

DISTRIBUTION OF TITANIUM AND PHOSPHORUS IN OCEANIC BASALTS AS A TEST OF ORIGIN

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ABSTRACT

DISTRIBUTION OF TITANIUM AND PHOSPHORUS IN OCEANIC BASALTS AS A TEST OF ORIGIN

By

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A model is proposed to explain the distribution of titanium and phosphorus in oceanic basalts. This model is based on, the existence of titanium and phosphorus as primary components of specific mineral phases, the use of volumetric considerations to predict the stabilities of these phases and the existence of water as OH in the mantle. If this model is correct then the distribution of titanium and phosphorus and their ratio may be used to test models for the origin of oceanic basalts. The amount of titanium and/ or phosphorus is dependent on (in order of importance), the percent water in the original melt, amount of fractionation of silicate phases, and the depth. The ratio is largely dependent only on depth of partial melting provided titanium and phosphorus are not depleted in the mantle by partial melting. A x² analysis of the frequency distributions of these elements and their ratio is preformed in



order to test several models for the origin of basalts. From this analysis it is concluded that partial melting is the primary process for the generation of basalts but the degree of partial melting is relatively small and that the alkalinity of basalts increase with depth of partial melting.



DISTRIBUTION OF TITANIUM AND PHOSPHORUS IN OCEANIC BASALTS AS A TEST OF ORIGIN

Bу

Stephen I. Chazen

A THESIS

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INTRODUCTION

Several hypotheses exist for the generation of basaltic magmas (Kushiro, 1973a; Green, 1971; O'Hara, 1968). These schemes have been based largely on experimental evidence. Since these hypotheses yield differing results in terms of percent partial melting, depth, and mode of origin for each basaltic composition it is apparent that some method of testing these hypotheses using evidence other than laboratory experiments would be useful.

Of the major elements only the "incompatible"¹ ones bear any promise of differentiating between various origins for each rock composition. The nomenclature of igneous rock classification depends on the amount of major elements such as calcium, silicon, aluminum. Those elements that are independent of this classification scheme and that have predictable trends in distribution are the only ones that may be used for testing hypotheses concerning the origin of basalts.

Two of these "incompatible" elements, titanium and phosphorus, are unique in that they form minerals that

^LElements K, P, Ti, U, and Th are defined as incompatible by Green and Ringwood (1967).



contain these elements as primary components rather than existing only as traces in silicates. Stabilities of minerals such as rutile, ilmenite, sphene, perovskite, and apatite will control the distribution of titanium and phosphorus in melts since the bulk of the whole rock titanium and phosphorus is in these minerals rather than silicates.



PREVIOUS WORK

Several hypotheses exist that are used to explain the distribution of titanium and phosphorus in basaltic systems. The central problem that needs to be explained is the enrichment factors of titanium and phosphorus. That is, how does, for example, titanium increase from .71% in estimated mantle compositions to 3-4% in some alkali basalts. This is especially puzzling since rocks thought to be most deeply formed often have the greatest enrichment.

It has been suggested that the earth is zoned with respect to these elements (Green and Ringwood, 1967). In Green and Ringwood's model this zonation has been caused by repeated passing of heat through the earth which drives the "incompatible" elements out of silicate mineral structures in which they do not fit very well (Harris, 1957). This process of zone refining is not applicable to titanium and phosphorus because of their tendency to form their own mineral phases (e.g., rutile, ilmenite, apatite) rather than being included as traces in silicates. Experimental attempts to duplicate this process envisioned by Harris (1957) for rock systems have not been very successful for titanium and phosphorus (Vinogradov, Yaroshevsky, and Ilyin, 1971).

O'Hara (1968) suggests that titanium and phosphorus are incompatible with eclogites. If as O'Hara suggests eclogites are an intermediate product of partial melting between mantle compositions and basalts it may be possible to obtain the appropriate enrichment of titanium and phosphorus. This argument, while it may be correct does not explain the reason for the enrichment but only reports that it occurs.

Experimental studies in the system MgO-SiO₂-TiO₂ (MacGregor, 1968) show that with increasing pressure more titanium is forced into the partial melt. The shift, while present, is insufficient to account for the enrichment of titanium observed in rock systems. The choice of this particular system is unfortunate since magnesium titanates are extremely rare in nature.

Flower (1971) analyzed a specimen of phlogopite thought to be derived from the mantle. He found about 6% TiO_2 in this specimen. He postulated that the distribution of titanium was controlled by the breakdown of phlogopite in the mantle. There are few phlogopite crystals found with as much TiO_2 as this specimen (Deer, Howie, and Zussman, 1962), but even if this were common the percent phlogopite in the mantle is certainly less than 1%. Therefore only a maximum of .06% TiO_2 in the mantle could be accounted for with phlogopite.



Green and Ringwood (1967) have suggested that rising plutons absorb titanium and phosphorus from the wall rock to yield the appropriate enrichment. The criticism of O'Hara (1968) seems proper in that it is unlikely that this mechanism would work as well the second time a magma passed through a conduit to the surface as it did the first time.

The bulk of the current notions concerning the distribution of these two elements either use a trace element approach to their distribution or some theory that is untestable.

Kushiro (1973b) has done some work in basaltic systems with TiO_2 and P_2O_5 added. He reports that additions of small amounts of either element will shift the invariant point to the alkalic compositions. This work does not provide a source for the TiO_2 and P_2O_5 . Some other mechanism is needed to provide the titanium and phosphorus to the melts.

MODEL FOR THE DISTRIBUTION OF TITANIUM AND PHOSPHORUS

Titanium and phosphorus occur dominantly in mineral phases that contain either element as a major component and for that reason cannot be considered as trace elements. Due to the relatively low geothermal gradient in the mantle volumetric (ΔV) relationships should be the most important factor controlling the trends in the stability of phases (Fyfe, 1970). These trends are therefore predictable based on ΔV relationships of model reactions. If we assume that water exists primarily as OH⁻ in the mantle (Hamilton, Burnham and Osborn, 1964) then the stability of iron and calcium titanates can be predicted. For example:

1. FeTiO₃ + 20H⁻ = Fe(OH)₂ + TiO₃⁼

has a negative ΔV for all pressures. Thus larger amounts of TiO₃⁼ would be found in melts formed under increasingly higher pressures. Similar relationships can be described for calcium titanates. Therefore with increasing pressure more titanium would be forced into partial melts.

The stability of ilmenite and sphene (or perovskite) with respect to rutile decreases with increasing pressure. Ilmenite (FeTiO₃) will be increasingly replaced by rutile (TiO₂) with depth and thus the source for reaction (1)



decreases in abundance. Rutile is relatively insoluble in OH⁻ and therefore there will be smaller rate of increase of titanium with increasing depth of partial melting.

The stability of apatite, the primary phosphate bearing phase, can be written:

2.
$$Ca_5(PO_4)_3OH + 9 OH = 3PO_4^2 + 5Ca(OH)_2$$

Using estimates of the compressibility of apatite and portlandite $(Ca(OH)_2)$ (Clark, 1966) the ΔV for this reaction becomes increasingly negative with depth. No known, OH^- insoluble, phosphate phases, replace apatite with depth and the phosphorus content of the melt will increase un-impeded with depth of partial melting.

Thus if OH⁻ is present in the mantle, both elements will increase, in the melt, with depth of partial melting. Due to the limiting effects on the availability of ilmenite (reaction [1]) by increasing rutile stability with pressure and the lack of limits on the availability of apatite the proportion of titanium to phosphorus will decrease with depth. This ratio will depend primarily on the interrelationships of titanium bearing mineral stabilities and apatite stability at a particular pressure.

This proportion will be largely independent of reasonable amounts of partial melting since limited melting affects the absolute amount but not their proportion. The presence of titanium and phosphorus in all basalts would be expected only if the degree of partial melting was not





enough in almost all cases to use up either element. If these elements were commonly used up in partial melting processes many basalts would be expected that had very little of either element. In all rocks thought to be residual products of partial melting (e.g., lherzolites) discernable amounts of both titanium and phosphorus are found (Wyllie, 1967). On these bases it is concluded that the degree of partial melting for most rocks cannot be sufficient to use up all of titanium and phosphorus in the source. Since the titanium and phosphorus are not depleted by partial melting then the ratio in the melt will be responsive to the pressure at which the melting occurred.

In the source rock some titanium may be tied up as a trace element in silicates. The effect of pressure on these silicates is to force the titanium out of the lattice into melts (Verhoogen, 1962). This effect approximates the trend due to reaction [1].




EFFECTS OF FRACTIONAL CRYSTALLIZATION

The effect of fractional crystallization on the titanium to phosphorus ratio must be considered. The effect on the ratio $\text{TiO}_2/\text{P}_2\text{O}_5$ of fairly large amounts of fraction-ation, in sills and other igneous complexes is negligible since only trace amounts of titanium or phosphorus are incorporated into solid phases until at least 40% of the liquid is solidified (Wager and Brown, 1967; Walker, 1969; Anderson and Greenland, 1969). The remaining liquid, after some fractionation, will have essentially the same ratio as the initial ratio. In the analysis discussed below, since a large number of samples are used, errors due to liquid fractionation if present will be minimal.

Of the primary silicate phases in basaltic rocks only clinopyroxene can contain more than a trace amount of titanium. The amount of clinopyroxene that would be formed by fractional-crystallization of basaltic magmas is in the range of 5-10% of the total magma with a maximum of 20%. A maximum estimate of the titanium content of the pyroxene from basaltic rocks is 2%. Using this maximum estimate, combined with the maximum estimate of pyroxene fractionated from basaltic magmas, not more than .4% of the whole rock titanium would be in the fractionated pyroxene (a more



realistic estimate would be .1-.2%). If one does not consider individual samples but rather element distributions with large numbers of samples the effect of .4% titanium on the trends of titanium and TiO_2/P_2O_5 would be quite small. The net effect may be quite close, to the analytical error associated with the analyses used.

The ratio $\text{TiO}_2/\text{P}_2\text{O}_5$ is not correlated with olivine (normative) content (product-moment correlation in oceanic regions of about .05). The independence from olivine content is a further indication that fractionation of primary silicate phases does not effect the ratio.



A TEST OF GREEN'S PETROGENETIC GRID

Green (1971) has presented a comprehensive model for the generation of basaltic magmas. His petrogenetic grid (Figure 1), based on reconnaissance experiments in water deficient basaltic and pyrolitic systems, relates magma types to depth of partial melting of a pyrolite source and amount of water present. Although Green's model needs further experimental verification, it can be tested by comparing the theoretical magma types of his petrogenetic grid with the real patterns of distribution of certain elements in the equivalent basaltic rock types that occur in oceanic areas.

In order to test Green's model, ten rock types, defined in the same manner as Green and Ringwood (1967) were selected from his petrogenetic grid (Figure 1). Sample frequency distributions for 1870 non-continental Cenozoic basalts, grouped by rock type, were obtained for the parameters TiO_2 , P_2O_5 and TiO_2/P_2O_5 from RKNFSYS (Chayes, 1970).

In any suite of rocks, the trends in frequency distributions of titanium and phosphorus (in chemical analyses as TiO_2 and P_2O_5) should be sensitive to depth of origin and amount of water in the melt. The amount of water effects the amount of each element due to the

Figure 1.--Petrogenetic grid for mantle derived basalt based on partial melting of pyrolite containing .1% water. Coordinates and compositions of rock types based on Green's model. Numbers in parenthesis refer to percent normative olivine in melt.

PER CENT PARTIAL MELTING

1	e	e D	e			
28	Olivine Tholeiit (5-15)	Olivine Tholeiit (15-20)	Olivine Tholeiit (20-25)	Picrite (30-35)	ç	
17	Tholeiite (0-5)				Ŀ.	
12	Quartz Tholeiite		Alkaline Olivine Basalt (20-30)	Olivine-Rich Basanite (20-30)	1	
ŝ			Olivine-Rich Basanite (15-25)	Olivine Nephelinite (20-25)	4	
	▶ ⊢	· 1 ∞	16	55	1	
			ראבסטטאב			
	PRFSSURF (KB)					

shifting of reactions [1] and [2] to the right with increasing OH⁻. The ratio of the two elements will be relatively constant at a particular depth since the AV which controls the equilibrium of the reactions is pressure dependent and the source of titanium and phosphorus is "unlimited" for reasonable degrees of partial melting. For any given amount of water in the melt the amount of titanium and phosphorus in the melt should increase with depth, and similarly, at any given depth the amount of water increases.

If Green's model is viable, the ratio (TiO_2/P_2O_5) should shift downward with increasing depth and most of the variation should be between various depths. In the case of the individual elements, the most pronounced effect should be an increase in the elements with percent water in the proposed melt and a lesser increase in the elemental abundance with increasing depth.

A χ^2 contingency table analysis was performed on the frequency distributions (Cochran, 1954) (see Appendix), of the rock types in order to test the predicted distribution of TiO₂/P₂O₅ and TiO₂ and P₂O₅ with depth and amount of water in the suggested melt. For rock types that have the same proposed depth of origin, their TiO₂/P₂O₅ frequency distributions were added together and compared with other depth groups. Similarly, for rock types that have the same suggested percent water (or degree of partial melting), their frequency distributions for the parameters TiO₂ and



 P_2O_5 (separately) were added together and compared with other percent water groups. Trends in the ratio table (Table 1, part a) that parallel the proposed pressure were tested while trends in the individual elements' table (Table 1, parts b and c) paralleling both the degree of partial melting and the percent water, were tested. A significant negative correlation was obtained between pressure and the ratio, TiO_2/P_2O_5 , indicating as the ratio decreases the pressure increases. A significant positive correlation was obtained between the amount of water in the proposed melt and each of TiO_2 and P_2O_5 .

The χ^2/df column in each part of Table 1 gives a measure of relative importance of each source of variation. Table 1, part a indicates that the grouping of TiO₂/P₂O₅ based on depth of origin yields relatively more important variation than does the within depth variation. The within depth variation may be, in part, explained by several possible depths of origin for each of the rock types. The linear correlation with pressure is clearly the most important factor in explaining the variation between rock groupings.

In Table 1, parts b and c both elements show insignificant correlation with degree of partial melting but highly significant and important correlation with percent water in the melt. The grouping based on percent water in the melt explained the bulk of variation between rock types. The within percent water also yielded significant variation

TABLE l χ^2 Analysis Breakdown of Frequency Dis Figure l.	tribu	ltions of	Rock Types Shov	ni nv
Source	df	××	Significance	χ^2/df
Part a				
Due to depth grouping Linear correlation with pressure Curvilinear correlation	35 35 35	125.41 78.76 46.65	Sig. Sig. Not Sig.	3.48 78.76 1.33
Within Depth	72	149.46	Sig.	2.076
Part b				
Due to percent water grouping Correlation with degree of partial melting Correlation with percent water Curvilinear correlation	4 4 1 1 0 4 0 4	366.08 2.13 175.78 188.17	Sig. Not Sig. Sig. Sig.	8.72 2.13 175.78 4.71
Within percent water grouping	84	336.83	Sig.	4.01
Part c				
Due to percent water grouping Correlation with degree of partial melting Correlation with percent water Curvilinear correlation	5 1 55 55	251.47 .03 48.37 203.07	Sig. Not Sig. Sig. Sig.	4.41 .03 48.37 3.69
Within percent water grouping	114	235.77	Sig.	2.07
* Results were tested at the .05 level. contingency tables using coordinates shown in Fi measure of relative importance of listed source quency distributions grouped by depth of origin. grouped by percent water in melt. (c) TiO2 freq percent water in melt.	Trend gure of va (b) uency	l analysis 1. The X 1.ation: P205 fre distribu	was performed 2/df column giv (a) TiO2/P205 quency distribu tions grouped b	on ves a fre- utions oy



which to a large extent is due to depth of origin, but it is not as relatively important as the correlation with water content. Therefore, in each of the three χ^2 parts of the table the method chosen to group the rock types (either by depth or percent water) yielded the relatively most important variation.

By using the distribution of these elements in oceanic basaltic rocks, it is clear that the $\text{TiO}_2/\text{P}_2\text{O}_5$ ratios are consistent with Green's depth of partial melting, and the absolute abundances are compatible with his proposed distribution of water in the melt. In other words, we would have had to reject his model if these comparisons were not significant. The lack of correlation with percent water in the melt may indicate that Green's melting curves require too large percentage of partial melting (Wyllie, 1971). More appropriate values would show a smaller range in percent partial melting than Green currently shows.

TEST OF OTHER MODELS FOR BASALT PETROGENESIS

Other models for the origin of basalts may be tested using the distribution of titanium and phosphorous. Kushiro (1973a) has suggested a model which relates alkalinity with depth. In a general sense, Green (1971) has done this in his grid but some rock types are out of place (e.g., basanite [15-25] with a model based on parallel alkalinity and depth). If we group $\text{TiO}_2/\text{P}_2\text{O}_5$ for the 10 rock types shown in Figure 1 in a manner such that there is decrease in silica saturation the following rock types would be grouped:

- 1. Quartz Tholeiite
- 2. Olivine Tholeiite and Tholeiite
- 3. Alkaline Olivine Basalt
- 4. Olivine Basanite and Olivine Nephelinite

The first group is therefore quartz normative, the second is olivine normative but not nepheline normative, the third has less than 5% nepheline in the norm and the fourth has more than 5%. Picrites were placed in the appropriate groups based on their nepheline content.

The results of the χ^2 analysis on the frequency distributions of TiO₂/P₂O₅ ratio for the rock types grouped as above is shown in Table 2. As can be seen by comparing this table with Table 1, part a this method of grouping is



clearly superior to Green's grouping. This can be seen by comparing the size of the "Due to Depth" χ^2 values and by noting the lack of significant (at the 5% level) "Within Depth" factors in Table 2.

TABLE 2.-- χ^2 Analysis of Frequency Distributions for 10 Rock Types Shown in Figure 1 for the Parameters TiO₂/P₂O₅.*

Source	df	x ²	Sig. (5% level)	χ^2/df
Due to Depth	36	203.1345	Sig.	5.64
Within Depth	72	71.7349	Not Sig.	1.00

Rock types were grouped according to silica saturation. The within depth portion is largely caused by partial melting affects on the ratio.

It might be argued that the ratio TiO_2/P_2O_5 is correlated in some heretofore unknown way with alkalinity and not with depth per se. Two observations strongly suggest that this is not the case.

First, the frequency distributions for the ratio are clearly polymodal in all rock types examined. This would be expected only if the ratio were correlated with some variable, such as depth, that had several possible values for a given rock type. Due to the tight restraints on the rock type compositions it is unlikely that compositional control, by the major elements, would give patterns such as those shown for these rocks.



Second, the oceanic regions have different depth relationships for the origin of rock types than circumoceanic regions (Dickinson, 1970), and if we compare three rock types found in large numbers in both island arcs and oceanic regions we should see this depth difference if the ratio is a measure of depth. If it is strictly a compositional indicator there should be no differences between regions only possible differences between rock types. The three rock types chosen were quartz tholeiite, tholeiite (0-5) and olivine tholeiite (5-15). These three types are extremely common in both areas and are the only basaltic rock types with sufficient number of analyses in the island arcs to work with. Table 3 shows the result of this analysis. There is no significant difference (at the 5% level) between rock types. There is a large, highly important, very significant difference due to region indicated. If the ratio truly measures only composition there should have been only differences between rock types. The ratio must therefore be a measure of some genetic factors.

TABLE 3.-- χ^2 Analysis of Frequency Distributions Comparing Quartz Tholeiite, Tholeiite (0-5), and Olivine Tholeiite (5-15) between Oceanic and Island Arc Regions, for the Parameter TiO₂/P₂O₅.

Source	df	x ²	Sig. (5% level)	χ^2/df
Due to rock type	28	41.133	Not Sig.	1.47
Due to region	42	525.842	Sig.	12.52



The melting relationships proposed by Wyllie (1971) for the fusion of a garnet peridotite source is a scheme that might be tested. Relatively small (compared to Green, 1971) amounts of melt are produced in Wyllie's system. This model is likely to give results comparable to the degree of partial melting that best fits the distribution of TiO_2 and P_2O_5 . That is, his system would give a smaller range of partial melting than Green has proposed. Unfortunately sufficient data does not exist to rigorously test this model.

The model of O'Hara (1968) (O'Hara and Yoder, 1967) is more difficult to evaluate than the other schemes because of its reliance on fractional crystallization for many compositional differences. In a general sense, this type of model may also be evaluated using the distribution of titanium and phosphorus.

If fractional crystallization is an important process then plots of TiO_2 vs P_2O_5 will have good correlations. The amount of titanium and phosphorus should increase with fractionation but the relative amount of each (the ratio) should be the same. Figure 2 illustrates this for Hawaiian volcanics while Figure 3 is for Icelandic volcanics. Both are tholeiites. Both clearly have important fractionation components in their origin. The Icelandic series has a deeper origin than the Hawaiian (as indicated by the slope). This is supported by geophysical evidence independent of



Figure 2.--Plot of TiO₂ vs P₂O₅ for 52 analyses from Kilauea Volcano (Wright and Fiske, 1971). Values shown are in weight percent of the oxide. A strong correlation (r = .9577) exists between TiO₂ and P₂O₅ for this differentiated tholeiitic series. The slope is .1353 (ratio estimate 7.4).





Figure 3.--Plot of TiO₂ vs P₂O₅ for 10 analyses from Thingmuli Volcance, Iceland (Carmicheel, 1964). Values shown are in weight percent of the oxide. (Carmicheel, 1964). Values shown are in weight percent of the oxide. differentiation exists (r = .0156) between TiO₂ and P₂O₅ for this differentiated tholeiltic series. The slope is .302 (ratio estimate 3.3).





chemical reasoning for both regions (Carmichael, 1964; Wright and Fiske, 1971). The correlation between titanium and phosphorus in both cases is very high.

In an area where partial melting is more important than fractionation, the correlation between titanium and phosphorus will be low. That is all the rocks will cluster around a particular value yielding a low correlation coefficient but a small variance of each of TiO_2 and P_2O_5 .

In order to evaluate the entire oceanic region each area within it would have to be considered separately. An approximation to this more involved process can be made by looking at a product moment correlation between titanium and phosphorus for some of the previously defined rock types. Table 4 shows some values for oceanic regions. This type of approach is only an approximation since it does not take into account regional differences but it does give some indication of the relative importance of processes. Not surprisingly the more undersaturated rocks are derived by partial melting (or some complex combination of partial melting and fractionation and partial melting again) while the more silica rich rock types have important evidence of fractionation in their origin.

It is clear that the distribution of titanium and phosphorus can be useful in determining whether a series of rocks had been fractionated or had a simple partial melting origin. Other major elements would not be as useful as this



Rock Type	Significance Level of Correlation
Quartz Tholeiite	gtr. than .001
Tholeitte (0-5)	gtr. than .001
Olivine Tholeiite (5-15)	gtr. than .001
Olivine Tholeiite (15-20)	gtr. than .001
Olivine Tholeiite (20-25)	Not Sig.
Olivine Rich Basanite (15-25)	Not Sig.
Picrite	Not Sig.
Olivine Rich Basanite (20-30)	Not Sig.
Alkaline Olivine Basalt	Not Sig.

TABLE 4.--Significance of Correlations (Product-Moment) * Between TiO_2 and P_2O_5 for Rock Types from Oceanic Regions.

* Minimum significance level was .10.

pair for several possible reasons. First, often pairs of elements are correlated because of numerical necessity (Chayes, 1949, 1971, etc.). Secondly, titanium and phosphorus travel together and respond to the same factors except under the most extreme conditions of fractionation.



CONCLUSION

One of the clearest observations concerning the distribution of titanium and phosphorus is their regularity within regions and rock types. The trends in frequency distributions were as predicted by the model for the occurrence of these elements and is generally consistent with accepted models for the origin of basaltic magmas. The change in the ratio, in the case of Green's model was closely parallel with the change in pressure. Since alkalinity increase with pressure underlies all models for oceanic regions it would be expected that most other models would also linearly correlate the TiO_2/P_2O_5 ratio with pressure.

The absolute amount of each element is dependent on the pressure and percent water in the melt. Green's percent water direction is nearly an increasing normative olivine direction with decreasing water. The apparent negative logarithmic-type correlation (similar to percent water in melt) between percent olivine and TiO_2 and P_2O_5 distributions could easily explain the apparent enrichment of TiO_2 and P_2O_5 in basalts. The amount of titanium (or phosphorus) in picrites is not much greater than the amount of titanium assumed to be in the mantle. With a log-type increase in water in melts the titanium and phosphorus would increase logarithmically also.


A model that would be consistent with the distribution of TiO_2 and P_2O_5 and their ratio should contain each of the following characteristics:

- The model should be based primarily on partial melting but locally important fractionation at shallow depths may be used to generate more siliceous rock types.
- The degree of partial melting should be relatively small (a smaller range than Green has suggested), perhaps as small as 10% maximum.
- 3. The trends and water contents in basaltic magmas must be similar to those suggested by Green.
- The model should relate increasing alkalinity with depth.

Most models currently suggested meet the above criteria, at least generally. Consideration of the distribution of these two "incompatible" elements should be useful as a guide to further experimental work in basaltic systems. The distribution of these elements clearly puts limits on what is and is not possible for generation of magma compositions similar to basalts that exist in oceanic regions.

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APPENDIX

A description of the χ^2 analysis used in this work may be obtained from Maxwell (1961). Deviations from chance for frequency distributions between groups may be evaluated by using χ^2 analysis. The expected value of the χ^2 is equal to the number of degrees of freedom. This number is calculated by creating a contingency table and multiplying the number of rows minus one times the number of columns minus one. Deviations from this expected value are evaluated using a χ^2 table. A significant result means that there are differences between categories, within the contingency table, that deviate significantly from chance.

In this analysis (see Table 1, part a), for example, a contingency table was made that had a $\text{TiO}_2/\text{P}_2\text{O}_5$ frequency distribution for each rock type (10 rock types and 12 divisions within each frequency distribution). A χ^2 value was obtained for this "Total" table. Another table was made that grouped and added the frequency distributions of the rock types that were thought to have the same depth (4 depth groups and 12 divisions of the distributions). The χ^2 value obtained for this table was the "due to depth" value. The difference between this value and the value for the "Total" table is ascribed to "within depth."

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Trends in these tables may also be tested. Using a table that has both the vertical and horizontal axis in a natural order we can test to see if a continuous variable underlies the distribution. That is, is the shift in the frequency distribution continuous and is the shift related to the assigned coordinates for each cell of the table.

In this analysis, the contingency table with the 4 depth groups and the 12 divisions of the distribution was examined to see if the frequency distributions shifted to one direction continuously and if this shift parallels the change in pressure in magnitude and direction. The χ^2 value gives the significance of the regression coefficient with one degree of freedom.

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