5. COMPUTER MODELING OF MAJOR AND TRACE ELEMENT VARIATIONS OF HOLE 504B DIABASE AND BASALT¹

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ABSTRACT

Four computer modeling techniques were used to examine the intersample variation in Hole 504B basalt and diabase: (1) a liquid-line-of-descent calculation (the CHAOS program, Nielsen [1985, 1990]); (2) Pearce element ratio analysis (Pearce, 1968); (3) a least-squares-fit parent-daughter calculation (Bryan et al., 1969); and (4) correlation coefficient pattern analysis (the DARWIN program, Cox and Clifford [1982]). The first two techniques require few input assumptions, and can be used to identify what phases are fractionating, the compositions of those phases, and the relative proportions of those phases. The other two techniques require a considerable amount of input assumptions, and are primarily useful for testing petrologic models. The liquid-line-of-descent calculation suggests that fractional crystallization of plagioclase An74,4, augite Wo41,7En48,6Fs9,7, and olivine Fo_{85.3} from an initial mid-ocean-ridge basalt parent could explain the range of compositions observed in the 504B data set. The complementary gabbro would have the cumulus mineral assemblage 57.5% plagioclase, 23.3% augite, and 19.3% olivine plus an unknown amount of intercumulus liquid. Pearce element ratio analysis suggests that fractional crystallization of plagioclase An₇₉₋₈₆, augite Mg#₈₂₋₈₃, and olivine Fo₇₈₋₇₉ could explain the range of compositions observed in the 504B data set. The complementary gabbro would have a cumulus mineral assemblage of 62% to 67% plagioclase, 23% to 27% augite, and 8% to 12% olivine plus an unknown amount of intercumulus liquid. All four computer models are consistent with a differentiation scheme for 504B magmas in which an initial high Mg# parent fractionates plagioclase, augite, and olivine to produce a series of daughter magmas with lower Mg#s. None of the models require significant amounts of assimilation or more than one parent magma composition to explain the variation observed in the 504B data. Fraction of the observed 1726 m of basalt and diabase at Site 504B would require a minimum thickness of 573 m of gabbro if we assume 0% trapped liquid, or 1042 m of gabbro if we assume 45% trapped liquid. The lower crustal section at Hole 504B is probably thicker and more primitive than that calculated.

INTRODUCTION

The development of modern automated equipment for the analysis of whole-rock samples allows petrologists to collect larger, more complete, and more accurate data sets than were possible using wetchemical methods. A number of computer methods have been developed to model the intersample variation observed in these extensive data sets. We have applied four of these techniques to basalt and diabase analyses from Hole 504B: (1) a liquid-line-of-descent calculation (the CHAOS program, Nielsen [1985, 1990]); (2) Pearce element ratio analysis (Pearce, 1968); (3) a least-squares-fit parent-daughter calculation (Bryan et al., 1969); and (4) correlation coefficient pattern analysis (the DARWIN program, Cox and Clifford [1982]). Each of these methods requires the user to make some assumptions about the differentiation process, and then provides a set of relationships compatible with those assumptions. In addition to comparing these four methods, and trying to determine how the 504B magmas differentiated, the models generated by these methods can be used to predict the composition of the gabbros that might be encountered at depth in Hole 504B as a complement to the basalts and diabases recovered to date.

More than 500 whole-rock analyses have been made of Hole 504B basalts and diabases from the 1726 m of igneous core recovered through Leg 140. To minimize the effect of interlaboratory variations, we have selected a set of 273 X-ray fluorescence (XRF) analyses of basalts and diabases of group D composition from laboratories using similar standards and data reduction procedures (Autio and Rhodes, 1983; Kempton et al., 1985; Autio et al., 1989; Shipboard Scientific

Party, 1992; Sparks, this volume). From this set of analyses, a subset of 92 aphyric to sparsely phyric samples (0%–2% phenocrysts) was selected to best represent the range of group D magma compositions in the 504B section (Fig. 1). Only the least altered samples (Cu ≥45 ppm; Zr/Y = 1.6-2.45) were used in this subset to minimize the effects of pervasive hydrothermal alteration (e.g., Sparks, this volume). The calculated means, standard deviations, and ranges of major element oxides and selected trace elements for this suite are presented in Table 1.

More than 98% of the analyzed basalts and diabases from Hole 504B fall in group D of Autio and Rhodes (1983). Compositionally they can be classified as olivine-normative to slightly quartznormative tholeiites with compositions similar to moderately evolved mid-ocean-ridge basalts (MORB). They are unusually depleted in incompatible elements, but have incompatible element ratios similar to those of normal MORB. Although 504B samples cover a range of differentiation (Mg# = 67.8–53.1), standard Harker diagrams (Fig. 2) are of limited use in determining the processes of differentiation that operated on these magmas.

LIQUID-LINE-OF-DESCENT CALCULATIONS

The availability of thermodynamic and phase equilibria data for basaltic liquids and associated liquidus minerals allows the liquidus temperature and liquidus assemblage of most basaltic compositions to be calculated with a reasonable degree of confidence. A number of programs have been written that take advantage of these calculations to determine the differentiation history or liquid-line-of-descent for a wide range of basaltic starting compositions. The user can then compare the calculated daughter-liquid compositions with the compositions of the more evolved magmas in the data set. In general, in this type of calculation a computer program is used to determine the liquidus assemblage of a given magma. The program then subtracts a small increment of that assemblage to produce a new magma composition. The program then calculates the liquidus assemblage of the

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Figure 1. Selected group D MORB samples for this study. Open symbols represent 273 XRF analyses of group D samples (Autio and Rhodes, 1983; Kempton et al., 1985; Autio et al., 1989; Shipboard Scientific Party, 1992; Sparks, this volume); solid symbols represent a selected subset of 93 least-altered, aphyric samples.

new magma and subtracts a small increment of that assemblage. By this method, the initial magma composition is incrementally crystallized, while the phases removed and the changing magma compositions are recorded.

The program CHAOS (Nielsen, 1985; 1990) has been used to determine three liquid-line-of-descent models for a typical primitive magma composition (Mg# = 62.6) from Hole 504B. One of the advantages to using a program like CHAOS is that the user does not have to make any assumptions about the phases that are fractionated. Users need only to input the composition of the parent magma, the composition of any assimilant, the oxygen fugacity, whether equilibrium or fractional crystallization has occurred, a few control parameters (the calculation increment, the output increment, etc.) and data on how often and how much the differentiating magma chamber is recharged, how often and how much assimilation occurs, and how often and how much eruption occurs. The three models run for this study specified fractional crystallization with no assimilation, no recharge, no eruption, and oxygen fugacities of QFM, 1 log unit below QFM, and 1 log unit above OFM. The models were run until the resulting daughter magma had a Mg# approximating that of the most evolved 504B magma.

The model run at QFM calculates a daughter magma with a Mg# = 52.9 after 30.1% crystallization of olivine Fo_{85.3} (5.8%), augite Wo_{41.7}En_{48.6}Fs_{9.7} (7.0%), and plagioclase An_{74.4} (17.3%) (Table 2). The model predicts that olivine + plagioclase would be the initial liquidus phases (0%–15% crystallization), followed by plagioclase + augite + olivine (15.1%–30.1% crystallization). The model run at 1 log unit below QFM predicts slightly more olivine (6.1%) and slightly less augite (6.7%) but otherwise produced similar results. The model run at 1 log unit above QFM calculated slightly less olivine (5.4%) and slightly more augite (7.4%) but otherwise produced similar results. These three models suggest that the gross variation seen in the 504B magmas can be explained by shallow (crustal level) crystal-

Table 1. Means, standard deviations, and ranges of major elements and selected trace elements in 92 aphyric to sparsely phyric samples, Hole 504B.

	Mean	Std. dev.	Min.	Max.
SiO ₂ (%)	50.2	0.5	48.5	51.1
TiO ₂	0.96	0.11	0.71	1.24
Al ₂ Õ ₃	15.15	0.71	13.80	16.90
Fe2O2*	10.45	0.72	8.83	12.50
MnO	0.18	0.02	0.15	0.26
MgO	8.42	0.43	7.16	9.57
CaO	12.76	0.35	11.69	13.27
Na ₂ O	1.96	0.17	1.59	2.51
K ₂ Õ	0.03	0.06	0.00	0.36
P2Os	0.07	0.02	0.04	0.13
Zr (ppm)	48	6	35	64
Y	25	2	20	30
Sr	57	8	43	78
Ni	102	23	55	164

Note: Fe2O3* is total iron as Fe2O3.



Figure 2. Harker plot of % MgO vs. % SiO_2 for the samples used in this study. Symbols as in Figure 1.

lization of plagioclase, augite, and olivine from an initial MORB parent. The complementary gabbro would have the cumulus mineral assemblage 57.5% plagioclase, 23.3% augite, and 19.3% olivine plus an unknown amount of intercumulus liquid. A number of more complex models could be run using CHAOS to better fit the major and trace element compositional variation in the 504B data set (Fisk et al., 1992), but that is beyond the scope of this paper.

PEARCE ELEMENT RATIO ANALYSIS

Pearce element ratio analysis (Pearce, 1968, 1990; Nichols and Russell, 1990) can be applied easily to a data set using any advanced spreadsheet-plotting program on a personal computer. The technique first converts analyses to cation percents, and then plots various ratios of petrologic interest. In general, a conserved element (i.e., one that does not enter any of the fractionating phases and has not been mobilized during alteration) is used as the denominator. Plots of excluded element ratios can be used to identify co-genetic suites because ratios of excluded elements remain constant during fractional crystallization. Plots of included elements divided by a common conserved element can be used to identify fractionated mineral phases, because cation ratios have predictable variation patterns for each fractionated mineral. For example, if olivine, (Mg, Fe)₂SiO₄, is fractionated, the change in Fe + Mg will be twice that of the change in Si, so that a plot of (Fe + Mg)/Zr vs. Si/Zr will have a slope of 2.0 if olivine is the only fractionated phase. The use of cation ratios, instead of weight percent (wt%) variations, results in plots that are not sensitive to the addition or subtraction of elements that do not appear in the plots (this is particularly useful in working with data sets in which the user suspects that

Table 2. Output from the three CHAOS models run with a single 504B composition.

	QFM	QFM + 1	QFM-1
Parent Mg#	62.7	62.7	62.7
Parent liquidus (°C)	1203	1216	1203
Daughter Mg#	52.9	52.8	52.8
Daughter liquidus (°C)	1179	1180	1177
Total % fractionation	30.1	30.1	30.1
% olivine fractionation	5.8	6.1	5.4
Olivine/total crystals	0.193	0.203	0.179
Average olivine (Fo%)	85.3	84.7	86.4
% plagioclase fractionation	0.575	0.575	0.575
Plagioclase/total crystals	17.3	17.3	17.3
Average plagioclase (An%)	74.4	74.5	74.3
% augite fractionation	7.0	6.7	7.4
Augite/total crystals	0.233	0.223	0.246
Average augite (Wo:En:Fs)	42:49:10	42:48:10	42:49:9
Average augite Mg#	83.4	82.7	84.4

one or more elements have been mobilized during alteration). An additional advantage of applying Pearce element ratio analysis to large data sets is that all of the analyses in the data set are used to determine the final fractionation model. Like the CHAOS model described above, Pearce element ratio analysis does not require any assumptions about the phases that are fractionated, only some basic assumptions about whether the data set is the result of fractional crystallization or assimilation, and whether the data set represents a co-genetic suite. The Pearce element plots in this paper are based on the two data sets described above with open symbols used for the set of 273 group D analyses and filled symbols used for the subset of 92 least-altered aphyric samples. All of the calculated slopes are based on the subset of 92 aphyric samples; for each calculated slope the correlation coefficient (R) for the best-fit regression line and the 95% confidence limits on the slope are also given.

On a plot of Y/Ti vs. Zr/Ti (Fig. 3A) the 504B samples form a tight cluster, indicating that Ti, Y, and Zr are conserved elements in this suite, and that the samples represent a series of magmas that, if not comagmatic, have had similar histories during partial melting, transport, and differentiation. On a plot of P/Ti vs. K/Ti (Fig. 3B) the spread of values indicates that K (and to a lesser extent P) does not behave as a conserved element in this suite.

A plot of F'/Ti vs. Si/Ti (where $F' = 0.5 \cdot (Fe + Mg) + 2 \cdot Ca + 3 \cdot$ Na) can be used to test a simple model that postulates that intersample variation in this suite is the result of the crystallization of olivine, augite, and plagioclase. The formula for F' was selected so that its value for olivine ([Fe, Mg]₂ SiO₄; F' = 1), augite (Ca_{0.67}[Fe,Mg]_{1.33}Si₂O₆; F'= 2), anorthite (CaAl₂Si₂O₈; F' = 2), or albite (NaAlSi₃O₈; F' = 3) will be equal to the number of Si cations in the mineral. On a plot of F'/Ti vs. Si/Ti (Fig. 4A) the addition or subtraction of olivine, augite, or plagioclase in any proportions will result in a line with a slope of 1.0, while the addition or subtraction of orthopyroxene will result in a line with a slope of 0.5, and the addition or subtraction of any Si-free and Ti-free oxide (chromite, magnetite) will result in a trend with a slope of ∞ . The 504B data yield a slope of 1.044 (R = 0.983; $\pm 95\% = 1.004$ to 1.084) confirming that orthopyroxene and Fe-oxides are not important fractionating phases in these rocks. The slightly higher than expected slope may be the result of the fact that the calculation assumed an augite composition of Ca_{0.67}(Fe + Mg)_{1.33}Si₂O₆. An augite composition of Ca_{0.80}(Fe + Mg)_{1.20}Si₂O₆ would result in a slope of 1.10. The crystallization of a typical gabbro with 10% olivine, 30% augite (Ca0 80 (Fe + Mg)_{1,20}Si₂O₆), and 60% plagioclase (An₈₅) would result in a slope of 1.034, similar to that observed.

A plot of F"/Ti vs. Si/Ti (where $F'' = AI + 0.5 \cdot (Fe + Mg) - 4 \cdot Ca - 4 \cdot Na$) can be used to separate the effects of olivine crystallization from augite and plagioclase crystallization. On such a plot (Fig. 4B) olivine crystallization will result in a line with a slope of 1.0, orthopyroxene crystallization will result in a line with a slope of 0.5, and plagioclase or augite crystallization will result in a trend with a slope



Figure 3. A. Excluded element ratio plot of 504B group D MORB. The tight clustering of group D samples indicates that Y, Zr, and Ti are all behaving as conserved elements. Symbols as in Figure 1. The fields for type T (asterisks) and type M MORB (crosses) (Autio and Rhodes, 1983) are indicated. B. Excluded element ratio plot of 504B group D MORB. The sample distribution indicates that K, and to a lesser extent P, are not behaving as conserved elements in this data set. Symbols as in Figure 1.

of -1.0. The 504B data yield a slope of -0.8165 (R = 0.949; $\pm 95\% = -0.7598$ to -0.8732) confirming a model dominated by augite and plagioclase, with a small but significant olivine component.

A plot of F'''/Ti vs. Al/Ti (where $F''' = 2 \cdot Ca + Na$) can be used to separate the effects of augite and plagioclase crystallization. On such a plot (Fig. 5A) plagioclase crystallization will result in a trend with a slope of 1.0, and augite crystallization will result in a trend with a slope of ∞. Neither olivine nor orthopyroxene crystallization will have an effect on this diagram because neither contains significant amounts of Ca, Na, or Al. The 504B data yield a slope of 1.386 (R = 0.971; $\pm 95\%$ = 1.314 to 1.457), confirming a model with significant augite crystallization, but dominated by plagioclase crystallization. Pearce element ratios can also be used quantitatively to calculate the relative proportions of the fractionated mineral phases. On a plot of Na/Ti vs. Al/Ti (Fig. 5B), the slope is a direct function of the composition of the average fractionated plagioclase and is independent of any other fractionated phase (slope = Xab/[2 - Xab]) (see Appendix). The 504B data has a slope of 0.0959 (R = 0.683; $\pm 95\% = 0.0744$ to 0.1174), indicating an average plagioclase composition of $An_{82,5}$ ($An_{79,0}$ to $An_{86,2}$). The low R value for this plot may result from Na mobilization in some samples during alteration, and from the fact that a range of plagioclase compositions has crystallized from this suite.

If we assume a plagioclase composition of $An_{82.5}$, we can determine the relative proportions of plagioclase and augite from the slope of F''/Ti vs. Al/Ti (slope = [Xcpx + 1.2 · Xan + 0.6 · Xab]/[1.2 · Xan + 0.6 · Xab] for Ca_{0.67}[Fe + Mg]_{1.33}Si₂O₆ or slope = [1.2 · Xcpx + 1.2 · Xan + 0.6 · Xab]/[1.2 · Xan + 0.6 · Xab] for Ca_{0.80}[Fe + Mg]_{1.20}Si₂O₆)



Figure 4. **A.** Pearce element ratio plot of 504B group D MORB samples. The fractionation of olivine (OL), augite (CPX), and plagioclase (PLG) will result in a trend parallel to a slope of 1.0; fractionation of orthopyroxene (OPX) will result in a trend parallel to a slope of 0.5. Symbols as in Figure 1. **B.** Pearce element ratio plot of 504B group D MORB samples. The fractionation of olivine (OL) will result in a trend parallel to a slope of 1.0; fractionation of orthopyroxene (OPX) will result in a trend parallel to a slope of 0.5; fractionation of orthopyroxene (OPX) will result in a trend parallel to a slope of 0.5; fractionation of augite (CPX) and plagioclase (PLG) will result in a trend parallel to a slope of -1.0. Symbols as in Figure 1.

(Fig. 5A). The 504B data yields an augite/(augite + plagioclase) of 0.297 (0.256 to 0.334) for augite with 33% Wo component and 0.260 (0.223 to 0.294) for augite with 40% Wo.

If we know the plagioclase composition and the relative proportions of augite and plagioclase (and assume orthopyroxene crystallization = 0) we can determine the amount of fractionated olivine from the slope of F"/Ti vs. Si/Ti (slope = [Xol - 1.2 · Xan - 1.8 · Xab - 1.5 · Xcpx]/[Xol + 1.2 · Xan + 1.8 · Xab + 1.5 · Xcpx] for Ca_{0.67}[Fe + Mg]_{1.33}Si₂O₆ or slope = [Xol - 1.2 · Xan - 1.8 · Xab - 1.95 · Xcpx]/[Xol + 1.2 · Xan + 1.8 · Xab + 1.5 · Xcpx] for Ca_{0.80}[Fe + Mg]_{1.20}Si₂O₆) (Fig. 4B). The 504B data yields an olivine/(olivine + augite + plagioclase) of 0.121 (0.084 to 0.157) for augite with 33% Wo component and 0.130 (0.091 to 0.167) for augite with 40% Wo.

An independent check of olivine/(olivine + augite) can be obtained from a plot of (2 · Ca + Na - Al)/Ti vs. (Fe + Mg)/Ti (Fig. 6A) where slope = $Xcpx/(2 \cdot Xol + Xcpx)$ for augite with 33% Wo or slope = (1.2 \cdot Xcpx)/(2 \cdot Xol + 0.9 \cdot Xcpx) for augite with 40% Wo. The 504B data yield a slope of 0.4874 (R = 0.863; $\pm 95\% = 0.4302$ to 0.5447), which gives olivine/(olivine + augite) of 0.345 (0.295 to 0.398) for augite with 33% Wo and 0.439 (0.3995 to 0.486) for augite with 40% Wo. Combined with the results from F""/Ti vs. Al/Ti this yields olivine/ (olivine + augite + plagioclase) of 0.089 for augite with 33% Wo and 0.095 for augite with 40% Wo. It is interesting to note that the details of this plot are consistent with the CHAOS model in that the initial fractionation (from the upper right toward the middle of the plotted points) has a relatively shallow slope, indicating that it is dominated by olivine, while the final fractionation (from the middle of the plotted points toward the lower left) has a relatively steeper slope, indicating that it is dominated by augite. The calculations above using the slope of the best-fit line give the average fractionation trend.



Figure 5. **A.** Pearce element ratio plot of 504B group D MORB samples. The fractionation of plagioclase (PLG) will result in a trend parallel to a slope of 1.0; fractionation of augite (CPX) will result in a trend parallel to a slope of ∞ ; fractionation of olivine or orthopyroxene will have no effect on this diagram as neither contains significant amounts of Ca, Na, or Al. Symbols as in Figure 1. **B.** Pearce element ratio plot of 504B group D MORB samples. The fractionation of albite (Ab) will result in a trend parallel to a slope of 1.0; fractionation of anorthite (An₁₀₀) will result in a trend parallel to a slope of 0.0. Symbols as in Figure 1.

Because both olivine and augite have significant amounts of Fe and Mg, the compositions of these solid solution series cannot be independently determined using Pearce element ratios. A plot of Mg/Ti vs. (Fe + Mg)/Ti (Fig. 6B), however, yields an average Mg# for olivine and augite (slope = XMg/[XMg + XFe]). The 504B data yield a slope of 0.8046 (R = 0.992; $\pm 95\% = 0.7830$ to 0.8261), which gives an average Mg# of 80.5. Assuming KD^{Fe}/_{Mg} ^{ol}/_{lq} = 0.30 (Roeder, 1974) and KD^{Fe}/_{Mg} ^{cpx}/_{lq} = 0.23 (Grove and Bence, 1977), and using the values for olivine/augite previously calculated, the distribution of Mg and Fe between augite and olivine can be calculated; the Mg# for olivine = 78.0–78.8 and the Mg# for augite = 82.2–82.8.

All of the mineral proportions calculated using Pearce element ratios are in cation %. To compare with mineral proportions calculated by other computer models these have to be converted to wt% by multiplying by the molecular weight of each phase, dividing by the number of cations in the phase, and then renormalizing to 100%. For samples in which the olivine and augite have high Mg#s and the plagioclase has a high An%, the conversion from cation % to wt% makes only a minor change in the mineral percentages. The Pearce element data for the 504B suite are summarized in Table 3. Four separate models are presented; Model 1 uses Figures 5A, 5B, 4B, and 6B and assumes an augite of Ca_{0.67}[Fe + Mg]_{1.33}Si₂O₆, Model 2 uses Figures 5A, 5B. 4B, and 6B and assumes an augite of Ca_{0.80}[Fe + Mg]1 20Si2O6, Model 3 uses Figures 5A, 5B, 6A, and 6B and assumes an augite of Ca_{0.67}[Fe + Mg]_{1.33}Si₂O₆, and Model 4 uses Figures 5A, 5B, 6A, and 6B and assumes an augite of Ca_{0.80}[Fe + Mg]_{1.20}Si₂O₆. The robustness of the method is illustrated by the fact that the four models yield similar results.

LEAST-SQUARES-FIT PARENT-DAUGHTER CALCULATIONS

Least-squares-fit mixing models (Bryan et al., 1969; Wright and Doherty, 1970; Bryan, 1986) are standard fare for igneous petrology. In such models, the user inputs a parent magma composition, a daughter magma composition, and the compositions of fractionated mineral phases and/or assimilated xenoliths. In some versions of the program, the user can specify how each element is to be weighted in the model, so that elements that are known to be accurately determined and not affected by alteration can be more heavily weighted than elements less well determined or those suspected to have been affected by alteration. The program then does a multivariate least-squares fit to determine the best proportions of parent magma, fractionated minerals, and assimilated xenoliths that can be mixed to produce the daughter composition. There is no unique solution, so a successful least-squares-fit does not necessarily mean that the user has correctly modeled the differentiation that has occurred. On the other hand, not every mixture of parent, daughter, and fractionated or assimilated phases will yield a successful least-squares-fit (i.e., one in which the residuals for each element are within experimental error), and there is no control on whether a particular phase is added to or subtracted from the parent magma, so that in some cases where there is a successful fit mathematically, the mixing proportions suggest an unreasonable model (i.e., a model in which a fit is achieved by adding an unreasonably large amount of one phase compensated for by subtracting an unreasonably large amount of another phase). A disadvantage of this method is that the user needs to specify the compositions of the fractionated and assimilated phases. Electron microprobe data on phenocrysts, if available, usually provide a good starting point. If mineral composition data are not available, a trial and error approach must be used to determine the compositions of the phases that will best describe the process. An additional disadvantage of this model for a large data set is that only two compositions (one parent and one daughter) are modeled at a time. The program is best suited for situations in which the general scheme of differentiation is known (or suspected) and the user wishes to determine the relative proportions of the phases involved.

In this exercise a single parent with a high Mg# (62.7) and a single daughter with a low Mg# (53.2) were used (Table 4). Mineral compositions were taken from the phenocryst assemblage observed in Hole 504B samples (e.g., Natland et al., 1983; Kempton et al., 1985). This simple approach has resulted in a solution with low element residuals and petrologically reasonable mixing proportions. The removal of 5.0% olivine, 8.0% augite, and 14.8% plagioclase from a high Mg# parent results in a low Mg# daughter after 27.6% total crystallization. The cumulus assemblage in the complementary gabbro would be 18.1% olivine, 29.1% augite, and 53.8% plagioclase (Table 5).

CORRELATION COEFFICIENT PATTERNS

The processes affecting the evolution of a suite of cogenetic igneous rocks, be they magma mixing, multiphase fractionation, or wallrock assimilation, will result in predictable compositional relationships, if the processes and chemical data for all components are known. A unique way of looking at these relationships is to calculate the correlation coefficients between all analyzed elements. The resultant correlation coefficient matrix can then be compared, graphically, with similar matrices that have been calculated from various petrologic models. A simple, single-stage process such as fractionating olivine from a liquid, or mixing two magmas of constant composition, results in correlation coefficients that are either +1, or -1 (or 0, in the rare case where the abundance of an element is the same in both endmembers). Additional stages, or complexities, will reduce these correlations depending on the processes and compositions involved. Cox and Clifford (1982) describe this correlation method in detail, and have written a computer program named DARWIN to test various simple or complex evolutionary scenarios. They emphasize that this



Figure 6. **A.** Pearce element ratio plot of 504B group D MORB samples. The fractionation of olivine (OL) or orthopyroxene (OPX) will result in a trend parallel to a slope of 0.0; fractionation of augite (CPX) will result in a trend parallel to a slope of 1.0; fractionation of plagioclase will have no effect on this diagram. Symbols as in Figure 1. **B.** Pearce element ratio plot of 504B group D MORB samples. The fractionation of fayalite (Fa), and/or hedenbergite (Hd) will result in a trend parallel to a slope of 0.0; fractionation of forsterite (Fo) and/or diopside (Di) will result in a trend parallel to a slope of 1.0. Symbols as in Figure 1.

approach is meant to complement, not replace, other modeling tools. The striking advantage to this approach is its ability to easily examine the behavior of a large number of elements, providing greater detail to the selected model, or alerting the user to possible difficulties.

To use DARWIN, the compositions of an initial liquid and each modifying phase or component are first specified. Next, whether components are to be added or subtracted, and by what percentages, must be stipulated. The program then calculates a mean rock composition and the correlation coefficients between the initial composition and the new mean. With each successive stage of evolution (i.e., a new fractionating phase or added magma), DARWIN calculates a new mean rock composition and correlation patterns. These patterns are printed out graphically, allowing a large number of modeling options to be tested quickly. Cox and Clifford stress that it is not important to match the observed patterns exactly. Instead, the patterns are meant for qualitative comparisons, matching or excluding patterns from various models.

This method was tested with two data sets: (1) the 93 aphyric to sparsely phyric basalt and diabase samples described above, and (2) a series of synthetic compositions calculated by the computer program CHAOS (Nielsen, 1985; 1990) that cover the same range of Mg#s as the natural suite. Correlation coefficients for both of these data sets (Table 6) were calculated for SiO₂, TiO₂, Al₂O₃, total iron as Fe₂O₃ (Fe₂O₃*), MnO, MgO, CaO, Na₂O, Zr, Y, Sr, and Ni, using a computer spreadsheet. DARWIN was set up to simulate a multistage fractionation of approximately 6% olivine, 20% plagioclase, and 11% clinopyroxene from an initial primitive liquid, and the resulting correlation matrix is presented in Table 6. Mineral proportions are similar to those calculated earlier by the least-squares-fit mixing program.

Table 3. Results from Pearce element ratio analysis of 504B samples.

Model	1	2	3	4
Assumed augite (Wo%)	33	40	33	40
Cation % Olivine/total crystals Plagioclase/total crystals Augite/total crystals	12.1 61.8 26.1	13.0 64.4 22.7	8.9 64.1 27.1	9.5 66.9 23.6
Weight % Olivine/total crystals Plagioclase/total crystals Augite/total crystals	11.4 62.3 26.3	12.2 65.0 22.8	8.3 64.4 27.2	8.9 67.4 23.7
Mineral compositions Average olivine (Fo%) Average plagioclase (An%) Average augite Mg#	78.4 82.5 82.5	78.8 82.5 82.8	78.0 82.5 82.2	78.4 82.5 82.5

Table 4. Compositions used as input for DARWIN and least-squares-fit calculations.

	Initial liquid	Olivine	Plagioclase	Augite
SiO ₂ (%)	50.30	40.50	46.60	52.90
TiO ₂	0.91	0.00	0.00	0.57
Al ₂ Ô ₃	15.31	0.00	33.46	2.40
FeO	9.50	12.20	0.18	5.60
MnO	0.18	0.16	0.00	0.15
MgO	8.95	46.39	0.25	16.80
CaO	13.01	0.34	17.76	21.30
Na ₂ O	1.83	0.00	1.53	0.28
K ₂ Ô	0.01	0.00	0.00	0.00
P ₂ O ₅	0.06	0.00	0.00	0.00
Zr (ppm)	44	0	0	7
Y	25	0	0	13
Sr	55	0	99	11
Ni	107	930	0	150

Note: Total iron as FeO.

Table 5. Res	sults of least-se	quares-fit ca	alculations.
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	$\begin{tabular}{ c c c c } \hline Evolved liquids \\ \hline Observed & Calculated \\ \hline $1.35 & $51.29 \\ 1.26 & $1.19 \\ 13.98 & $14.01 \\ 11.39 & $11.62 \\ 0.21 & $0.22 \\ 7.25 & $7.24 \\ 11.85 & $11.94 \\ 11.85 & $11.94 \\ 12.5 & $2.72 \\ 0.01 & $0.01 \\ 0.08 & $0.08 \\ Σ t2 = $ \\ \hline Mixing proportions & Percentages \\ \hline $1.381 & $100.00 \\ -0.069 & $-5.00 \\ -0.205 & $-14.84 \\ -0.111 & $-8.04 \\ \hline \end{tabular}$			
	Observed	Calculated	Residual	
SiO ₂ (%)	51.35	51.29	-0.06	
TiO ₂	1.26	1.19	-0.07	
Al2Õ3	13.98	14.01	0.03	
FeÕ	11.39	11.62	0.23	
MnO	0.21	0.22	0.01	
MgO	7.25	7.24	-0.01	
CaO	11.85	11.94	0.09	
Na ₂ O	2.25	2.18	-0.07	
K ₂ Ô	0.01	0.01	0.00	
P2Os	0.08	0.08	0.00	
2-3		$\sum r^2 =$	0.08	
	Mixing proportions	Percentages		
Initial liquid	1.381	100.00		
Olivine	-0.069	-5.00		
Plagioclase	-0.205	-14.84		
Augite	-0.111	-8.04		
Evolved liquid	0.996	72.12		

Note: Total iron as FeO.

The compositions of the fractionated phases (Table 4) are in reasonable agreement with analyses from Hole 504B (e.g., Natland et al., 1983; Kempton et al., 1985) and 1-atm equilibrium compositions (e.g., Roeder and Emslie, 1970; Drake, 1976) calculated by the program CHAOS.

In the 504B data set, TiO_2 exhibits moderate to strongly positive correlations (+0.5 to +0.9) with SiO_2 , $Fe_2O_3^*$, MnO, Na₂O, Zr, and Y; strongly negative correlations (-0.7 to -0.8) with A_2O_3 , MgO, CaO,



Figure 7. Correlation coefficient patterns for Ti, Zr, and Y. Symbols: filled boxes and solid lines = Hole 504B suite; open triangles and dotted lines = output from DARWIN; open boxes and dashed lines = output from CHAOS.

and Ni; and low correlations (+0.1) with Sr. The patterns produced by subtracting olivine, plagioclase, and clinopyroxene via DARWIN display the same general pattern as the selected 504B samples (Fig. 7), with the exception of Al_2O_3 and CaO, which show almost no correlation (-0.1, +0.1). The pattern resulting from the liquids calculated by CHAOS corresponds well with SiO₂, Al_2O_3 , $Fe_2O_3^*$, MnO, MgO, Na₂O, Zr, Y, and Ni, but misses CaO (0.0) and Sr (+1.0). Yttrium and Zr correlation patterns for both natural and calculated compositions are comparable to those of TiO₂.

The patterns for compatible elements Al₂O₃, MgO, and CaO (Fig. 8) are much less coherent. In the 504B data set, MgO is positively correlated with Al2O3, CaO, and Ni (+0.5 to +0.7), and negatively correlated with SiO₂, TiO₂, Fe₂O₃*, Na₂O, Zr, Y (-0.5 to -0.8); MnO and Sr show almost no correlation with MgO. The MgO correlation values from DARWIN are in reasonable agreement with the more incompatible elements TiO₂, Zr, Y, and compatibles SiO₂, Na₂O, and Ni, but the values for Al2O3, Fe2O3*, and CaO are correlated in the opposite sense. The CHAOS pattern, on the other hand, is a slightly better match. It is roughly the same as the observed 504B pattern, except for Sr, which is strongly correlated (-0.97) in the calculated compositions, but not in the rocks (-0.1). The pattern matching for Al2O3 and CaO ranges from poor to nonexistent, respectively. CHAOS matches the Al₂O₃ pattern slightly better than DARWIN does, but neither program effectively mimics the observed CaO correlation pattern in the 504B data set.

Changing the proportions of olivine, plagioclase, and clinopyroxene does not drastically affect these patterns, if the proportions are

	Correlation coefficient matrix-504B basalts and diabases										
	SiO_2	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	Zr	Y	Sr
TiO ₂	0.67										
Al ₂ Õ ₂	-0.66	-0.74									
Fe On	0.55	0.82	-0.87								
MnO	0.19	0.52	-0.56	0.54							
MgO	-0.67	-0.78	0.48	-0.64	-0.14						
CaO	-0.58	-0.73	0.51	-0.68	-0.21	0.65					
Na ₂ O	0.26	0.49	-0.22	0.29	0.12	-0.51	-0.48				
Zr	0.49	0.89	-0.55	0.62	0.48	-0.62	-0.60	0.41			
Y	0.54	0.89	-0.78	0.89	0.49	-0.66	-0.70	0.38	0.76		
Sr	-0.04	0.05	0.36	-0.36	-0.19	-0.07	-0.07	0.29	0.34	-0.22	
Ni	-0.72	-0.80	0.79	-0.76	-0.41	0.72	0.58	-0.49	-0.66	-0.77	0.10
			C	Correlation	n coefficie	ent matrix	—DARW	'IN			
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	Zr	Y	Sr
TiO ₂	0.84										
Al ₂ O ₃	0.18	-0.09									
Fe ₂ O ₃	0.15	0.63	-0.68								
MnO	0.48	0.84	-0.58	0.94							
MgO	-0.77	-0.50	-0.77	0.32	0.05						
CaO	0.65	0.13	0.59	-0.65	-0.34	-0.79					
Na ₂ O	0.74	0.81	0.49	0.24	0.43	-0.82	0.32				
Zr	0.76	0.98	0.00	0.66	0.68	-0.58	0.05	0.87			
Y	0.82	1.00	0.05	0.64	0.69	-0.52	0.13	0.83	0.99		
Sr	0.36	0.15	0.98	-0.52	-0.55	-0.87	0.61	0.67	0.21	0.17	
Ni	-0.86	-0.58	-0.67	0.27	0.19	0.99	-0.83	-0.81	-0.55	-0.57	-0.79
			1	Correlatio	on coeffici	ient matri	x—CHAC	OS			
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	Zr	Y	Sr
TiO ₂	0.98										
Al ₂ O ₂	-1.00	-0.99									
Fe ₂ O ₃	0.97	1.00	-0.98								
MnO	0.99	1.00	-0.99	1.00							
MgO	-1.00	-0.99	1.00	-0.98	-0.99						
CaO	0.20	0.02	-0.16	-0.04	0.04	-0.13					
Na ₂ O	0.97	1.00	-0.98	1.00	1.00	-0.99	-0.03				
Zr	0.98	1.00	-0.98	1.00	1.00	-0.99	-0.01	1.00			
Y	0.98	1.00	-0.99	1.00	1.00	-0.99	0.00	1.00	1.00		
Sr	0.95	0.99	-0.97	1.00	0.99	-0.97	-0.10	1.00	1.00	0.99	
Ni	-0.99	-0.97	0.99	-0.95	-0.97	0.98	-0.25	-0.95	-0.96	-0.96	-0.93

Table 6. Correlation coefficient matrices from natural and calculated compositions.

varied within reasonable limits. The simulated patterns could be made to more closely approach those of the natural samples if steps were taken to fine tune the model by adding different liquid compositions to simulate the effect of variable primary liquid compositions, adding evolved liquids to simulate a periodically refilled magma chamber, or adding small amounts of some of the alteration minerals. It is not clear, however, that such fine tuning would add any new geologic insights to the model.

The application of the correlation method to the 504B data suggests several points to consider when using this approach. Correlation coefficients between moderate to highly incompatible elements (Ti, K, P, Nb, Zr, Y, Rb, Ba, La, Ce, etc.) are easier to match than those for some of the compatible elements (Al, Mg, and Ca). SiO2, Fe2O3*, and Ni, on the other hand, commonly agree with the fractionation model. This observation is in agreement with the results of Cox and Clifford (1982) for their East Iceland, Mahabaleshwar, and Rooi Rand suites. Although incompatible elements are preferred for this kind of modeling, the unusually low concentrations of many incompatible elements in Hole 504B samples (Nb ≤1.5 ppm; Rb <0.4 ppm; Ba <2 ppm; K <200 ppm; P2O5 <0.13 %), limits their usefulness for this exercise. In addition, K, Rb, and possibly Sr and Na have been affected by hydrothermal alteration (e.g., Alt et al., 1986). Another difficulty to consider is the relative homogeneity of the Hole 504B samples (Table 1). Suites of rocks that show little variation tend to have lower correlation coefficients and are more likely to be affected by outlying values for both the observed rocks and phase compositions (Cox and Clifford, 1982). In such cases, analytical error plays an important role because correlation coefficients become highly variable and difficult to match with seemingly small variations in composition.

Despite these difficulties, however, useful information has come out of this exercise. If only the relatively incompatible elements plus SiO_2 and $Fe_2O_3^*$ are considered, the patterns are consistent with a model of olivine, plagioclase, and clinopyroxene fractionation to explain the compositional variations in the 504B suite.

CONCLUSIONS

Four computer models have been used to examine the compositional variation in the 504B samples. The first two models, a liquidline-of-descent calculation (CHAOS) and Pearce element ratio analysis, require few input assumptions, and can be used to identify: (1) what phases are fractionating, (2) the compositions of those phases, and (3) the relative proportions of those phases. The other two models, least-squares-fit parent-daughter calculations and correlation coefficient patterns analysis (DARWIN), require a considerable amount of input assumptions, and are primarily useful for testing models (the least-squares-fit parent-daughter calculations do, however, yield the relative proportions of fractionating phases). All four computer models are consistent with a differentiation scheme for 504B magmas in which an initial high Mg# parent fractionates plagioclase, augite, and olivine to produce a series of daughter magmas with lower Mg#s. None of the models require significant amounts of assimilation or more than one parent magma composition to explain the variation observed in the 504B data.

If it is assumed that fractionation occurred in a crustal level magma chamber, the average composition of the residual gabbro can be calculated. The primary unknown in such a calculation is the amount of trapped liquid. Model gabbros have been calculated assuming 0%,

Table 7. Calculated average gabbros for Hole 504B.

CHAOS models					Pearce	Pearce element ratio models			Least-squares-fit models			
% pore magma	0.00	15.00	30.00	45.00	0.00	15.00	30.00	45.00	0.00	15.00	30.00	45.00
% olivine	19.10	16.24	13.37	10.51	10.20	8.67	7.14	5.61	17.92	15.23	12.54	9.86
% plagioclase	57.50	48.88	40.25	31.63	64.80	55.08	45.36	35.64	28.83	24.51	20.18	15.86
% augite	23.40	19.89	16.38	12.87	25.00	21.25	17.50	13.75	53.25	45.26	37.28	29.29
SiO ₂	48.60	48.84	49.08	49.32	47.94	48.28	48.62	48.96	47.32	47.75	48.19	48.62
TiO	0.13	0.26	0.38	0.51	0.13	0.26	0.38	0.50	0.16	0.28	0.40	0.52
Al ₂ Õ ₂	19.16	18.56	17.96	17.36	22.44	21.35	20.25	19.16	18.51	18.01	17.50	17.00
FeO	4.07	5.03	5.98	6.94	3.70	4.71	5.72	6.74	3.90	4.88	5.86	6.85
MnO	0.09	0.11	0.12	0.13	0.06	0.08	0.10	0.12	0.07	0.09	0.10	0.12
MgO	12.71	12.07	11.42	10.78	8.54	8.52	8.50	8.48	13.29	12.56	11.83	11.10
CaO	13.55	13.43	13.31	13.20	15.84	15.38	14.91	14.45	15.66	15.22	14.79	14.35
Na ₂ O	1.71	1.75	1.79	1.82	1.33	1.42	1.52	1.61	0.90	1.06	1.21	1.37
K ₂ Ô	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.00	0.00	0.01	0.01
P205	0.00	0.01	0.02	0.03	0.00	0.01	0.02	0.03	0.00	0.01	0.02	0.03
Total	100.03	100.05	100.07	100.10	99.98	100.01	100.04	100.07	99.81	99.86	99.92	99.98



Figure 8. Correlation coefficient patterns for Mg, Al, and Ca. Symbols as in Figure 7.

15%, 30%, and 45% trapped liquid of average 504B composition using the cumulus mineral proportions calculated by: (1) liquid-lineof-descent calculations, (2) Pearce element ratio analysis, and (3) least-squares-fit parent-daughter calculations (Table 7). Given that the most primitive magmas (aphyric, unaltered whole-rock compositions) from Hole 504B are approximately Mg# = 68, and that the average magma is approximately Mg# = 60.5, we can calculate that the average aphyric rock in the section has fractionated approximately 25% (TiO₂ = 0.72% at Mg# = 68 and 0.99% at Mg# = 60.5, fractionation = 27.6%; Y = 19 ppm at Mg# = 68 and 25 ppm at Mg# = 60.5, fractionation = 23.1%; Zr = 38 ppm at Mg# = 68 and 50 ppm at Mg# = 60.5, fractionation = 24.1%). Fraction of the observed 1726 m of basalt and diabase would require a minimum thickness of 573 m of gabbro at Site 504B if we assume 0% trapped liquid, or 1042 m of gabbro if we assume 45% trapped liquid.

The calculated residual gabbro derived from these calculations only represents the material necessary to account for the observed differentiation in the basalts and sheeted dikes in the upper 2 km of Hole 504B. The lower crustal section at Hole 504B is also likely to contain magmas that were injected into the crust and solidified in place, and some of these magmas may be more primitive than those observed in the upper part of the section. It is also possible that phenocryst-rich or xenocryst-rich magmas were intruded into the crust and contributed transported crystals to the lower crustal gabbros. The calculated gabbros, therefore, probably represent a minimum estimate; the lower crustal section at Hole 504B is probably thicker and more primitive than that calculated.

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REFERENCES*

- Alt, J.C., Honnorez, J., Laverne, C., and Emmermann, R., 1986. Hydrothermal alteration of a 1 km section through the upper oceanic crust, Deep Sea Drilling Project Hole 504B: mineralogy, chemistry, and evolution of seawater-basalt interactions. J. Geophys. Res., 91:10309–10335.
- Autio, L.K., and Rhodes, J.M., 1983. Costa Rica Rift Zone basalts: geochemical and experimental data from a possible example of multistage melting. *In* Cann, J.R., Langseth, M.G., Honnorez, J., Von Herzen, R.P., White, S.M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office), 729–745.
- Autio, L.K., Sparks, J.W., and Rhodes, J.M., 1989. Geochemistry of Leg 111 basalts: intrusive feeders for highly depleted pillows and flows. *In Becker*, K., Sakai, H., et al., *Proc. ODP, Sci. Results*, 111: College Station, TX (Ocean Drilling Program), 3–16.
- Bryan, W.B., 1986. Linked evolutionary data arrays: a logical structure for petrologic modeling of multisource, multiprocess magmatic systems. J. Geophys. Res., 91:5891–5900.
- Bryan, W.B., Finger, L.W., and Chayes, F., 1969. Estimating proportions in petrographic mixing equations by least-squares approximation. *Science*, 163:926–927.

^{*} Abbreviations for names of organizations and publications in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

- Cox, K.G., and Clifford, P., 1982. Correlation coefficient patterns and their interpretation in three basaltic suites. *Contrib. Mineral. Petrol.*, 79:268–278.
- Drake, M.J., 1976. Plagioclase-melt equilibria. Geochim. Cosmochim. Acta, 40:457–465.
- Fisk, M.R., Nielsen, R.L., Harvey, P.K., Pezard, P., and Laverne, C., 1992. Magma chamber size, mantle recharge, and eruption at Site 504B, Costa Rica Rift. *Eos*, 73:496.
- Grove, T.L., and Bence, A.E., 1977. Experimental study of pyroxene—liquidinteraction in quartz normative basalt 15597. Proc. Lunar Sci. Conf., 8:1549–1579.
- Kempton, P.D., Autio, L.K., Rhodes, J.M., Holdaway, M.J., Dungan, M.A., and Johnson, P., 1985. Petrology of basalts from Hole 504B, Deep Sea Drilling Project, Leg 83. In Anderson, R.N., Honnorez, J., Becker, K., et al., Init. Repts. DSDP, 83: Washington (U.S. Govt. Printing Office), 129–164.
- Natland, J.H., Adamson, A.C., Laverne, C., Melson, W.G., and O'Hearn, T., 1983. A compositionally nearly steady-state magma chamber at the Costa Rica Rift: evidence from basalt glass and mineral data, Deep Sea Drilling Project Sites 501, 504, and 505. *In* Cann, J.R., Langseth, M.G., Honnorez, J., Von Herzen, R.P., White, S.M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office), 811–858.
- Nicholls, J., and Russell, J.K., 1990. Pearce element ratios: an overview, example, and bibliography. *In Russell, J.K., and Stanley, C.R. (Eds.)*, *Theory and Application of Pearce Element Ratios to Geochemical Data Analysis.* Short Course Notes, Geol. Assoc. Canada, 8:11–21.
- Nielsen, R.L., 1985. EQUIL.FOR: a program for the modeling of low-pressure differentiation processes in natural mafic magma bodies. *Comput. Geosci.*, 11:531–546.

—, 1990. Simulation of igneous differentiation processes. In Nicholls, J., and Russell, J.K. (Eds.), Modern Methods of Igneous Petrology: Understanding Magmatic Processes. Mineral. Soc. Am., Rev. Mineral., 24:65–105.

Pearce, T.H., 1968. A contribution to the theory of variation diagrams. Contrib. Mineral. Petrol., 19:142–157.

—, 1990. Getting the most from your analytical data: applications of Pearce element ratio analysis. *In* Russell, J.K., and Stanley, C.R. (Eds.), *Theory and Application of Pearce Element Ratios to Geochemical Data Analysis.* Short Course Notes, Geol. Assoc. Canada, 99–130.

- Roeder, P.L., 1974. Activity of iron and olivine solubility in basaltic liquids. Earth Planet. Sci. Lett., 23:397–410.
- Roeder, P.L., and Emslie, R.F., 1970. Olivine-liquid equilibrium. Contrib. Mineral. Petrol., 29:275–289.
- Shipboard Scientific Party, 1992. Site 504. In Dick, H.J.B., Erzinger, J., Stokking, L.B., et al., Proc. ODP, Init. Repts., 140: College Station, TX (Ocean Drilling Program), 37–200.

Wright, T.L., and Doherty, P.C., 1970. A linear programming and least squares computer method for solving petrologic mixing problems. *Geol. Soc. Am. Bull.*, 81:1995–2008.

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APPENDIX

The slope on a Pearce element ratio diagram is equal to the change in the Y-axis numerator divided by the change in the X-axis numerator. Because these values are in cation percent, the effect of the addition or removal of the various possible fractionated minerals can be easily evaluated. In Figure 5B, Na/Ti vs. Al/Ti, the slope is equal to Δ Na/ Δ Al. Because plagioclase is the only phase with significant amounts of Na or Al, the change in Na is equal to the fraction of albite (Xab) in the crystallization assemblage, and the change in Al is equal to the fraction of albite (Xab) plus twice the fraction of anorthite (2 · Xan). Therefore:

slope = Xab/[Xab + $(2 \cdot Xan)$] = Xab/[Xab + $(2 \cdot (1 - Xab))$] = Xab/[2 - Xab]

or Value (2 alassa)/(1 to

 $Xab = (2 \cdot slope)/(1 + slope)$

If more than one mineral phase is involved, the number of cations in each phase must also be considered. In Figure 5A, $(2 \cdot Ca + Na)/Ti$ vs. Al/Ti, the slope is equal to $(2 \cdot \Delta Ca + \Delta Na)/\Delta Al$. Plagioclase and augite are the only phases with significant Ca, Na, or Al, but plagioclase has five cations per formula unit, and augite has only four. As a result, the change in Ca resulting from augite fractionation has to be multiplied by 5/4 so that the ratio of minerals obtained from the slope remains in cation percent. If we assume an augite composition of Ca_{0.67}[Fe + Mg]_{1.33}Si₂O₆, $\Delta Ca = (5/4 \cdot 2/3 \cdot Xcpx + Xan)$, $\Delta Na = Xab$, and $\Delta Al = (2 \cdot Xan + Xab)$. Therefore:

 $slope = [2 \cdot (5/4 \cdot 2/3 \cdot Xcpx + Xan) + Xab]/[2 \cdot Xan + Xab]$ $slope = [1.6667 \cdot Xcpx + 2 \cdot Xan + Xab]/[2 \cdot Xan + Xab]$

Normalizing to 1 Xcpx:

slope = $[Xcpx + 1.2 \cdot Xan + 0.6 \cdot Xab]/[1.2 \cdot Xan + 0.6 \cdot Xab]$

stope = $[Xcpx + 1.2 \cdot Xan + 0.0 \cdot Xab]/[1.2 \cdot Xan + 0.0 \cdot Xab]$ Replacing Xan with (1 - Xcpx)AN and Xab with (1 - Xcpx)AB and

rearranging:

 $Xepx = [(slope - 1) \cdot (1.2 \cdot AN + 0.6 \cdot AB)/[1 + (slope - 1) \cdot (1.2 \cdot AN + 0.6 \cdot AB)]$

where AN and AB refer to the anorthite and albite contents of the fractionated plagioclase (AN + AB = 1).