compositions that were involved in the differentiation. It is important therefore, to be able to portray significant differences in chemistry between individual analyses or suites of analyses.

The work of Pearce (1968, 1970) introduced a new and improved method for the representation of chemical data in variation diagrams. His element ratio diagrams have the ability to discriminate between rival petrologic hypotheses which are inseparable in other kinds of variation diagrams. Although his papers adequately introduced the method and graphically demonstrated the power of these diagrams, they have received limited use in petrology. Exceptions are Syme and Forester (1977), Beswick (1982), Nicholls et al. (1986) and Russell and Nicholls (1987).

In this paper we explore several petrologic problems that illustrate the power of Pearce element ratios in testing specific petrologic hypotheses. These examples will demonstrate that Pearce element diagrams yield insights into igneous processes that are not obvious or quantitatively expressed when portrayed on other variation diagrams. In other variation diagrams many petrologic hypotheses cannot be rejected, whereas in Pearce element ratio diagrams few hypotheses can be accepted. Presumably these few hypotheses contain the correct process.

Pearce element ratios

Pearce element ratios are most effective for studying systems that change in amount during physical-chemical processes. The most important attribute of Pearce element ratios is the presence of a conserved constituent in the denominator. There must be one constituent whose amount does not change during the process in order for the system change to be accurately portrayed (Pearce 1968). The unchanging constituent is a conserved one (Nicholls 1988).

There are two problems associated with the analysis of data on oxide-oxide wt.% variation diagrams. First, data in wt.% format is not easily related to mineral formulae or compositions. For example to determine the wt.% CaO in stoichiometric diopside requires a simple but tedious calculation (25.9 wt.%). The problem is exacerbated by non-stoichiometry and solid solution whereas, the molecular or atomic proportions of Ca:Si is readily ascertained to be 1:2 for diopside-hedenbergite pyroxenes. Second, the wt.% oxide data suffer from the constant sum effect (Chayes 1964; 1971; Skala 1979; Aitchison 1981; 1984) and further suffer in that a large part of the variance resides in the denominator (sum of the wt. fractions). Consequently, the variables are correlated and the constant sum may create enhanced positive or negative correlations between oxide components. This raises the problem of interpreting the relationships between various oxides. The question is: How much of the element's variation is due to closure and how

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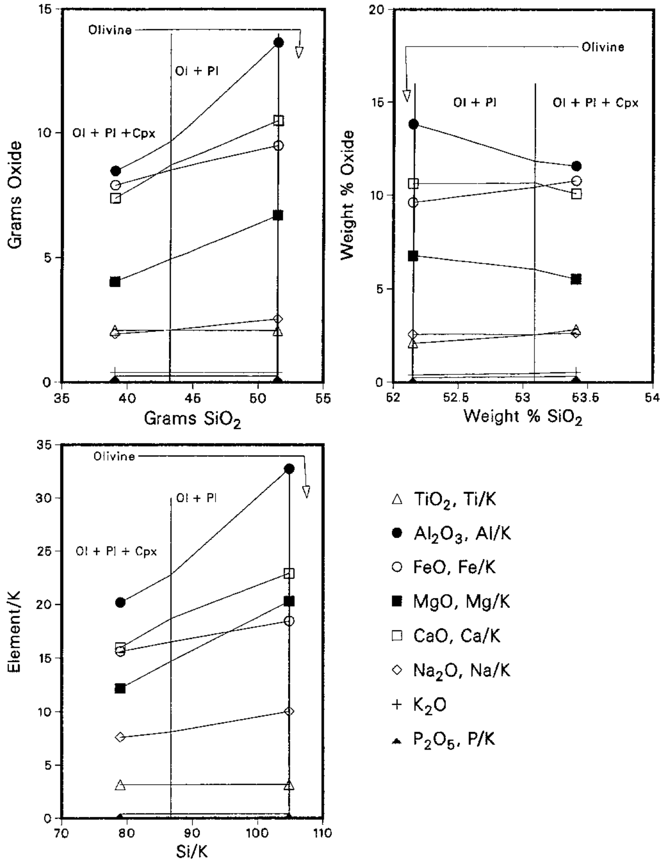

Fig. 1 a–c. Variation diagrams for the crystallization of 100 grams of the 1984 Mauna Loa magma. **a** grams of oxide vs grams of SiO_2, **b** wt.% oxide vs wt.% SiO_2, **c** Pearce element ratios plotted against Si/K

much has arisen through the magmatic process? The effect of closure on compositional trends is illustrated in Fig. 1. We have modeled the crystallization of 100 grams of a Mauna Loa lava. The residual liquid compositions that result from 20% crystallization of olivine, olivine + plagioclase, and olivine + plagioclase + clinopyroxene are plotted in terms of extensive variables (grams), intensive variables (wt.%), and Pearce element ratios. Figure 1a illustrates the true variation of the oxides with increasing crystallization. The grams of the oxides remaining in the residual melt are plotted against the grams of SiO_2 in the melt. The absolute amounts of each oxide except the conserved ones (e.g. K_2O), decrease with crystallization as we expect. The absolute variation in oxide constituents is accurately portrayed in this diagram. If we had this information about a natural system we would be able to unravel igneous processes exactly.

However, chemical analyses of rock compositions are reported as weight percentages. Figure 1b illustrates the same data transformed into a weight percent basis. The significance of variations of these oxides is no longer straight forward. In fact, some of the apparent inter-oxide relationships illustrated in Fig. 1b are opposite to the known relationships (e.g. Al_2O_3). Once the data are in a weight percent basis, the elemental variations due to crystallization are no longer apparent and the absolute relationships of the masses are lost and not recoverable. Therefore the interpretation of geochemical variations in terms of specific minerals becomes complicated. Pearce element ratios preserve information related to variations in absolute units. This relationship is apparent on Fig. 1a–c. Pearce element ratio diagrams ensure that the true elemental variations are represented whether expressed against other element ratios or a physical dimension (see below).

The element ratios are calculated in two steps. All wt.% oxides are first converted to the element fractions, e_i, by:

$$e_i = W_i A_i / MW_i \tag{1}$$

where W_i, A_i and MW_i are the wt. percentages, the number of cations in the oxide formula and the molecular weight of oxide i. The Pearce element ratio of element i is:

$$r_i = e_i / e_z \tag{2}$$

where z is a conserved element.

The means to determine an appropriate conserved element are discussed by Nicholls (1988). We can test whether both elements of a pair are conserved by comparing the variance of the ratio in the data with the uncertainty expected from analytical error (Nicholls 1988; see appendix A). This concept is critical to the recognition of cogenetic rock suites. Ratios calculated from conserved element concentrations remain constant throughout the process. Ratios with elements in the numerator that are involved in the process will vary according to their stoichiometry in the separated phases. This stoichiometry is represented in the slopes of chemical trends on Pearce element diagrams and provides the signature by which the phases involved can be identified. For example, olivine has a cation to silica ratio of 2 and would define a slope of 1 in a diagram with axes $Y = 0.5$ $[Mg + Fe]/n$, $X = Si/n$, where n is a conserved element. Slopes intermediate between those expected for end members of a solid solution series provide an estimate of the composition of the solid solution. Consequently, the whole rock chemistry can be precisely interpreted in terms of the modes and chemistry of the participating phases.

Recognition of comagmatic lavas

Discussion of a suite of rock analyses in terms of magmatic differentiation, implies that the compositions are derived from a single lineage. Usually the assumption of a comagmatic relationship is taken a priori. Pearce element ratios can be used to test this primary premise. If we cannot reject the comagmatic hypothesis then the suite deserves further scrutiny. Conversely, rejecting the hypothesis indicates a more complex history. The hypothesis testing is carried out by using ratios of conserved elements. The choice of element ratios will vary depending on the composition of the system being investigated. As our examples are basaltic, K, P, and Ti remain conserved for a significant period of the crystallization history. Figure 2 is an example of how Ti/K and P/K can be used to test the comagmatic hypothesis. If these elements remain incompatible with respect to differentiation, comagmatic rocks will define a tight cluster. Ideally, they would plot as a point.

Two sets of data are plotted in Fig. 2. Analyses of Uwekahuna laccolith (Kilauea Volcano, Hawaii) (solid circles) define a single cluster whose dispersion is less than expected from analytical error. The data plotted as squares and open circles are from the 1967–68 eruption of Kilauea volcano (Jackson et al. 1975, Wright et al. 1975). Included in these

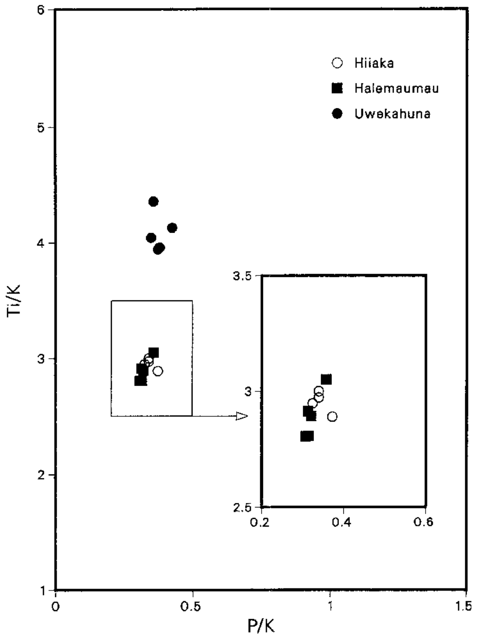

Fig. 2. Two suites of data are plotted in terms of ratios of elements that are conserved during basalt crystallization. Basaltic rocks that are comagmatic will plot as a tight cluster. Dispersion of data in this diagram would imply that the analyses are not from comagmatic rocks or that at least one of the elements was not conserved. The *filled circles* are data from the Uwekahuna laccolith (Murata and Richter 1961). The remainder of analyses are from the 1967–68 eruptions of Kilauea Volcano, at Hiiaka Crater (*open circles*) and Halemaumau Crater (*squares*)

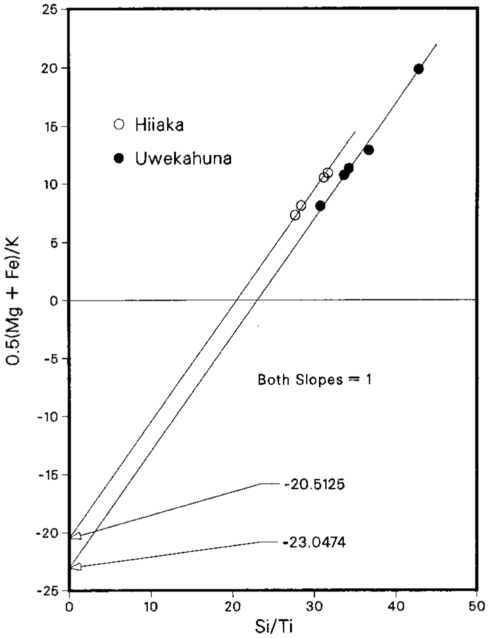

Fig. 3. The data from Uwekahuna laccolith and Hiiaka Crater are plotted in the Pearce variation diagram that uses the olivine indices. Both suites of data are adequately explained by the removal or addition of olivine. Different magmatic lineages undergoing the same differentiation process will define identical slopes but yield different intercepts. The intercepts are a trait of the initial magma

analyses are MgO-rich picrites erupted at Hiiaka Crater (open circles) and basalts from the summit eruption at Halemaumau Crater (squares). These analyses define a cluster that is distinct from the Uwekahuna data and also show less variation than expected from analytical error. The incompatible element plot demonstrates several points clearly. The Uwekahuna rocks are consistent with the comagmatic hypothesis and are chemically distinct from other lavas which have also undergone olivine fractionation (e.g., Halemaumau and Hiiaka suites). The similarity in incompatible ratios betwen the Hiiaka and Halemaumau lavas ensures that the lavas could represent differentiation products of a single magma. The data for the two suites from Kilauea Volcano justify further research into the nature of the differentiation processes that produced the chemical variations.

We can also discriminate between magmatic lineages using other Pearce element ratio diagrams. The Hiiaka Crater and Uwekahuna laccolith analyses are plotted in Fig. 3. Compositions related through olivine separation or accumulation will lie along a trend with a slope of 1.0 in this diagram. Both data sets are consistent with the predicted olivine slope. Notice that although the two slopes are the same, the intercepts are distinct. The intercepts are a function of the initial magma chemistry. Hence different magma batches subject to the same differentiation process can still be distinguished on the basis of Pearce element diagrams.

Dispersion of element ratios or dispersion of the intercept (Nicholls 1988) implies that at least one of the elements is not conserved. If *no* element is conserved, one or more of the following must be true:

i) the chemical variation has resulted, at least in part, from diffusional processes (e.g. the Soret effect).
ii) the system has been affected by an influx of foreign material (e.g. assimilation or mixing of non-cogenetic magmas).
iii) the rocks did not form from comagmatic parents (e.g. an inhomogeneous source region).
iv) differentiation has affected all of the elements (e.g. fractionation of amphibole, apatite, and Fe-Ti oxides).

It is easier to constrain hypotheses about the origin of rocks that pass the comagmatic test; there are no longer an infinite number of possibilities. On the other hand, suites that are not comagmatic have poorly constrained origins because petrologic methods used to solve the problem have more degrees of freedom to restrict. For example, mass balance calculations for non-comagmatic rocks can never be secure because there is not a unique liquid line of descent and postulated parental compositions are difficult to define. Hence, calculated mass changes remain speculative, regardless of the goodness-of-fit.

Similarly, Pearce element ratios comprising conserved elements restrict hypotheses about the cause of compositional hiatuses, such as the *Daly Gap*. If the end members on either side of the hiatus are shown to be comagmatic, then the missing intermediate products probably did not erupt. Otherwise, it is possible that the missing intermediate members never formed.

Uwekahuna laccolith – olivine settling

The Uwekahuna laccolith has been cited as an example of a rock body with chemical variations caused by olivine settling (Murata

Table 1. Results of least squares regressions of data from Uwekahuna laccolith. A) $X = Si/Ti$; $Y = 0.5[Mg + Fe]/Ti$ and B) $X = Fe/Ti$; $Y = Mg/Ti$. The calculated parameters (M and b) are reported with 1σ uncertainties. R is the Pearson correlation coefficient (York 1966)

Data	X	Y	M	b	R^2
A	Si/Ti	0.5[Mg+Fe]/Ti	0.976 ±0.041	−22.181 ±0.685	0.995
B	Fe/Ti	Mg/Ti	4.940 ±0.058	−16.339 ±0.393	0.999

Table 2. Whole rock data for the Uwekahuna Laccolith (Murata and Richter 1961). The FeO and Fe_2O_3 are calculated for QFM buffer at 1200° C (Kilinc et al. 1983). Also reported are the Pearce element ratios n/Ti

Sample No. Height (ft)	1 0.0	2 3.0	4 10.5	5 23.5	6 28
SiO_2	48.37	48.25	46.32	48.56	49.50
TiO_2	1.88	1.75	1.44	1.92	2.14
Al_2O_3	11.19	10.72	8.58	11.62	12.67
Fe_2O_3	1.17	1.08	0.99	1.17	1.28
FeO	10.12	10.23	11.30	9.87	9.34
MnO	0.17	0.17	0.17	0.16	0.16
MgO	15.16	16.45	21.98	14.65	11.55
CaO	8.94	8.79	7.11	9.36	10.05
Na_2O	1.76	1.61	1.28	1.74	1.99
K_2O	0.28	0.25	0.21	0.26	0.32
P_2O_5	0.16	0.16	0.11	0.14	0.18
Si/Ti	34.213	36.664	42.774	33.632	30.759
Al/Ti	9.328	9.600	9.338	9.485	9.279
Fe/Ti	6.609	7.118	9.415	6.326	5.452
Mn/Ti	0.102	0.109	0.133	0.094	0.084
Mg/Ti	16.088	18.632	30.254	15.123	10.697
Ca/Ti	6.775	7.156	7.035	6.945	6.691
Na/Ti	2.414	2.372	2.292	2.337	2.397
K/Ti	0.253	0.242	0.247	0.230	0.254
P/Ti	0.096	0.103	0.086	0.082	0.095

and Richter 1961). We use this example to demonstrate how easily such hypotheses can be tested with Pearce element ratios. The data on the Uwekahuna laccolith are summarized in Table 2 and Fig. 4. The five rock analyses were taken from a single 28 foot vertical section across the sill. The wt.% FeO and Fe_2O_3 have been recalculated for the QFM oxygen buffer at 1200° C (Kilinc et al. 1983) to remove the effects of secondary oxidation. All samples contain variable quantities of phenocrystic olivine. The olivine phenocrysts are described as 4–5 mm in diameter, with a composition of Fo_{85} (a single wet chemical analysis). The modal abundance of olivine across the sill is illustrated in Fig. 4 and attests to the effects of crystal sorting. Figure 4 also demonstrates the parallel variation in rock chemistry. The wt.% oxides plotted as a function of position show relative increases and decreases in concentration that are consistent with olivine accumulation and loss. MgO and FeO increase with their maximum concentrations coinciding with the highest modal olivine. On the other hand CaO, Al_2O_3 and SiO_2 all show concentration decreases. In the case of the Uwekahuna laccolith the variations in CaO, Al_2O_3 and SiO_2 are sympathetic. Without the field and petrographic data the interpretation of Fig. 4 is ambiguous. Given only a table of data, one could interpret the variations of CaO, Al_2O_3 and SiO_2 as a consequence of MgO and FeO increase or as a response to clinopyroxene and plagioclase segregation. The cause of the MgO and FeO distribution in a more complex rock suite will be uncertain as well. Pearce ratios remove this ambiguity.

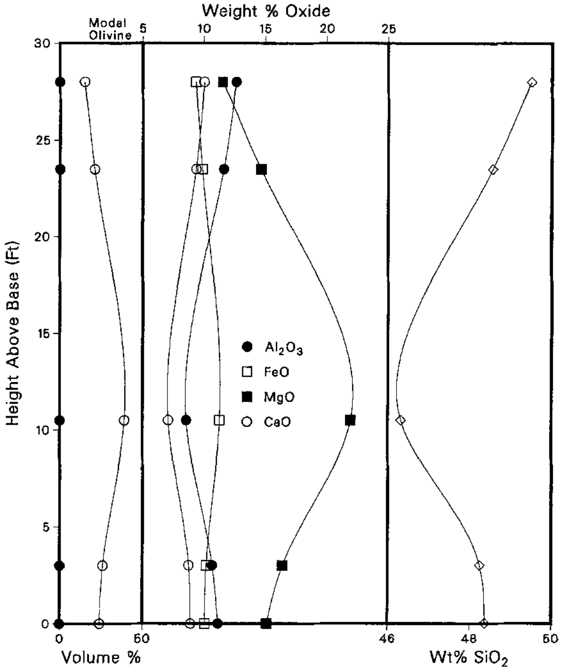

Fig. 4. The data reported by Murata and Richter (1961), including volume% olivine and wt.% oxides as a function of distance above the base of the Uwekahuna laccolith

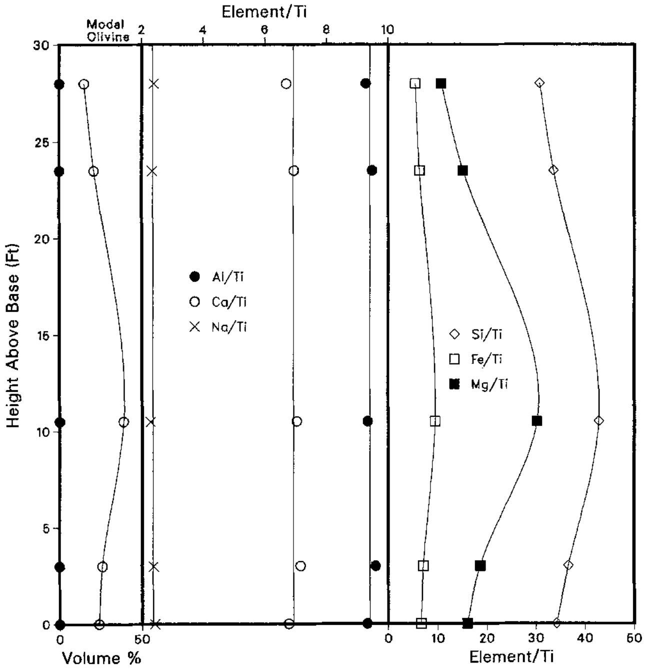

Fig. 5. Pearce element ratio representation of the same data plotted in Figure 4. The element ratios employ Ti as the denominator. The true variations of the remaining elements are illustrated as a function of position. As expected from olivine separation, the elements Mg, Fe, and Si vary while all other elements (Ca, Al, Na etc.) are constant and were not involved in the differentiation process (see text and Table 3)

A plot analogous to Fig. 4 that employs Pearce element ratios is illustrated in Fig. 5. The element ratios were constructed using Ti as the denominator because it is one of the elements independent of the olivine crystallization and settling. Any element that behaves incompatibly during such processes would work equally well. The

Table 3. Results of least squares linear regression of Uwekahuna laccolith data. *X* is distance (feet) and *Y* is the element ratio *n*/Ti. The estimated slope (*M*) and standard error (S.D.) are listed for each element that is expected to be conserved

n/Ti	*M*	S.D.
Al	−0.0030	0.0046
Mn	−0.0008	0.0006
Ca	−0.0065	0.0062
Na	−0.0006	0.0018
K	−0.0002	0.0003
P	−0.0003	0.0003

Pearce element ratios in Fig. 5 illustrate the actual variations of the elements across the sill. The element ratios fall into one of two categories; those ratios that have a constant value across the sill and those ratios which vary with position. Any element ratio comprised of conserved elements will define a straight line when plotted against height (Na/Ti, Al/Ti etc.). If the element ratio does not define a vertical line in Fig. 5, then one of the following could be true:

a) the analyses being examined are not comagmatic. The presence of several constant ratios is evidence that the rocks from Uwekahuna are comagmatic.

b) the denominator element (Ti) is not independent of the process being investigated. Ti is a conserved element because several ratios are constant.

c) the element in the numerator is involved in the differentiation of the magma. Ratios that vary will provide information on the phases that were involved in the differentiation of the rock body.

Figure 5 shows that there are no variations in the absolute amounts of Al, Mn, Ca, K, and P across the sill. The least squares linear regressions of the Uwekahuna element ratio data ($Y = n/\mathrm{Ti}$) against position (X) are reported in Table 3. The slopes of the regressions for the conserved element ratios are all close to zero. We cannot reject the hypothesis that the calculated slopes (M_n) of the regressions for Al, Mn, Ca, K, and P are equal to the predicted slope ($M^* = 0.0$) at the 95% confidence level (Student's *t* test). This guarantees that these elements and Ti are independent of the differentiation of the Uwekahuna laccolith.

Figure 5 shows the true variation in elements that were affected by olivine settling. Variations in Mg/Ti, Fe/Ti and Si/Ti parallel the observed increase in modal olivine. We expect and observe that ratios with these three elements in the numerator increase in response to olivine accumulation. Because of the stoichiometry of olivine, the changes in Mg/Ti and Fe/Ti together should equal 2 times the changes in Si/Ti.

Testing the settling hypothesis

The Uwekahuna laccolith provides an excellent example to demonstrate the ability of element ratios to discriminate between rival petrologic hypotheses. We wish to determine: 1) whether the whole rock chemistry of the sill is consistent with a single magma undergoing differentiation through olivine segregation and 2) whether the process of differentiation is by the accumulation or loss of the observed olivine phenocrysts (Fo_{85}). Theory predicts that the derived rock compositions that result from the equilibrium crystallization, fractional crystallization or the crystal accumulation of olivine must be different (e.g. Nicholls et al. 1986). Presumably the data will fit one hypothesis better than the others.

Figure 5 is consistent with the elements Mg, Fe and Si alone being involved in the differentiation process. In addition to olivine, these elements are sensitive to the stoichiometry of Ca-poor pyroxene. It may have been involved in the differentiation process in addition to or in place of olivine. The Pearce element ratio diagram discriminates between olivine, orthopyroxene, olivine + orthopyroxene or olivine + another phase acting in the differentiation process because the axes can be chosen to display the element stoichiometry of specific phases. A similar approach in Harker space would require us to ascertain the weight proportions of CaO, MgO, FeO, and SiO_2 in all compositions of olivine, augite, etc.

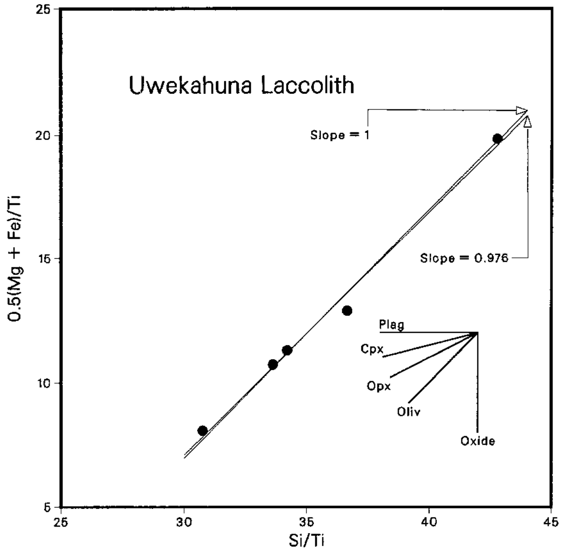

Fig. 6. Uwekahuna compositions plotted on a Pearce element ratio diagram to test for the effects of olivine *controlled* differentiation. Compositions that are consistent with the olivine hypothesis define a slope of 1.0. The calculated regression has a slope of 0.976 which is not different from 1.0 at the 95% confidence level

Bearing this in mind, it is evident that selecting 0.5 [Mg + Fe]/Ti as the Y-axis and Si/Ti as the X-axis will ensure that chemical compositions that are related solely by the addition or subtraction of olivine will define a slope of 1.0. The addition of any other phase that contains Mg, Fe or Si will cause the data to deviate from this slope of 1.0. For example, Ca-poor pyroxene has a slope of 0.5 in this space while the slopes for plagioclase and augite fractionation are 0.0 and 0.25 respectively. Hence the effects of any of these phases will cause a shallower slope than 1.0. The separation of a phase that does not contain any of the elements Mg, Fe, and Si will not affect this diagram. This theoretical slope is unique to the mineral olivine and will not change with the amount of olivine involved nor with the composition of the olivine. Initially, it may look as if we are losing information. However any information that is lost by ignoring solid solution is recovered by choosing other axes (see below). At this point, the primary question concerns the identity of the separating phase.

The olivine index 0.5 [Mg + Fe]/Ti vs Si/Ti is plotted in Fig. 6 and the data have been fit to a straight line by least squares linear regression (Russell 1986). The calculated slope ($M = 0.976$) is indistinguishable from the predicted slope ($M^* = 1.0$) at the 95% confidence level (Table 1). Therefore the whole rock chemical variation observed in the sill is consistent with olivine sorting.

While Figs. 5 and 6 guarantee that the rock compositions are explained by olivine segregation, the actual process has not been determined. Are the Uwekahuna rock analyses

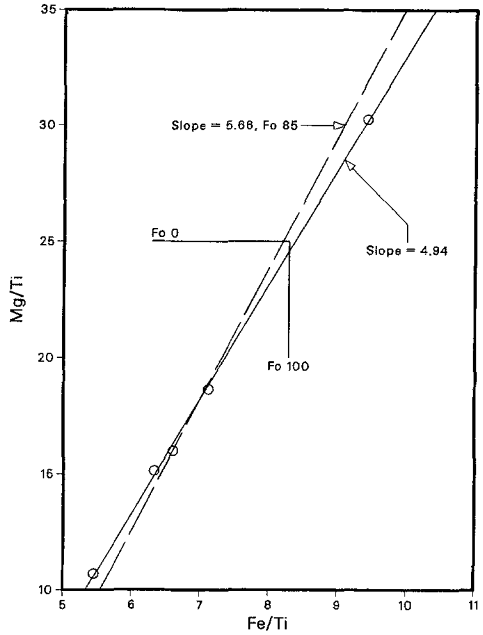

Fig. 7. The composition of olivine involved in the differentiation of the Uwekahuna laccolith is ascertained with the element ratios Mg/Ti and Fe/Ti. The best fit linear regression for the natural data is plotted with a solid line ($M = 4.94$). The appropriate slope for compositions related by Fo_{85} is illustrated with the broken line ($M^* = 5.66$). See text

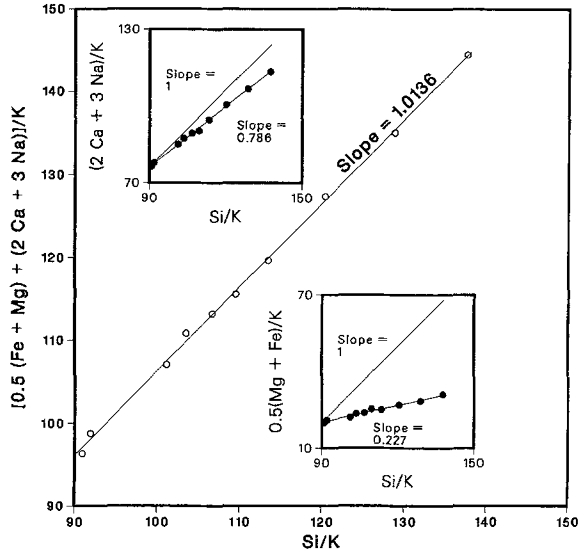

Fig. 8. The Diamond Craters basalts. Test of whether the chemistry is consistent with differentiation by crystal separation of olivine (*inset*) or plagioclase (*inset*) or both. The basalt chemistry defines straight line trends for either mineral index, however, slopes are inconsistent with individual mineral segragation

consistent with the products of olivine accumulation, fractional or equilibrium crystallization, or combinations of these end-member processes? We expect that the analyses can be explained by the gravitative settling of olivine (Murata and Richter 1961). If the range of rock compositions resulted from the separation of olivine, then the variation of Mg/Ti vs Fe/Ti will relate to the olivine composition. A diagram with the axes Mg/Ti and Fe/Ti has the attribute that each olivine composition generates a unique slope. In Fig. 7, rock compositions related by different amounts of forsterite will define a vertical line. Fayalite will generate a line with a slope equal to zero. Every intermediate composition of olivine has a constant slope between zero and infinity. If the Uwekahuna rocks are related by crystal sorting (accumulation or loss of unzoned olivine phenocrysts) the rock compositions will define a straight line in this Pearce element ratio diagram. The slope of this linear trend will reflect the olivine composition. On the other hand if the rocks resulted through fractional or equilibrium crystallization, a curvilinear trend must result. The curve would reflect the variable olivine compositions generated down the crystallization path and the slope of the tangent to such a curve would yield the equilibrium or instantaneous olivine composition.

There are two points to evaluate. The first is whether the data adequately define a straight line and second, whether the slope of the linear regression fits the model slope for Fo_{85} accumulation or loss. The results of the linear regression are listed in Table 1. Based on a χ^2 test, the results are consistent with a straight line model at the 95% confidence level. The slope of a straight line generated by the loss or gain of Fo_{85} will be 5.66 (see Table 5). A broken line with this slope is drawn to pass through the intermediate composition of the Uwekahuna analyses. The solid line is the calculated linear regression curve. Its slope and standard error (4.94 ± 0.06) is consistent with an olivine composition of Fo_{83}. Based on Student's t statistic the calculated slope is different from the theoretical slope at the 95% confidence level. These results are consistent with olivine accumulation but the rock analyses suggest that Fo_{83} rather than Fo_{85} is a more appropriate composition for the settling phase. This discrepancy could arise from analytical uncertainty in olivine analysis or small inhomogeneities due to olivine zoning. These possibilities could be evaluated by electron microprobe study.

Crystal sorting of two phases

Quaternary basalt lavas at outcrop at the Diamond Craters volcanic field in S.E. Oregon, have glomerocrysts and microphenocrysts of olivine and plagioclase (Russell and Nicholls 1987). The lavas are thought to be comagmatic as they were erupted over a short period of time, share the same phenocryst assemblage, and exhibit a narrow range of whole rock chemistry. The petrography, whole rock chemistry and thermodynamic modeling suggest that compositional variations between lavas may be explained by crystal sorting of one or both phenocrysts. Pearce element ratio diagrams discriminate between the three rival hypotheses: gain or loss of olivine, gain or loss of plagioclase, gain or loss of both. As with the Uwekahuna sill the first hypothesis is easily tested by plotting the olivine indices, thereby guaranteeing that rocks which are cogenetic and related solely by olivine separation will define a straight line with a slope of 1.0. The denominator can be any element which is conserved during olivine or plagioclase crystallization (e.g. Ti, K, P). The Diamond Craters basalts are plotted with K in the denominator (Fig. 8: inset). The

Table 4. Summary of least squares linear regressions performed on Diamond Craters lavas (Russell and Nicholls 1987). All variables (Y/n) are regressed against Si/n, where n is one of the elements K, Ti or P. Estimated slopes (M) and intercepts (b) are reported with 1σ standard errors

Y/n		Si/K	Si/Ti	Si/P	Theoretical slope
0.5(Mg+Fe)	$M\pm$	0.227 ± 0.009	0.237 ± 0.022	0.224 ± 0.100	Olivine=1.0
	$b\pm$	-0.369 ± 0.531	-0.632 ± 0.526	0.139 ± 1.151	
	R^2	0.992	0.960	0.991	
2Ca+3Na	$M\pm$	0.786 ± 0.010	0.759 ± 0.034	0.801 ± 0.150	Plagioclase=1.0
	$b\pm$	5.294 ± 0.594	3.788 ± 0.825	8.622 ± 1.827	
	R^2	0.999	0.990	0.998	
0.5(Mg+Fe)+2Ca+3Na	$M\pm$	1.014 ± 0.012	0.996 ± 0.038	1.024 ± 0.016	Olivine+Plagioclase=1.0
	$b\pm$	4.923 ± 0.683	3.125 ± 0.923	8.778 ± 1.905	
	R^2	0.999	0.993	0.999	
1.5Ca+(Mg+Fe)	$M\pm$	0.632 ± 0.080	0.664 ± 0.026	0.616 ± 0.130	Olivine+Clinopyroxene=1.0
	$b\pm$	-4.710 ± 0.450	-3.729 ± 0.625	-6.824 ± 0.1557	
	R^2	0.999	0.993	0.998	

least squares linear regression of the data produces an excellent fit ($R=0.9920$, Table 4). However, the calculated slope ($M=0.227$) is considerably less than 1.0. Therefore we reject the hypothesis: *Olivine sorting alone can explain the chemical variation of these lavas.*

Similar arguments can be used to demonstrate that plagioclase alone cannot reproduce the chemical variations in the Diamond Craters lavas (Fig. 8 and Table 4). The Pearce element ratio plot (X-Si/n and $Y=[2\text{Ca}+3\text{Na})/n$) guarantees that rocks related solely by the separation of plagioclase will generate a slope of 1.0. The Diamond Craters lavas plotted in Figure 8 fit a straight line model but the slope ($M=0.786$) is inconsistent with the process of plagioclase segregation. A more logical hypothesis based on the petrography of the rocks is that olivine and plagioclase are both involved in the process. The combined index, $[0.5(\text{Mg}+\text{Fe})+2\text{Ca}+3\text{Na}]/n$ vs Si/n, requires that rocks related by gain or loss of olivine and plagioclase define a slope of 1.0. Figure 8 and the data in Table 4 are consistent with the hypothesis: *The Diamond Craters lavas can be interpreted as comagmatic and related through the removal or addition of plagioclase and olivine.*

The linear relationship in Figure 8 is not affected by changes in phase chemistry or proportions. This diagram can be employed with rock suites that have undergone an extended period of crystallization where compositions and proportions of phases are changing continuously. Such rocks could result from equilibrium or fractional crystallization or by the mechanical segregation of phenocrysts. The linear regressions for olivine alone and plagioclase alone (Fig. 8) combine to give the requisite slope of 1.0. The ratios of the slopes should be equal to the proportions of the phases involved. In the Diamond Craters example, the plagioclase regression produced a slope much closer to 1 than did the olivine regression. This suggests that plagioclase dominated olivine in the phenocryst assemblage which is in agreement with the observed ratio in the lavas (1.5, Russell and Nicholls 1987).

These least squares linear regressions utilize K as the conserved element which was chosen because of our knowledge of the phenocryst chemistry. P and Ti are two other conserved elements that could have been used. The intercepts that result from using these elements in the denominator are different but the slopes remain the same. This is shown in Table 4. As the slope is the parameter which characterizes the segregated phases, our interpretations will remain the same regardless of which conserved element is used in the Pearce ratio.

The chemical variations in the phenocrysts should be evident in the chemistry of the lavas. The axes, 2 Na/K vs Al/K, portray the chemical variation in plagioclase composition (Fig. 9). Gain or loss of anorthite will generate a horizontal trend, whereas albite will generate a slope of 2. Intermediate plagioclases will generate intermediate slopes (Table 5), such that the composition of the separated plagioclase is related to the slope (M) by:

$$X_{\text{Ab}}=2M/(2+M) \tag{3}$$

The range of plagioclase phenocryst compositions, including the most An-rich groundmass ($\text{An}_{74}-\text{An}_{67}$) is represented by the region within the two solid lines. The band originates at the most aluminous Diamond Craters lava. The fact that the lavas plot within this field is consistent with the conclusion that crystal sorting and accumulation generated the chemical variations of the lavas. Evidently,

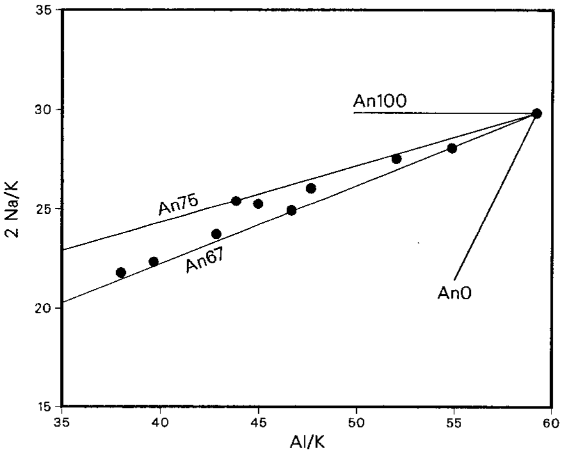

Fig. 9. The range in plagioclase compositions in the differentiation of the Oregon lavas is estimated by plotting 2Na/K vs Al/K. The slope of any straight line in this diagram is equal to $2X_{\text{Ab}}/(2\text{-}X_{\text{Ab}})$ (Table 5). The *solid lines* represent the bounds on the phenocryst compositions observed in the Diamond Craters lavas. The region includes all of the observed lavas, save one

Table 5. Summary of Pearce element ratios used in the evaluation of petrologic hypotheses. Element n is a conserved constituent. Element ratios are combined to test: one (1), two (2) and three (3) phase segregation and to estimate mineral compositions (4)

	Phase(s)	X/n	Y/n	M: expected	Other Phases
1	OL	0.5(Mg+Fe)	Si	OL=1.0	CPX=0.25; PL=0.0
	PL	2Na+Al	Si	PL=1.0	CPX=OL=0.0
	CPX	2Ca+Na-Al	Si	CPX=1.0	PL=OL=0.0
2	OL+PL	0.5(Mg+Fe)+2Ca+3Na	Si	OL+PL=1.0	±CPX>1.0
	PL+CPX	2Ca+3Na	Si	PL+CPX=1.0	±OL<1.0
	OL+CPX	0.5(Mg+Fe)+1.5Ca	Si	OL+CPX=1.0	±PL<1.0
3	PL	2Ca+Na	Al	CPX=∞	±OL=no effect
	CPX			PL=1.0	
				[CPX+PL]/PL=M	
4	OL	Fe	Mg	Fo=En=Di=∞	$M=X_{Mg}/X_{Fe}$
	PYROX			Fa=Fs=Hd=0.0	
	PL	2Na	Al	An=0.0	$M=2X_{Ab}/(2\text{-}X_{Ab})$
				Ab=2.0	

it is possible to infer something about phase chemistry from the variations in the whole rock chemistry.

Testing for the third phase

The slopes on Pearce element ratio diagrams reflect the stoichiometry of the minerals. If three phases form, the slopes combine and it is difficult to separate the effects of three phases on a two dimensional diagram. This problem is circumvented in part, by selecting axes that reduce the effects of at least one phase to a single point. One factor to consider is whether the element selected as a conserved constituent can be expected to remain so. The risk of an element losing its conserved status increases as the number of crystallizing phases increase. For example, if Fe-Ti oxides fractionate or accumulate, Ti is no longer conserved. Many basalts crystallize olivine, clinopyroxene and plagioclase as phenocrysts. The following example illustrates how Pearce element ratios test whether compositions are consistent with crystallization of one, two, or all three of these phases. The approch provides a means of evaluating i) whether clinopyroxene was involved in the process, ii) the molar proportion and clinopyroxene fractionated relative to plagioclase, and iii) the composition of the melt when the second and third phases began to crystallize.

Experimental MORB compositions

Our first example is part of a series of 1 atm. melting experiments on the phase relations of several MORB glasses (Grove and Bryan 1983). In their experiments a crystallization sequence of olivine, olivine+plagioclase, and olivine+plagioclase+clinopyroxene was generated (AII-96-6-42, starting material). Grove and Bryan (1983) provide electron microprobe analyses for the glasses representing the residual melt compositions. Our question is: Can the crystallization history of the sample be unambiguously reconstructed from the glass compositions? A Harker diagram (Fig. 10a) illustrates the range in glass chemistry. Figure 10b is the diagram from which we can reconstruct the crystallization history. The experiments that produced glass, glass+olivine or glass+olivine+plagioclase are plotted as dots and the experiments that produced glass+olivine+plagioclase+clinopyroxene are plotted as squares. The scatter in the data probably reflects the difficulty of accurately analysing silicate glasses from experimental charges. The smooth, curvilinear trends evident in the Harker diagram suggest that the glass data are related by a simple process but provide little indication of what phases crystallized, what was the order of crystallization, nor what were the compositions of the phases.

The Pearce element ratio diagram has Ti in the denominator because Ti is conserved throughout the crystallization

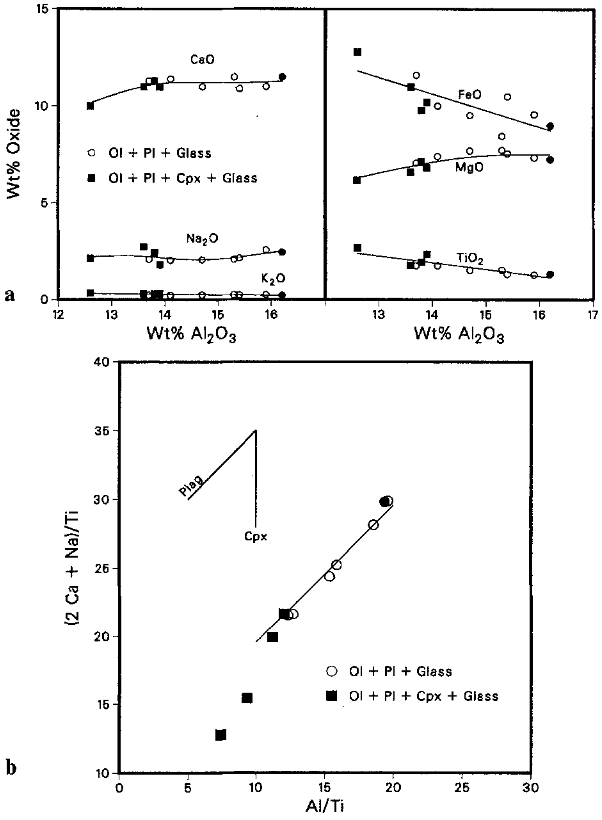

Fig. 10a, b. The electron microprobe glass analyses of Grove and Bryan (1983). **a** (*Top*) Harker diagram **b** (*Bottom*) Pearce element ratio diagram. Assemblages are glass, glass+olivine, or glass+olivine+plagioclase (*circles*) and glass+olivine+plagioclase+clinopyroxene (*squares*). Starting composition shown by *filled circle*

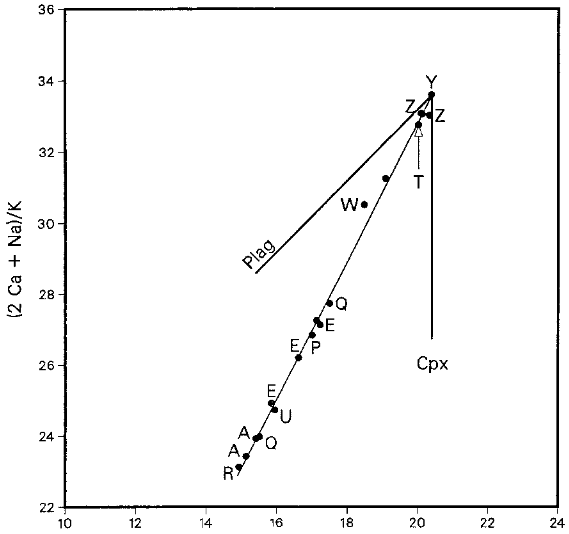

Fig. 11. The 1955 Kilauea lavas (Wright and Fiske 1971). The labels A–Z refer to the relative chronology of the eruptions (*A*: early, *Z*: late)

sequence and is one of the more precisely analysed elements in silicate glasses. A diagram with $X = \mathrm{Al/Ti}$ vs $Y = [2\mathrm{Ca} + \mathrm{Na}]/\mathrm{Ti}$ has the attribute that compositions related by olivine or orthopyroxene fractionation will plot as a single point. The effects of these phases are eliminated from this diagram. Consequently, the effects of plagioclase and clinopyroxene fractionation can be seen. If an element other than Ti (e.g. K or P) was selected as the conserved element, then the effects of Fe-Ti oxide fractionation would also be eliminated. Fractionation or accumulation of clinopyroxene with or without olivine, orthopyroxene, etc. will define a vertical trend. Rock compositions related through plagioclase fractionation will define a slope of 1. Therefore magmatic lineages that involve plagioclase or clinopyroxene will define very different trends on this diagram. Chemical compositions that result from both plagioclase and clinopyroxene crystallization will define trends with slopes between 1 and infinity.

The experiments that resulted in charges with glass, glass + olivine or glass + olivine + plagioclase (dots) clearly fall on a line with a slope of 1. The experiments that resulted in charges saturated with clinopyroxene (squares) deviate significantly from the plagioclase fractionation path. It is possible to estimate the point on the plagioclase trend at which pyroxene first begins to crystallize. The tangent (M) to the second curve gives the instantaneous molar proportions of plagioclase to pyroxene in the fractionating mineral assemblage: $[\mathrm{Pl}/(\mathrm{Pl} + \mathrm{Cpx}) = 1/M]$. The glass chemistry is therefore consistent with the observations of Grove and Bryan (1983).

1955 Kilauea Eruptions

The 1955 eruption products of Kilauea volcano are described by Tilley (1960) and Wright and Fiske (1971). The lavas have phenocrysts of olivine, augite, plagioclase and less commonly orthopyroxene and Fe-Ti oxides. The lavas erupted over a period of 3 months and over an extent of 10 miles. They were labelled chronologically from A to Z (Wright and Fiske 1971) and it was noted that the most differentiated lavas erupted early and were generally followed by less differentiated ones.

The data are plotted in Fig. 11 with their chronological labels. The data fall into two groups. The later eruptions (Y–Z) are tightly clustered indicating that the effects of plagioclase and augite crystallization are minimal. The early eruption products however, define a simple linear trend on the diagram that is consistent with subequal amounts of plagioclase and augite fractionation. The first erupted lavas can be related to the later lavas by simple crystallization and separation of augite and plagioclase (± olivine, orthopyroxene, etc). These results are consistent with the conclusions of Ho and Garcia (1987).

Analysis of liquid lines of descent

The unique liquid lines of descent produced by crystallization of magma systems are a function of the initial magma composition, the mode of differentiation (fractional vs equilibrium crystallization) and pressure. Variations in these parameters cause significant changes in the order of crystallization and change in the phase assemblages. The differences in liquid lines of descent can be analysed in terms of the fractionated minerals and the cotectic compositions. These constrain inferences about the physicochemical conditions attending differentiation.

The basalts from the 1967–68 Halemaumau Crater eruptions are possible differentiates of the comagmatic Hiiaka Crater picrites (Nicholls et al. 1986; Nicholls and Stout 1988; also see p. 27). The two data sets are plotted on Fig. 12. The olivine fractionation trend for the Hiiaka lavas (see Fig. 3) intersects one data point from Halemaumau; an additional corroboration of the comagmatic relationship of the rocks. Further, it indicates that olivine fractionation of the picrites can generate at least one basaltic composition. The Halemaumau lavas define a trend with a slope different from that due to olivine fractionation, indicating that other phases have joined the fractionating assemblage.

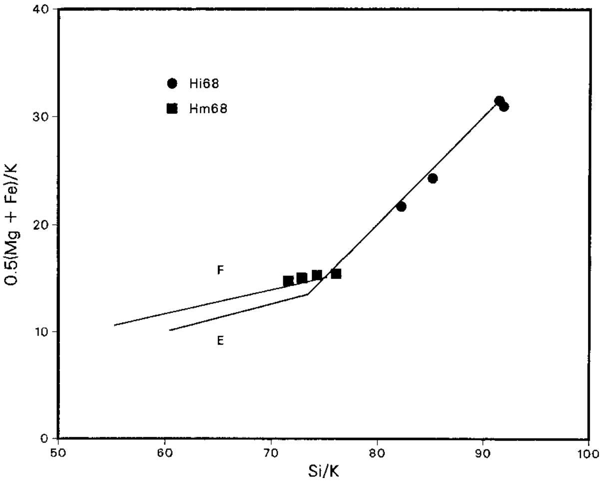

Fig. 12. The compositions of residual liquids calculated for the fractional (*F*) and equilibrium (*E*) crystallization of the high-Mg Hiiaka lavas. The Hiiaka lavas (*solid circles*) are related through crystallization of olivine alone. The Halemaumau lavas (*squares*) can be derived from the Hiiaka magma through fractional crystallization, but not through equilibrium crystallization. The discontinuity in slope marks the cotectic between olivine and the later phases

This is consistent with the phenocryst assemblages in the rocks (Jackson et al. 1975; Nicholls and Stout 1988). The discontinuity in slope is interpreted as the point at which the fractionating liquid reached the cotectic between olivine and the other phases, plagioclase and augite. Figure 12 also illustrates the calculated liquid lines of descent for equilibrium and fractional crystallization (e.g. Ghiorso and Carmichael 1985; Russell and Nicholls 1985; Nicholls et al. 1986). The fractional crystallization path produced through thermodynamic modeling is consistent with the lava chemistry for the Halemaumau and Hiiaka rocks, whereas equilibrium crystallization produces a liquid line of descent that does not coincide with the observed summit lava compositions.

A paradigm for testing hypotheses

Igneous hypotheses are created to explain the structure of a data set. Like all hypotheses, they are not proven constructions but are assumed for purposes of argument. Pearce element ratio diagrams can be used to disprove hypotheses that are not consistent with the chemistry of the rock suite. Those hypotheses that are not disproved can be granted the status of theory, in that they are now shown to be consistent with the evidence.

In addition, the diagrams yield new insights into the nature of processes that generate chemical variations. Pearce element ratio variation diagrams can be employed to identify the phases involved in igneous differentiation, to estimate the molar proportions of phases and to place limits on the compositions of the phases involved. Consequently, it is possible to evaluate a wide variety of hypotheses concerning igneous processes. While the very nature of scientific hypothesis testing precludes proving that one of them is true, Pearce element ratios facilitate the recognition and eventual rejection of unfounded hypotheses. In conjunction with mineral chemistry and physical-chemical modeling, Pearce element ratio diagrams strengthen igneous interpretations.

The premise of olivine control lines (Powers 1955) is that they represent comagmatic eruptive products related by gain or loss of olivine. In reality these trends are strictly linear *only* when there is a single composition of olivine involved in the process. The effects of olivine fractionation result in unique curvilinear trends. The olivine control lines that have played such an integral part in the study of Hawaiian volcanism, could be improved upon by considering the analogous Pearce element ratio diagram. First, the slope on a Pearce element ratio diagram immediately confirms whether olivine or some other phase affected the chemistry of the lavas. Second, the stoichiometry of olivine deviates so little from its ideal formula that scatter in the trend alerts the petrologist to the fact that additional phases, source material or processes contributed to the chemical variations.

In summary, we advocate using the following three Pearce element ratio diagrams to begin the study of basaltic suites. This minimum number of plots will provide a test of most hypotheses appropriate to the early crystallization of basalt magmas. The initial step is to ensure that the data justify the premise that they represent a single lineage. To this end, the chemical data should be plotted on a Pearce element ratio diagram with P/K vs Ti/K. These elements are conserved throughout much of the early crystallization history of basalts. Consequently, basaltic rocks which are cogenetic will define a single cluster. Second, plot the data in a diagram with Si/n as the X-axis and $0.5[\mathrm{Mg}+\mathrm{Fe}]/n$ as the Y-axis. Differentiation that involves a single ferromagnesian phase will define a linear trend whose slope is equal to one half the stoichiometric ratio of iron plus magnesium to silica in the separated phases. Consequently the identities of the early crystallizing phases are easily ascertained. As well, the cotectic liquid composition and cotectic assemblage can be identified by discontinuities in the slopes. Next, plot the data on a diagram with $X=\mathrm{Al}/n$ and $Y=[2\mathrm{Ca}+\mathrm{Na}]/n$. The early crystallization of basaltic rocks often involves three phases. This particular Pearce diagram is valuable in portraying the effects of one, two and three phase crystallization in basalt systems. In particular, sequences of crystallization involving olivine, orthopyroxene, Fe-Ti oxides, clinopyroxene, and/or plagioclase can be distinguished. From Pearce variation diagrams it is possible to: i) identify the phases involved in the differentiation process, ii) establish the order of crystallization and iii) identify the cotectic liquid compositions.

Table 5 gives a summary of Pearce element ratios that test a variety of petrologic hypotheses in basaltic systems. Suites involving other rock types may require other ratios to trace the course of differentiation. However, as long as the principles of the element ratios are maintained, this approach will work (Nicholls 1988).

Conclusions

Our successful analysis of igneous processes with Pearce element ratios encouraged development of Pearce's (1968, 1970) original work. Given the questions this approach has answered, we have investigated some of the reasons that the diagrams have not found widespread use in testing petrologic hypotheses. It has become clear that high quality data is a prerequisite. Data with large uncertainties, whether analytical or geological (e.g. secondary alteration) will not stand up to careful scrutiny. Quite often imprecise data will still define *reasonable* trends in Harker variation diagrams, whereas the Pearce element ratio representation shows increased scatter. In the case of altered rocks, the scatter results from a combination of the original igneous process and the subsequent alteration (Nicholls 1988). Conversely, we have shown that precisely measured compositions yield remarkable insights into igneous processes. The last point raises the issue of analytical precision in conventional whole rock analysis. It is critical to measure the concentrations of the conserved elements such as K, Ti, and P as precisely as possible. At a minimum, petrologists should select the analytical method that provides the highest precision for each of these elements. The significance of this approach also urges us to investigate improving the available analytical procedures.

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Appendix A

The variance in the ratio (σ_r^2) due to analytical uncertainty in the oxide analysis (σ_i^2) can be calculated from:

$$v_i = \sigma_i^2 / e_i^2 \tag{4}$$

$$v_z = \sigma_z^2 / e_z^2 \tag{5}$$

$$\sigma_r^2 = r^2 (v_i + v_z) \tag{6}$$

Equation 6 assumes that any covariance between e_i and e_z arising from analytical measurements is zero.