49. TRACE ELEMENT GEOCHEMISTRY OF BASALTS FROM HOLE 504B, PANAMA BASIN, DEEP SEA DRILLING PROJECT LEGS 69 AND 70¹

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ABSTRACT

Deep basement penetration during Legs 69 and 70 at Hole 504B in the Panama Basin allowed the recovery of a 561.5-meter sequence of basaltic pillows, thin flows, and breccias interspersed with thick massive flows. The lavas, which are aphyric to moderately plagioclase-olivine-clinopyroxene phyric, are petrologically indistinguishable from typical mid-ocean-ridge basalts (MORB). Some units are distinctive in that they carry accessory chrome-spinel micro-phenocrysts or emerald green clinopyroxene phenocrysts.

Major and trace element analyses were carried out on 67 samples using X-ray fluorescence techniques. The basalts resemble normal MORB in terms of major elements. However, the trace element analyses show that most of the basalts are characterized by very strong depletion in the more incompatible elements compared with, for instance, normal (N type) MORB from the Atlantic at 22°N. Interdigitated with these units are one or two units that have distinctly higher incompatible element concentrations similar to those in basalts of the transitional (T) type from the Reykjanes Ridge (63°N in the Mid-Atlantic Ridge).

All the basalts appear to have undergone some high-level crystal fractionation, although this has not proceeded to the extent of yielding ferrobasalts as it has at the adjacent Galapagos Spreading Center or along the East Pacific Rise. The magnetic anomalies are of lower amplitude than in the latter two regions, which suggests that the absence of ferrobasalts may be a general feature of the ocean crust generated at the Costa Rica Rift. The presence of two distinct magma types, one strongly depleted and the other moderately enriched in incompatible elements, suggests that magma chambers at the spreading center are discontinuous rather than continuous and that there is some chemical heterogeneity in the underlying mantle source. Observed variations in incompatible element ratios of basalts from the more depleted group could, however, reflect mixing between these two magma types. In general it would appear that the Mid-Atlantic Ridge.

INTRODUCTION

Legs 68, 69, and 70 of the Deep Sea Drilling Project were undertaken principally to study the problems of hydrothermal circulation in young oceanic crust. The deep penetration and good recovery of basaltic basement, particularly at Site 504, for these hydrothermal studies also provided the opportunity to study the igneous geochemistry and petrogenesis of the basalts in the Panama Basin. This part of the Panama Basin is floored by young ocean crust produced by spreading at the Costa Rica Rift (Fig. 1). The rift is a presently active ocean floor spreading center some 200 km long; it lies midway between the east-west-trending Carnegie Ridge and the northeast-southwest-trending Cocos Ridge and is approximately 500 km from the Colombian coast (Fig. 1). The Costa Rica Rift is the easternmost section of the Galapagos Rift System, which joins the East Pacific Rise at the Galapagos triple junction. The Costa Rica Rift is bounded on the west and east by the Ecuador and Panama fracture zones, respectively, two of several major transforms that form offsets on the Galapagos Rift System (Lonsdale and Klitgord, 1978).

Previous studies in this area of the eastern Pacific Ocean have established that the basalts that have erupted along the Cocos-Nazca Ridge, in the Galapagos Spreading Center, and along both the adjacent limbs of the East Pacific Rise are predominantly geochemically evolved basalts, in particular ferrobasalts (e.g., Clague and Bunch, 1976; Schilling et al., 1976; Vogt, 1979; Batiza and Johnson, 1980; Rosendahl et al., 1980). The ocean floor generated by spreading at these ridges is topographically smooth, with well developed high amplitude magnetic anomalies that are thought to reflect the presence of titanomagnetite-rich ferrobasalts (Anderson et al., 1975; Vogt, 1979; Vogt and Johnson, 1973). The Panama Basin is similarly floored by smooth ocean crust, with well developed magnetic anomalies up to 7.1 m.y. old and a moderate total spreading rate of 7.2 cm per yr. However, although the magnetic lineations in this basin are well developed, the magnetic anomalies are of lower amplitude than those associated with the presence of ferrobasalts.

During DSDP Legs 68, 69, and 70, eight holes were drilled at two different sites on the southern flank of the Costa Rica Rift. Sites 501 and 504 are essentially the same site, Site 504 being offset 0.5 km to the east of Hole 501. The sites are at 1°13.64'N, 83°43-89'W, approximately 250 km south of the Costa Rica Rift. They are on a negative magnetic anomaly between Anomalies 3A and 4 in ocean crust about 5.9 m.y. old. Five holes were drilled: Holes 501, 504, 504A, 504B, and 504C. Major basement penetration occurred in Hole 504B, in

¹ 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).



Figure 1. Location of drill sites from Legs 68, 69, and 70 plus previous DSDP drill sites in the vicinity of the Costa Rica Rift. Adapted from van Andel et al. (1973).

which 561 meters of basalt were cored. The basalt consisted of highly fractured pillows, flows, and breccias that were interspersed with massive flows. The overlying sediment was 264.5 meters deep and consisted mainly of pelagic siliceous oozes, chalks, limestones, and cherts. Site 505 is at 1°55.2'N, 83°47.3'W, almost 100 km north of Site 504 and between it and the Costa Rica Rift. Basement penetration and recovery were low at Site 505, and little material became available for detailed work.

This study concentrates on the characteristics of the material recovered from Hole 504B; initial shipboard petrographic and chemical data suggest that basalts from Sites 501 and 504 share the same petrographic and geochemical features, and recovery and penetration were better there than at other holes. The trace and minor element geochemistry of selected samples from Hole 504B is described, and within-hole chemical variations are evaluated with a view to developing an understanding of the genesis of the basalts.

IGNEOUS LITHOLOGY AND PETROGRAPHY OF HOLE 504B

The lithostratigraphy, igneous, and alteration petrographies of the basement section cored by Hole 504B are described in detail in the Site 504 chapter (this volume). The pertinent features are summarized below and in Figures 2 and 3. Three main petrographic groups of basalts are recognized:

1) Aphyric to moderately phyric plagioclase-olivine basalts, some with glomerophyric clumps of plagioclase and augite. Plagioclase is the most commonly observed phenocryst phase. The phenocrysts are generally small (0.2-0.7 mm long); however, a rare second population of slightly larger phenocrysts is present in some units. Compositional zoning is poorly developed, although resorption affects a few small phenocrysts.

2) Variably plagioclase-olivine phyric basalts with accessory chrome-spinel phenocrysts. The plagioclase phenocrysts often have well developed normal or oscillatory zoning; they often carry inclusions of glass and occasionally carry anhedral plagioclase laths. Olivine is found as phenocrysts or as granular or skeletal forms in the groundmass. Similarly, chrome-spinel phenocrysts are present as euhedral inclusions in plagioclase or olivine phenocrysts; skeletal varieties can also be found. Chrome-spinel is also present in the mesostasis.

3) Plagioclase-olivine-clinopyroxene phyric basalts. These basalts are notably more phenocryst rich (15-20% phenocrysts) than the other two petrographic types. Plagioclase phenocrysts with vaguely oscillatory zoned cores and more albitic rims are common. Rare glass inclusions and small anhedral plagioclase laths are found in plagioclase phenocrysts. Both plagioclase and the characteristic emerald green clinopyroxene crystals of this petrographic type commonly show signs of resorption.

Most of the basalt units described are aphyric to moderately plagioclase-olivine phyric; the chrome-spineland emerald green clinopyroxene-bearing basalts are less common. Vesicles are rare except in Lithologic Units 5 and 36 (Fig. 2); however, small, irregular miarolitic voids occur in some units.

The basalts are generally weakly to moderately altered. Clinopyroxene and plagioclase crystals are usually fresh in appearance, although clay minerals have been identified in the cleavage fractures of some plagioclase phenocrysts. The most noticeable alteration effects are the replacement of olivine and mesostasis by clay minerals. A scheme of nonoxidative alteration is inferred from the shipboard observations; it is charac-



Figure 2. Downhole variation in lithology, magnetic inclinations, and selected geochemical parameters for the basement section of Hole 504B cored during Leg 69.

terized by the replacement of olivine and filling of vesicles by saponite or (in regions of higher temperature) a talc-like mineral followed by Fe-Mg-rich smectites. Later stages of alteration appear to have taken place under oxidizing conditions, but the effects are more limited in extent than those of the earlier nonoxidative phase of alteration and result in the gradual conversion of smectite to iron oxyhydroxides and titanomagnetite to maghemite.

Pyrite, carbonates, and clay minerals can be found, especially in the chrome-spinel-bearing units, where some of the pyrite may be of primary igneous origin. Calcite appears to be limited to the units above 600 meters sub-bottom (Unit 27); below this unit pyrite is more abundant, particularly in vein fillings, and evidence for oxidative alteration diminishes.

The extent of alteration varies with lithology; the margins of pillow lavas and flows are more intensely altered than the more crystalline interiors, where observable alteration effects are generally limited to the areas immediately adjacent to fractures. Most of the samples analyzed in this study were selected from the relatively fresh pillow and flow interiors of the different units.

ANALYTICAL TECHNIQUES

Minicores or quarter-core sections were washed in distilled water to remove surface contamination and dried at 110° C overnight prior to being ground to a fine powder (less than 60 μ m) in an Agate TEMA swingmill. Powder briquettes 46 mm in diameter were made by binding 15 g of rock powder with about 20 drops of a 7% aqueous solution of polyvinyl alcohol under a pressure of 15 tons per square inch in a steel die with polished hardened surfaces. X-ray fluorescence (XRF) analysis was performed on the Leg 69 samples by using a Philips PW1450 automatic spectrometer with a PW1466 60 position sample changer. Count data from the spectrometer were processed by using a 32K Digital PDP 11-03 computer and the University of Birmingham's ICL 1906A computer. The major, minor, and trace elements were determined on the 46-mm briquettes using rhodium (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P on the major element program; Zr, Nb, Ni, and Cr on the trace element program), molybdenum (Y, Sr, Rb, Th, Pb, Ga, Zn, and Ba), and tungsten (Ce, La, and Nd) anode X-ray tubes. Instrumental repeatability was ensured by measuring a reference sample for major and minor elements after every fourth sample or at the beginning of every loading of 60 samples for trace elements.

Details of the analysis of major and minor elements using Rh anode excitation are given in Marsh et al. (1980). The analysis of trace elements (Y, Sr, Rb, Th, Pb, Ga, Zn, Ba) by Mo anode excitation and of Ce and La using W anode excitation is described in Tarney et al. (1979). For the analysis of the Leg 69 samples, Nd was added to the W anode program. The program used the L_{α} peak, a LiF₂₂₀ crystal, coarse collimation (0.55 mm), and a flow proportion detector (to measure argon/methane). The mutual overlap of Nd, L_{α} , and Ce L $\beta_{1, 4}$ was corrected. The remaining elements (Zr, Nb, Ni, and Cr) were determined by using Rh anode excitation, which provides improved sensitivity when compared with the W anode previously employed. Zr and Nb have a statistical lower limit of detection (2σ above background) of 0.15 ppm for a 100-s counting time; the previous limit of detection was 1 ppm. The practical limit of determination is still of the order of 1 ppm, however. The Rh tube was operated at 70 kV and 30 mA to excite the K_{α} wavelengths. Fine collimation (0.15 mm) and a LiF220 crystal were used, as well as the scintillation detector for Nb and Zr and the flow proportion detector for Cr and Ni.

Trace element calibrations were initially prepared from a wide range of rock types and pure silica spiked with an appropriate pure element compound (Leake et al., 1969). Total mass absorption was then corrected by using the Mo, K_{α} , and Rh K_{α} Compton scatter lines for elements with emission wavelengths shorter than the iron absorption edge (Reynolds, 1967). For the analysis of Cr, iron counts and Rh Compton intensity were used to estimate the absorption coefficients on

4	Core	Lithology	Unit	Petrography	1.0 Fe/Mg 1.8	Cr (ppm) 200 400	Zr (ppm) 30 90
	29	192-592	20	Aphyric		8	8
500-							
500	_	E CAN		plagioclase-			
	32		21	clinopyroxene		•	•
	33	00	22	Olivine-plagioclase			
	34		23	Chrome-spinel			
	35 36		24	Plagioclase-olivine	•	٠	•
	37 38		25	Chrome- spinel	•		•
-	39 40		27	Plagioclase—olivine	:	÷.	:
600-	41	200		Dia index allula		•	•
	43		28	Plagioclase—olivine	•	•	•
-	44		29	Plagioclase—olivine— clinopyroxene	٠	•	
	46		30	Plagioclase-olivine-	2	•	•
(m) 41	47	Breccia		clinopyroxene	•	•	•
om Dep	49		33	Plagioclase—olivine	•	•	•
Sub-bott	51 52 53		34	Plagioclase—olivine	•.	:	:
	54	393	-				98
700-	55 56		36	Vesicular, aphyric	•	•	•
-	57		37	Olivine		•	•
	58	Dike	38	Plagioclase-olivine		•	•
-	59	0 0	39	Plagioclase-olivine		•	
	61	Oer					
-	62		40	Plagioclase-olivine		•	
	63				•	•	•
_	64					•	•
	65 66		45	Plagioclase—olivine			•
800-		22365	46	Aphyric			
	67	F 3 2 3 A	47	Olivine- clinopyroxene			
-	69			Plagioclase-			
	70	र्ट्स्ट	48	clinopyroxene			
		74422					*



the long wavelength side of the iron absorption edge. For Zr, Nb, Ni, and Cr, the Rh Compton peak gave an improved estimate of the absorption coefficient when compared to the WL_{β} Rayleigh peak previously used. The peak is also clear of overlapping lines and is therefore superior to the Mo K_{α} Compton scatter lines, which must be corrected for Y interference. Ce, La, and Nd calibrations were obtained by using basalts previously analyzed by isotope dilution, because no improvement resulted from absorption corrections using tube scatter lines.

Trace element precision is high, as illustrated by Table 1, which shows the average concentrations of the internal reference BOB-1 measured on 23 consecutive days. However, a potential problem in projects that extend over a period of a year or more is long term drift in instrumental accuracy. This was minimized by using some 40 samples from Legs 49 and 58 together with other basaltic material that was selected to cover as wide a concentration range as possible for all the elements measured. These samples were analyzed together with the unknowns to ensure measurement consistency between different sample batches.

Trace element analyses on the Leg 70 samples were also performed on the Philips PW1450 spectrometer at the University of Birmingham using the techniques described above. However, major element analyses were performed on a Phillips PW1400 automatic X-ray spectrometer with a 72-position sample changer at the University of Leicester. Techniques similar to those described above were used to ensure consistency with the Leg 69 data. Count data from the PW1400 spectrometer were processed on line using a Phillips P851 minicomputer and X-14 software.

Values for the international reference samples BCR-1 and JB-1 are given in Table 1 to give some estimate of accuracy, although as yet basic reference materials do not cover the range of concentrations found in ocean-floor basalts.

Unfortunately, several of the trace elements in the Leg 69 and Leg 70 basalts have very low abundances that are close to, or lower than,

TRACE ELEMENT GEOCHEMISTRY OF BASALTS

Table 1. Analyses of standard reference samples.

a. Trace element analyses.

	Sample											
	BOB-1 ^a	BCR	JB-1	BOB-1								
Cr ^c (ppm)	251 ± 9	18	359	255								
Ni	103.4 ± 1.7	18	134	114								
Rb	4.8 ± 0.5	47	42	6								
Sr.	201.3 ± 0.9	329	442	197								
Y ^d	26.8 ± 0.4	36	23	25								
Zr ^e	108.5 ± 1.1	192	150	107								
Nb	4.8 ± 0.6	12	35	4								
Ba ^f	50.6 ± 3.4	690	500	53								
La	6.7 ± 1.0	25	38	3								
Ceg	14.9 ± 1.3	55	63	12								
Nd ^g	10.4 ± 0.9	28	20	10								
Pb	4.2 ± 1.3	16	10	6								
Th	0.2 ± 1.0^{h}	6	11	2								
Zn	62.2 ± 2.2	120	80	68								
Ga	17.5 ± 0.9	24	17	14								

^a Mean concentrations determined on 23 consecutive days, with 1σ standard deviation during this study (Univ. Birmingham).

- b Concentrations determined during this study (Univ. Leicester).
- ^c Not corrected for V interference.
- d Corrected for Rb interference.
- e Corrected for Sr interference.
- ¹ Corrected for Ce interference.
- ^g Corrected for mutual interference.
- h Below statistical lower limit of detection.

b. Major element analyses for BOB-1.

	Medium of Analysis								
	Powder Briquette ^a	Powder Briquette ^b	Fusion Bead ^C						
SiO ₂ (%)	50.9	50.8	51.02 ± 0.078						
TiO ₂	1.32	1.31	1.28 ± 0.004						
Al2O3	16.1	15.3	16.55 ± 0.012						
Fe2O3d	8.6	9.14	8.48 ± 0.013						
MnO	0.14	0.147	0.14 ± 0.001						
MgO	7.6	7.2	7.58 ± 0.030						
CaO	11.28	10.93	11.39 ± 0.027						
Na ₂ O	3.1	3.18	3.10 ± 0.074						
K2Õ	0.35	0.36	0.37 ± 0.003						
P205	0.128	0.141	$0.16~\pm~0.001$						
Total	99.52	98.51	100,07						

^a Values determined on a 46-mm-diameter powder briquette during this study (Univ. Birmingham).

b Values determined on a 46-mm-diameter powder briquette during this study (Univ. Leicester).

- ^c Mean anhydrous major element composition determined on six fusion beads with 1σ sigma standard deviation.
- d $\overline{Fe_2O_3}$ is total iron determined as Fe_2O_3 .

the theoretical lower limit of detection. At these low abundance levels, precision falls dramatically, and abundances near or below the lower limit of determination for a particular element should be treated with caution. The elements most affected are Nb (1 ppm), La (≈ 5 ppm), Ce (≈ 8 ppm), Nd (≈ 8 ppm), Pb (≈ 5 ppm), and Th (≈ 10 ppm).

We have not made a serious attempt to provide major element data by fusion techniques on the Leg 69 and Leg 70 samples. However, to provide additional data for interpreting our trace and minor element results, major element analyses were carried out on the powder briquettes. Fortunately, the samples have similar bulk chemistries, limiting potential variations to mineralogical effects. Al is expected to be the most aberrant element, as well as (to a lesser extent) Fe and Mg. For comparison, the various major element analyses performed on the internal reference sample BOB-1 are listed in Table 1.

TRACE AND MINOR ELEMENT TERMINOLOGY

Trace and minor elements may be either compatible or incompatible with respect to rock-forming minerals. For convenience in petrogenetic discussions, incompatible elements can be grouped semiguantitatively into less-hygromagmatophile (HYG) and more-hygromagmatophile types. Less-HYG elements are those with a bulk crystal/liquid distribution coefficient (D) of approximately 0.1. More-HYG elements have lower D values, often significantly less than 0.01. In the relatively anhydrous oceanic basalt systems, the more-HYG elements include (in order of increasing D) Cs, Rb, Ba, U, Th, K, Ta, Nb, La, and Ce. The less-HYG elements include Sr, Nd, P, Hf, Zr, heavy rare earth elements (HREE), Ti, and Y (Bougault et al., 1980; Bougault and Treuil, 1980; Saunders et al., 1980; Wood, Joron, et al., 1979). D values can vary according to the P-T-X conditions of the system considered; for example, during plagioclase crystallization, D values for Sr and Eu significantly increase and can exceed unity.

Trace and minor elements may also be grouped according to their ionic character. Large ions with low charge and ions with the ability to form hydration spheres (giving a low effective charge density) have been termed large ion lithophile (LIL) (Schilling, 1973) or low field strength ions (LFS) (Saunders et al., 1980). They include Cs. Rb. K. Ba. U. Th. and Sr. and to a lesser extent La and Ce. Several of these elements are easily mobilized during hydrothermal or ambient seawater alteration, particularly Cs, Rb, K, and U (Hart, 1971; Hart et al., 1974; Mitchell and Aumento, 1977). During extensive halmyrolysis, even La, Ce (Luddon and Thompson, 1979) and possibly Th are mobilized. Small ions with high charges are termed high field strength (HFS) ions and include Ta, Nb, P, Zr, Hf, the HREE, Ti, and Y. They are generally less susceptible to alteration processes and hence more likely to reflect igneous abundances (Pearce and Norry, 1979). These classifications are arbitrary, of course, because variations in both D values and charge density are gradational (Saunders et al., 1980).

RESULTS

The results of the chemical analyses are listed in Tables 2 and 3. All the basalts are similar in terms of major element chemistry, with 7.5 to 9.5% MgO, 9 to 11%total iron (as Fe₂O₃), and low Fe/Mg ratios. Figures 4 and 5 illustrate some of the main features of the major element chemistry. Although Fe/Mg ratio varies to some extent with alteration, it is still useful as a parameter for illustrating major element variations, especially for fresher material.

MgO and total iron (Fe_2O_3) contents correlate well with Fe/Mg, and apart from the samples from Lithologic Unit 1 (solid circles, Fig. 4), scatter is limited. CaO and Na₂O contents appear to be reasonably constant

Core	3	4	5	7	7	8	9	10	11	12	13	14	15	16	16	17	18
Section	1	2	2	2	4	2	1	2	2	2	2	1	3	3	4	1	1
Interval (cm)	131-134	114-117	68-71	27-30	84-87	84-87	48-51	26-29	134-138	65-69	109-112	144-148	108-112	45-50	14-19	57-61	63-66
Piece	257	307	379	454	502	530	572	629	693	736	782	858	972	992	1004	1039	1089
SiO ₂ (%)	48.8	49.6	50.1	49.5	49.4	48.1	49.5	47.9	49.0	50.6	49.7	49.0	49.5	50.3	49.1	47.7	49.9
TiO ₂	1.15	0.89	0.89	0.92	0.90	0.88	0.89	0.98	0.99	1.01	1.02	0.94	0.97	1.03	0.95	0.92	1.28
Al ₂ O ₃	14.6	15.4	15.8	15.8	15.5	15.8	15.8	14.1	14.8	15.2	15.3	14.7	15.1	15.4	15.4	14.2	15.6
Fe2O3a	12.2	9.8	9.8	9.9	9.2	8.5	9.1	9.6	10.2	9.0	9.1	10.7	9.8	9.6	9.4	9.2	9.6
MnO	0.18	0.19	0.17	0.17	0.21	0.15	0.17	0.15	0.17	0.18	0.15	0.18	0.17	0.16	0.19	0.15	0.17
MgO	8.8	9.2	8.2	8.5	8.5	8.6	9.0	8.3	8.1	9.0	8.6	8.1	8.4	8.8	9.5	9.1	8.9
CaO	11.84	12.55	12.78	12.71	12.49	12.13	12.61	12.21	12.13	12.41	12.23	12.30	12.31	12.30	12.19	11.98	11.83
NapO	2.21	2.05	2.08	2.21	2.08	2.15	2.00	2.08	2.13	2.23	2.42	2.03	2.04	2.17	2.10	1.78	2.39
K2Ô	0.111	0.027	0.133	0.080	0.004	0.005	0.007	0.136	0.328	0.127	0.174	0.233	0.253	0.128	0.140	0.074	0.399
P205	0.088	0.045	0.040	0.048	0.045	0.064	0.004	0.046	0.054	0.051	0.063	0.048	0.054	0.062	0.065	0.057	0.148
Total	99.98	99.75	99.99	99.84	98.33	96.38	99.12	95.50	97.90	99.81	98.78	98.23	98.60	99.95	99.03	95.16	100.22
Ni (ppm)	66	136	138	122	139	123	151	107	83	122	93	97	104	100	175	173	103
Cr	194	405	424	403	383	378	395	325	309	324	337	297	279	273	426	447	326
Zn	84	64	66	73	67	61	68	68	66	74	71	73	72	77	66	67	64
Ga	15	14	15	15	14	14	14	14	14	15	13	14	13	14	13	14	14
Rb	4	2	4	2	2	1	2	4	8	4	5	5	6	4	3	1	8
Sr	75	65	70	64	59	61	66	74	75	76	77	61	62	65	84	87	156
Y	28	22	25	23	22	22	21	24	23	24	24	24	24	25	23	23	26
Zr	53	44	46	47	46	43	45	50	49	50	50	43	45	45	53	54	89
Nb	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	10
Ba	12	6	7	9	5	9	6	3	3	15	8	8	5	<1	2	9	51
La	1	<1	<1	1	<1	<1	1	1	<1	<1	<1	1	<1	<1	<1	1	6
Ce	5	<1	<1	2	1	5	1	3	5	5	5	2	4	6	7	6	16
Nd	7	4	4	4	4	5	4	6	5	6	6	5	5	6	6	6	10
Pb	2	<1	4	<1	3	1	<1	2	2	<1	<1	2	2	<1	1	3	2
Th	<1	<1	2	2	1	<1	2	<1	<1	1	<1	<1	2	<1	<1	3	3
Fe/Mg	1.61	1.23	1.38	1.34	1.25	1.14	1.16	1.34	1.47	1.16	1.22	1.52	1.36	1.26	1.16	1.17	1.25
Zr/Nb	_		_		-	_			· · · · · ·		-		-	_	- <u>-</u>	-	8.9
Ti/Zr	130	121	116	117	117	123	119	117	121	121	122	131	129	137	107	102	86
CeN/YN	0.4		- 19 A	0.2	0.1	0.5	0.1	_	_	_	—		-		—	—	1.4
Lithologic Unit	1	2	2	2	2	2	2	3	3	3	3	3	3	3	4	4	5

Table 2. Analyses and element ratios for basalts from Hole 504B recovered during Leg 69.

^a Fe₂O₃ is total iron determined as Fe₂O₃.

Table 3. Analyses and element ratios for basalts from Hole 504B.

Core	32	33	34	36	37	38	39	40	41	41	42	43	44
Section	1	1	1	1	2	2	2	4	4	3	2	2	2
Interval (cm)	109-111	26-28	20-22	84-87	142-148	64-66	118-121	127-129	82-85	102-104	83-86	7-9	80-83
Piece	150	184	221	229	387	438	494	574	589	624	669	694	728
SiO ₂ (%)	49.0	49.2	49.0	48.3	47.0	47.2	47.9	47.5	47.0	47.5	47.8	48.1	48.7
TiO ₂	0.92	0.95	0.97	0.92	0.88	0.90	0.83	0.79	0.78	0.96	0.95	0.87	0.90
Al ₂ O ₃	14.8	15.2	14.7	14.5	12.7	13.5	15.6	15.8	15.7	14.9	14.7	14.8	14.6
Fe ₂ O ₃ ^a	10.7	10.2	10.3	10.3	11.1	11.1	9.6	9.2	9.2	10.3	9.96	10.2	10.5
MnO	0.18	0.16	0.17	0.15	0.17	0.17	0.15	0.14	0.14	0.15	0.15	0.15	0.16
MgO	7.9	8.8	8.5	8.0	7.5	7.3	8.5	8.3	8.4	6.9	8.0	8.5	7.7
CaO	12.48	12.42	12.37	11.89	12.50	12.83	12.23	12.16	11.96	12.05	11.90	11.82	12.33
Na ₂ O	1.881	2.08	2.20	2.07	1.78	1.96	2.01	1.89	1.89	2.17	2.13	2.08	2.09
K2Õ	0.200	0.109	0.139	0.018	0.107	0.048	0.025	0.023	0.022	0.015	0.023	0.017	0.013
P205	0.078	0.081	0.082	0.082	0.062	0.056	0.072	0.069	0.068	0.076	0.078	0.072	0.062
Total	98.14	99.20	98.43	96.23	93.80	95.06	96.92	95.87	95.16	95.02	95.69	96.61	97.05
Ni (ppm)	112	154	158	97	92	112	123	136	151	101	105	110	117
Cr	293	418	404	303	367	357	370	356	398	314	335	344	371
Zn	77	68	69	72	73	73	63	63	62	62	67	71	70
Ga	15	15	15	15	15	16	15	16	15	15	17	15	16
Rb	3	3	2	<1	1	<1	<1	<1	1	1	1	1	1
Sr	53	80	86	60	61	60	65	61	61	59	60	57	59
Y	22	21	22	24	24	25	20	19	19	22	25	24	21
Zr	39	51	53	44	42	42	39	36	37	43	42	40	40
Nb	<1	1	1	<1	<1	<1	1	1	1	1	1	1	1
Pb	1	1	<1	<1	1	<1	2	3	1	1	1	1	2
Th	<1	<1	<1	2	<1	2	<1	3	1	2	1	2	1
Fe/Mg	1.57	1.35	1.40	1.50	1.72	1.77	1.31	1.29	1.27	1.74	1.44	1.39	1.58
Zr/Nb		51	53	-			39	36		43	42		-
Ti/Zr	141	112	110	125	126	128	128	132	126	134	136	130	135
Lithologic Unit	21	22	22	24	25	25	27	27	27	27	28	28	29

^a Fe₂O₃ is total iron determined as Fe₂O₃.

Table 2. (Continued).

19	19	19	21	21	21	21	21	25	27	27	28	28	28	28	28	29	29
00.04	2 5	70 7	64 66	27 20	22.25	100 100		02.07	76 70	20 42	22.26	22.25	22 27	16.10	4 127 129	88 01	172 127
1125	1132	1143	1187	1203	1203	1216	1265	1412	1468	1480	1489	1505	1505	1522	1533	1542	123-127
49.5	49 7	50.2	48 7	50.04	49.1	50.4	49.2	48.2	49.4	49.2	49.9	49.8	49.0	49.4	48.6	48.9	49.9
1.32	1.00	1.36	1.04	1.01	1.02	0.75	0.81	1.00	1.02	1.07	1.05	0.98	0.98	0.98	0.98	1.02	0.97
15.0	15.7	14.9	14.7	14.9	14.8	16.9	14.1	13.5	14.9	15.6	15.2	14.6	14.8	15.1	14.7	14.5	15.7
93	8.8	97	10.5	10.4	10.4	8.9	10.5	10.6	10.5	10.1	10.2	10.5	10.1	10.2	10.3	10.4	10.5
0.21	0.15	0.19	0.15	0.21	0.18	0.16	0.18	0.20	0.16	0.16	0.18	0.17	0.17	0.19	0.18	0.20	0.19
9.0	9.2	8.6	8.5	8.4	8.2	8.5	8.9	8.0	7.8	8.6	8.5	8.5	7.9	7.8	7.3	8.7	8.1
12.54	12.04	12 47	12 11	12 27	12 25	13 27	12.97	12.40	12 12	11.84	12.80	12 72	12.09	12 79	12 53	12 37	12.86
2.19	2.14	2.24	2.18	2.26	2.335	1.98	1 78	1 99	2.26	2 41	2.127	2.08	2.06	2.01	2.02	2.17	2.00
0.134	0.094	0.158	0.110	0.171	0.113	0.068	0.069	0.100	0.441	0 191	0.095	0.136	0.247	0.115	0.262	0.102	0.147
0.140	0.057	0.174	0.089	0.055	0.095	0.037	0.056	0.042	0.058	0.088	0.073	0.072	0.055	0.069	0.076	0.066	0.079
99.33	98.88	99.99	98.08	99.72	98.49	100.96	98.56	96.03	98.66	99.26	100.12	99.56	97.40	98.65	96.95	98.43	100.45
122	155	122	96	108	92	120	123	96	77	79	183	145	118	143	106	92	85
327	481	343	374	298	376	358	358	283	272	372	374	253	228	267	281	271	263
66	70	75	65	81	69	65	63	71	71	64	69	75	75	67	70	70	69
14	15	15	15	14	15	15	13	12	13	15	15	15	14	15	14	14	15
3	2	2	3	5	3	2	2	3	9	5	2	3	6	2	5	3	5
176	94	170	96	67	94	57	54	67	67	95	108	52	51	57	60	68	61
26	23	32	24	28	25	19	23	25	25	25	26	25	23	26	25	25	26
98	55	90	55	53	56	32	34	50	49	59	59	40	42	44	42	49	45
13	<1	11	1	<1	1	<1	<1	<1	<1	<1	1	1	<1	<1	<1	<1	<1
64	12	n.d.	n.d.	8	n.d.	2	n.d.	4	5	10	n.d.	n.d.	5	n.d.	n.d.	8	n.d.
6	1	n.d.	n.d.	<1	n.d.	<1	n.d.	1	<1	1	n.d.	n.d.	1	n.d.	n.d.	1	n.d.
18	4	n.d.	n.d.	5	n.d.	5	n.d.	n.d.	3	2	n.d.	n.d.	5	n.d.	n.d.	4	n.d.
12	6	n.d.	n.d.	6	n.d.	6	n.d.	6	7	6	n.d.	n.d.	5	n.d.	n.d.	7	n.d.
3	1	1	<1	<1	<1	1	4	2	1	2	1	-	1	2	<1	3	<1
3	<1	2	<1	1	<1	<1	<1	1	<1	<1	1	1	2	<1	<1	1	2
1.30	1.10	1.31	1.43	1.43	1.48	1.22	1.37	1.54	1.56	1.36	1.39	1.43	1.47	1.52	1.64	1.39	1.50
7.5		8.2	55	—	56	-	-	-			59	40	—	—	-	-	
81	109	90	113	114	109	140	143	120	125	109	107	147	140	134	140	125	130
1.6	0.4	_	-	0.3		0.6	-	-	0.3	0.2		_	0.5	_	-	0.4	-
5	6	7	9	9	9	9	15	17	17	18	18	19	19	19	19	20	20

Table 3. (Continued).

46 1	47 2	49 2	51 1	52 2	55 1	57 1	58 1	60 1	62 1	63 2	64 2	66 2	70 2
74-76	123-126	83-85	113-115	89-92	98-101	88-91	115-116	37-40	94-97	118-121	28-32	25-28	19-21
775	835	946	985	1017	1092	1140	1203	1259	1325	1371	1424	1509	1564
47.4	48.5	49.4	49.1	48.2	49.8	49.9	49.6	48.5	48.4	47.8	48.4	48.0	48.3
0.92	1.02	0.89	0.83	0.86	1.41	1.02	0.93	1.06	1.03	0.98	1.18	1.0	0.90
13.0	13.8	14.6	15.7	15.4	14.4	14.4	15.7	14.3	13.7	13.6	13.8	13.6	14.8
10.9	11.1	10.8	9.7	9.7	11.0	10.4	10.5	10.7	11.8	11.2	11.8	10.9	10.2
0.18	0.15	0.18	0.15	0.15	0.20	0.16	0.17	0.16	0.17	0.17	0.18	0.19	0.1
7.3	6.9	8.3	9.0	8.1	8.9	9.3	7.8	7.9	7.0	8.3	6.4	8.0	9.2
12.57	11.17	12.74	12.86	12.70	11.87	12.46	12.7	11.80	13.03	12.08	11.35	12.38	12.49
1.90	2.02	1.95	1.95	2.01	2.41	2.10	2.01	2.11	1.68	1.75	2.04	1.8	1.80
0.007	0.014	0.028	0.016	0.019	0.034	0.013	0.013	0.022	0.015	0.016	0.021	0.004	0.011
0.057	0.088	0.062	0.067	0.077	0.138	0.070	0.076	0.094	0.063	0.063	0.102	0.071	0.070
94.23	94.76	98.95	99.37	97.22	100.16	99.82	99.50	96.67	96.89	95.96	95.27	96.04	97.94
92	82	89	116	113	91	129	93	97	132	127	69	107	142
305	133	254	352	347	254	328	262	278	313	303	143	307	443
75	84	71	64	64	75	69	68	73	82	77	84	78	68
16	17	16	17	16	18	16	16	15	16	15	18	16	15
1	1	1	1	1	<1	<1	<1	1	<1	1	<1	1	2
63	53	48	61	62	107	77	56	70	50	51	57	67	60
23	26	23	21	22	32	23	23	24	29	27	29	23	20
45	45	38	38	39	98	51	41	53	52	49	56	47	41
1	1	1	1	1	3	1	<1	1	<1	<1	1	<1	<1
1	1	3	1	1	4	2	<1	<1	1	1	<1	4	3
1	1	2	2	2	1	3	1	3	1	3	2	2	3
1.74	1.86	1.50	1.25	1.39	1.43	1.30	1.57	1.57	1.96	1.56	2.14	1.59	1.29
	45	-		_	33	51	_	53			56	-	-
123	136	140	131	132	86	120	136	120	119	120	126	127	132
30	30	33	34	34	36	37	38	39	40	40	43	45	49



Figure 4. Fe/Mg variation diagram of selected major and trace elements for samples from Leg 69. Symbols for lithologic units as in Figure 2.

with changing Fe/Mg except for Lithologic Unit 2 (open circles, Fig. 4), where CaO content seems to rise with increasing Fe/Mg. The decrease in Ni content with increasing Fe/Mg, with considerable overlap between the various units, suggests a general compositional consanguinity. Differences in chemistry between the lithologic units are revealed, however, by variations in trace and minor element abundances. For similar Fe/Mg ratios, TiO₂ contents cover a significant range. Samples from Lithologic Units 5, 7, and 36 (triangles and pluses, Fig. 4; designated datum, Fig. 5) have the highest TiO₂ contents, and those from Lithologic Unit 27 (Fig. 5) generally have the lowest, although one sample from Lithologic Unit 9 (solid triangle, Fig. 4) also has a very low TiO₂ content. That sample also has high Al₂O₃ and CaO contents suggestive of plagioclase accumulation.

Trace and minor element variations are illustrated by using Zr as an index of fractionation. Zr is particularly useful in this respect. It has a low bulk distribution coefficient in ocean-ridge basalt systems and appears to be immobile during the hydrous alteration of basalts. In addition, it is easily determined with high precision by XRF techniques (Tarney et al., 1979) (Figs. 6-11). TiO₂, Y, and particularly Sr exhibit strong colinearity with

Zr, even when the small number of samples and limited concentration ranges within most units are considered. Samples from Lithologic Units 5 and 7 (open triangles and pluses) have higher concentrations than most units of Zr, Ti, and Sr, as well as a higher Sr/Zr ratio, but lower Ti/Zr and Y/Zr ratios and only a small increase in Y concentration. Although the sample from Lithologic Unit 43 also has higher TiO₂, Zr, and Y contents and lower Ti/Zr and Y/Zr ratios than samples from most of the other units, no increase in Sr concentration or Sr/Zr ratio is apparent. Less marked differences in these trace element ratios are also seen between the other units. These differences are more clearly apparent in the Leg 69 data, where on average a larger number of samples per unit were analyzed. Unit 6 (asterisks) and the chrome-spinel-bearing units (Units 2, 4, and 18; open circles, open squares, and inverted open triangles) have slightly lower Ti/Zr and Y/Zr ratios than the aphyric to sparsely phyric units, whereas their Sr/Zr ratios are marginally higher on average.

The concentrations of La, Ce, and Nd are, apart from those of Unit 5 (and, we suspect, Lithologic Unit 7), very low. A plot of Ce versus Y (Fig. 12) shows considerable scatter, most of which is due to poor analytical



Figure 5. Fe/Mg variation diagram of selected major and trace elements for samples from Leg 70. For clarity, only lithologic units mentioned in the text are labelled.

precision for these low abundances. Nevertheless, the consistently low Ce concentrations and low chondritenormalized Ce/Y ratios suggest strong depletion in light rare earth elements (LREE). Lithologic Unit 5 samples (open triangles), however, appear to have LREE-enriched chondrite-normalized rare earth element (REE) patterns. Similarly, Nb concentrations in samples from all the units except Lithologic Units 5 and 7 are very low, generally less than 1 ppm, and the Zr/Nb ratios are correspondingly high (\approx 50). However, basalts from Lithologic Units 5 and 7 are distinctive in having 10 to 13 ppm Nb and Zr/Nb ratios of approximately 8.

Chemical differences between the lithologic units are not restricted solely to incompatible trace elements. Whereas Cr contents decrease with increasing Fe/Mg ratio (Fig. 13), the higher Cr contents of the chromespinel-bearing units of Lithologic Unit 6 are clearly apparent in Figure 13. Additional analyses of samples from Sites 504 and 505 are listed in Table 4.

ALTERATION EFFECTS

Before evaluating the igneous variations between the samples from Hole 504B, the possible effects of altera-

tion on the basalt chemistry need to be assessed. The LIL elements Rb, K, and to a lesser extent Ba and Sr are the most susceptible to alteration. A plot of K₂O versus an alteration-resistant element such as Zr (Pearce and Cann, 1971) (Fig. 14) exhibits considerable scatter, suggesting that K₂O contents in many samples have been modified by secondary processes. Rb abundances have been similarly affected, but Rb and K₂O contents still appear to co-vary with a K/Rb ratio of approximately 400 (Fig. 15), a feature possibly more characteristic of hydrothermal than of low-temperature alteration (halmyrolysis). Some of the scatter at very low values of K_2O (<0.05%) and Rb (<1 ppm) (as well as in the Ba data for <10 ppm, not shown) reflects low analytical precision. Sr appears to have been unaffected by alteration and still represents original igneous abundances, as indicated by the good positive correlation with Zr within most units (Figs. 10 and 11).

Generally, HFS ions are alteration resistant (Pearce and Cann, 1971; Pearce and Norry, 1979), and the good coherence between Zr, Ti, and Y concentrations (Figs. 6-9) supports this observation. Similarly, Cr and Ni (not shown) appear to have been unaffected, the Ni contents



Figure 6. Ti versus Zr for samples from Leg 69. Symbols for lithologic units as in Figure 2.



Figure 7. Ti versus Zr for samples from Leg 70.



Figure 8. Y versus Zr for samples from Leg 69. Symbols for units as in Figure 2.

of Unit 1 being an exception. P_2O_5 (Fig. 16) is also commonly assumed to be alteration resistant, although Marsh et al. (1980) found that P_2O_5 content was modified by alteration processes in the crystalline interiors of pillow lavas. This may well explain the scatter of the P/Zr ratios within individual units, as in Lithologic Units 1 and 2 (solid and open circles), for example. The P_2O_5 and Sr data probably reflect mineralogical control; the Sr is held in plagioclase, whereas in less crystalline samples P_2O_5 is held in the mesostasis and is more readily mobilized.

Changes in major element chemistry are less easily assessed. Most of the samples analyzed are from the least altered sections of flow or pillow interiors. Petrographically, the major alteration features are the partial to total replacement of olivine and the mesostasis, plus some filling of vesicles by clays. These features indicate that Fe, Mg, and Si have been mobile (Floyd and Tarney, 1979; Pritchard et al., 1979; Site 504 chapter, this volume). The good correlations between Fe/Mg and total iron or MgO contents; the general rise in Fe/Mg ratio with increasing TiO₂; and the falling Ni and Cr contents (Figs. 4, 5, and 13) suggest that although Fe and Mg may have been mobile, the major element data can still provide qualitative estimates of the original igneous compositions.



Figure 9. Y versus Zr for samples from Leg 70.



Figure 10. Sr versus Zr for samples from Leg 69. Symbols for units as in Figure 2.



Figure 11. Sr versus Zr for samples from Leg 70.



Figure 12. Ce versus Y for samples from Leg 69. Ce_N/Y_N indicates chondrite-normalized Ce/Y ratios (approximately equivalent to Ce_N/Ho_N). Symbols for units as in Figure 2.

DISCUSSION

Comprehensive studies of basalts from the North Atlantic Ocean have illustrated the chemical variability of the magmas being erupted at the mid-ocean ridges (e.g., Schilling, 1973; Hart et al., 1973; White et al., 1976; Rhodes et al., 1979; Bougault et al., 1979; Bougault and Treuil, 1980; Tarney et al., 1979; and Wood, Tarney, et al., 1979). On the basis of these studies three main ba-



Figure 13. A. Cr versus Fe/Mg for samples from Leg 69. B. Cr versus Zr for samples from Leg 69 showing the higher Cr contents of the chrome-spinel-bearing units and Lithologic Unit 6 plus the limited concentration ranges within individual units. Symbols for units as in Figure 2.

salt types characterized by different HYG element and isotope ratios have been defined (Sun et al., 1979; and Tarney et al., 1980). They are:

1) Normal or N type MORB (deleted tholeiitic oceanridge basalt), with low initial ⁸⁷Sr/⁸⁶Sr ratios (0.7023– 0.7027, Hart et al., 1973); high ¹⁴³Nd/¹⁴⁴Nd ratios (0.5131–0.5133, DePaolo and Wasserburg, 1976, and O'Nions et al., 1977); and low abundances of HYG elements, particularly the more-HYG elements, giving low ratios of more- to less-HYG elements compared to chondritic values.

2) Enriched or E type MORB (tholeiitic and alkalic ocean-ridge basalts), with moderate to high initial ⁸⁷Sr/ ⁸⁶Sr ratios (0.7027–0.7035, White et al., 1976); ¹⁴³Nd/ ¹⁴⁴Nd ratios of less than 0.5131 (O'Nions et al., 1977); high abundances of more-HYG elements; and high ratios of more- to less-HYG elements.

3) Transitional or T type MORB (tholeiitic ocean ridge basalt), with isotopic and HYG element characteristics intermediate between the N and E type MORB.

Representative analyses and selected ratios for each type of MORB are listed in Table 5 and illustrated in Figure 17.

A comparison of the data from Hole 504B with the different types of MORB illustrates some of the main geochemical features of these basalts. Although in terms of major element composition the basalts from Hole 504B are similar to N type MORB from the Mid-Atlantic Ridge (MAR 22°N), their HYG element abundances are in general lower (e.g., $Zr \sim 50$ ppm, Nb < 1 ppm, $TiO_2 < 1\%$; see Table 2). High values for Zr/Nb (≈ 50), Ti/Zr (≈ 120 , Figs. 6 and 7), Y/Zr (≈ 0.5 , Figs. 8 and 9), and low values of Ce/Y ratios (<0.5 when chondrite

normalized, Fig. 12) suggest that not only are the abundances of the HYG elements low but that the more-HYG elements are more severely depleted relative to the less-HYG elements than in N type MORB from MAR 22°N. This feature is clearly illustrated in Figure 17, where selected elements in representative samples have been normalized to the composition of the N type MORB from MAR 22°N. The elements are plotted in order of increasing estimated D values for typical mantle mineral assemblages (Mattey et al., 1980).

Samples from most of the units exhibit the progressive depletion of the alteration-resistant more-HYG elements (Nb, La, Ce, and Sr) in comparison to the less-HYG elements (Ti and Y). The depletion of the more-HYG elements is less marked in Lithologic Unit 4, whereas Lithologic Unit 5 appears to be identical to the T type MORB example, exhibiting progressively greater enrichment of Ce, La, Nb, and to a lesser extent Sr. Even if the reduced analytical precision for Nb, La, and Ce due to their low abundances in the more depleted units is taken into account, the element distribution patterns suggest that Lithologic Units 5 and 7 have significantly different more-HYG element ratios than the other units—Nb/La ratios of ≈ 2 and ≈ 1 , respectively, for example, and La/Ce ratios of ≈ 0.4 and ≈ 0.2 . Nonetheless, a general feature of all the samples from Hole 504B is their low Ti and Y contents compared to N type MORB, which has a similar Fe/Mg ratio and similar Ni, Cr, total iron, and MgO contents.

Detailed quantitative modeling of the possible chemical relationships between the units will have to await the acquisition of high precision data for other alterationresistant more-HYG elements. However, the present

Hole 504A 504A 505B 505 505B Core 24 6 7 3 6 Section 1 3 2 1 1 Interval (cm) 90-93 53-55 63-65 109-112 46-49 19 Piece 66 91 118 210 SiO2 (%) 48.1 49.3 49.5 48.8 49.4 TiO₂ 1.10 1.15 0.67 0.93 0.93 Al203 14.4 14.4 17.0 15.6 15.6 Fe2O3a 10.6 11.6 7.5 9.4 9.1 MnO 0.20 0.19 0.14 0.15 0.15 MgO 7.6 8.1 87 92 94 CaO 12.17 12.59 11.89 12.35 12.38 Na₂O 2.09 2.23 1.92 2.13 2.22 K₂Ō 0.245 0.169 0.058 0.049 0.066 P205 0.074 0.031 0.037 0.037 Total 96.32 99.18 98.22 99.27 98.66 Ni (ppm) 76 144 199 164 169 Cr 181 189 473 381 380 Zn 79 77 50 66 64 Ga 15 15 13 14 13 Rb 4 2 1 4 2 69 76 Sr 70 82 76 Y 28 28 16 24 25 Zr 54 53 52 37 53 Nb 1 < 1< 1< 11 Ba 8 11 18 10 6 La <1 2 1 <1 1 Ce 3 6 2 4 6 Nd 4 6 7 3 6 Pb <1 4 1 <1 2 Th <1 1 2 <1 1 Fe/Mg 1.62 1.66 0.99 1.19 1.12 Zr/Nb 54 53 Ti/Zr 122 130 109 107 105 0.2 CeN/YN 0.5 0.3 0.4 0.5

Table 4. Analyses and element ratios for basalts from Leg 69.

^a Fe₂O₃ is total iron determined as Fe₂O₃.

0.5 0.4 0.3 0.2

Figure 14. K_2O versus Zr for samples from Legs 69 and 70. Symbols for lithologic units for the Leg 69 samples as in Figure 2. Leg 70 samples are represented by small dots.



Figure 15. Rb versus K₂O for samples from Legs 69 and 70. Sample identification as in Figure 14.



Figure 16. P₂O₅ versus Zr for samples from Leg 69. Symbols for units as in Figure 2.

body of data still places a number of constraints on the mechanisms involved in producing these basalts.

Closed system fractional crystallization acting on a single magma or several magmas of similar composition cannot produce the observed differences in HYG element ratios between Units 5 and 7 and the other units. Units 5 and 7 have the highest more-HYG element abundances but still have lower Fe/Mg ratios and higher Cr and Ni contents than many other units. Closed system fractionation is also unlikely to produce the differences in Ti/Zr ratio that appear in the different depleted

	Basalt Type								
	Na	Tb	Ec						
SiO ₂ (%)	50.0	49.3	45.1						
TiO ₂	1.60	1.74	2.78						
Al2O3	16.20	14.01	12.71						
Fe2O3d	10.20	12.13	12.97						
MnO	_	0.19	0.16						
MgO	7.70	8.09	12.57						
CaO	11.30	11.65	8.76						
Na ₂ O	2.80	2.30	3.48						
K2Õ	0.22	0.18	1.80						
P205	1.25	0.22	0.81						
Ni (ppm)	138	106	342						
Cr	290	317	310						
Rb	1	4	36						
Sr	136	103	830						
Y	35	35	24						
Zr	88	110	281						
Nb	2.5	13	62						
Ba	12	70	460						
La	3	6	45.5						
Ce	10	19	93						
Fe/Mg	1.53	1.74	1.20						
Zr/Nb	35	8	4.5						
Ti/Zr	109	95	59						
CeN/YN	0.70	1.33	9.5						

Table 5. Representative analyses of different types of MORB from the Mid-Atlantic Ridge.

^a N type MORB from MAR 22°N (val-

ues compiled by Tarney et al., 1981). b T type MORB from Reykjanes Ridge

(values from Unit 409-3, Wood, Tar-

ney, et al., 1979). ^C E type MORB from Iceland, Sample ISL 79 (values from Wood, Joron, et

al., 1979). d Fe₂O₃ is total iron as Fe₂O₃.

units. Specifically, Lithologic Units 2 and 4 have higher Cr and Ni contents and lower Ti/Zr and Fe/Mg ratios than Lithologic Units 1 and 3. Crystal fractionation of the observed phenocryst phases (chrome spinel, plagioclase, olivine, and, more rarely, clinopyroxene) would be expected to leave the Ti/Zr (and Y/Zr) ratios unchanged or slightly reduced (Tarney et al., 1979).

Open system fractional crystallization as proposed by O'Hara (1977) provides a mechanism for preserving major element abundances while increasing both HYG element abundances and more-HYG/less-HYG element ratios, particularly those involving the least-HYG elements (i.e., Ti, Y, and the HREE). Saunders (in press) suggests that this process is the most likely explanation for the observed increases in the La/Yb, Zr/Y, and Zr/Ti ratios with increasing Zr content in the basalts recovered from the East Pacific Rise at the mouth of the Gulf of California. The changes observed there in Zr/Ti and Zr/Y ratios are comparable to the differences observed between Unit 5 and the depleted units, but they were accompanied by larger increases in the abundance of Zr (\approx 50 to 150 ppm), Ti (\approx 1.0 to 2.5%) and Y (\approx 25 to 50 ppm) than exist in the Hole 504B samples (Figs. 6 and 8). In addition, REE patterns remained LREE depleted and the Zr/Nb ratios were unchanged. Similarly, Mattey and Muir (1980) ascribe chemical variations in Galapagos Rift basalts and ferrobasalts to open system fractionation, where again the REE patterns remain LREE depleted and Ta/Hf (analogous to Zr/Nb) ratios remain constant. Theoretical modeling of high level open system crystal fractionation also produces similar results (Tarney et al., 1980; and Pankhurst, 1977), so it appears unlikely that the entire range of compositions shown by the Hole 504B basalts could be produced by crystal fractionation from a magma, or several batches of magmas of the same composition, at crustal levels.

Nevertheless, the Fe/Mg ratios, the Ni, Cr, and MgO contents, and the petrographic evidence all suggest that all the Hole 504B basalts have undergone some crystal fractionation and did not solidify as unmodified mantle melts. Variations in HYG element abundances and ratios could well reflect low-pressure open system crystal fractionation involving more than one parental magma.

One possible mixing scheme would involve a depleted parent magma with HYG element ratios similar to those of Lithologic Unit 1 diluting a magma with HYG element ratios similar to those of Lithologic Unit 5, the resultant mix then undergoing varying amounts of crystal fractionation to produce the basalts of Lithologic Units 2, 3, and 4. Batiza and Johnson (1980) explained the production of T type MORB at the East Pacific Rise close to the Siqueiros Fracture Zone by binary magma mixing during low pressure open system crystal fractionation. Additional trace element and petrographic data (Natland and Melson, 1980; Thompson and Humphris, 1980; and Humphris et al., 1980), however, suggest that their precise mixing scheme is not tenable and that independent magmas with a T type chemistry were more likely to have been involved.

Even allowing for the possibility of magma mixing during low pressure open system crystal fractionation, magmas of at least two distinct compositions are necessary to produce the HYG element variations within the Hole 504B basalts, one being similar perhaps to T type MORB and the other to N type MORB. Studies on basalts from the Mid-Atlantic Ridge in the FAMOUS area and on those from Iceland have shown that while it is possible to generate basalts with REE patterns ranging from moderately LREE enriched ($Ce_N/Yb_N \approx 2$) to LREE depleted (Ce_N/Yb_N ≈ 0.5) from an initially homogeneous mantle source by continuous batch partial melting (Langmuir et al., 1977) or dynamic partial melting (Wood, 1979b), ratios between the more-HYG elements remained essentially unaffected. Moreover, the differences in isotopic and more-HYG element ratios between N, T, and E type MORB appear to be adequately explained only by some degree of mantle heterogeneity (e.g., Tarney et al., 1980; and O'Nions et al., 1980). Evidence from the Atlantic suggests the veining of a host mantle depleted in more-HYG elements with respect to the less-HYG elements by material with high more-HYG/less-HYG element ratios and high abundances of more-HYG elements. The host mantle is the source of N type MORB, and by increasing the quantity of vein material T or E type magmas can be produced



Figure 17. Comparative element abundances in selected samples from Leg 69 normalized to N type MORB. Normalizing values are based on N type MORB from the Mid-Atlantic Ridge, 22°N, as compiled by Tarney et al. (1981). The example of E type MORB is from Iceland (ISL 79; Wood, Joron, et al., 1979), and that of T type MORB is from the Reykjanes Ridge (409-3; Wood, Tarney, et al., 1979). The basanite sample from southeastern Australia (2679; Frey et al., 1978) illustrates the possible composition of the vein material involved in generating T and E type MORB. Dashes connect estimated element abundances.

during partial melting. The favoured composition of the vein material would be similar to the compositions observed in many strongly undersaturated alkalic basalts (see Fig. 17).

The difference in Zr/Nb ratios and inferred differences in Nb/La and La/Ce ratios within the Hole 504B basalts, by analogy with basalts from the MAR, suggest that the mantle source feeding the Costa Rica Rift was heterogeneous with respect to more-HYG element contents. The depleted basalts at this site would have been produced by partial melting of the host mantle, possibly with a small and variable contribution from the vein material; the enriched magma that eventually gave rise to Unit 5 would have been produced by partial melting of a mantle with a higher vein content. However, the low contents of Ti, Y, and Zr plus the progressively increasing depletion of the more-HYG elements observed in most units in Hole 504B relative to 22°N MAR N type MORB suggest that the host mantle underlying this part of the Panama Basin is more severely depleted in HYG elements than the host mantle underlying the Atlantic.

The question remains as to how two apparently distinct magma compositions could exist at a ridge spreading at a moderate rate. Normal models of the spreading process envisage a continuous magma chamber. On slowly spreading ridges such as a Mid-Atlantic Ridge, basalts representing two or more separate magma types are not uncommon in cored sections, but this presents no difficulty if the magma chambers are only semicontinuous or discontinuous; small separate magma chambers can coexist. On a faster-spreading ridge there would be no

serious problem either if the enriched lavas were at the top of the cored section and could be regarded as the product of off-axis volcanism. However, in Hole 504B the enriched units occur at too deep a level to be considered off-axis lavas. In theory a continuous magma chamber should smooth out the trace element variations that result from different degrees of batch partial melting or small-scale mantle source heterogeneities. One possible explanation is that magma chambers along the Costa Rica Rift were long lived but not necessarily continuous, in which case separate magma types could be extruded, albeit to a very limited extent. Some of the trace element variations within the remainder of the lava sequence may have arisen through the mixing of the two magma types within semi-continuous magma chambers, although clearly the depleted magma type is dominant at Site 504.

In conclusion, the basalts sampled so far from the floor of the Panama Basin appear to be predominantly highly HYG-element-depleted mid-ocean-ridge basalts. Occasionally interdigitated with these depleted basalts are units with T type MORB characteristics. All the basalts have undergone some high-level crystal fractionation, although this has had far less effect on the composition of the erupted basalts than observed in the adjacent Galapagos Spreading Center or along the East Pacific Rise, where the magmas are commonly fractionated to ferrobasalts. Variations in HYG element ratios between different units could reflect some mixing between the two magma types at crustal levels, and a heterogeneous mantle source is necessary to explain the total range of HYG element ratios observed.

REFERENCES

- Anderson, R. N., Clague, D. A., Klitgord, K. D., Marshall, M., and Nishimori, R. K., 1975. Magnetic and petrologic variations along the Galapagos Spreading Center and their relation to the Galapagos melting anomaly. *Geol. Soc. Am. Bull.*, 86:683-694.
- Batiza, R., and Johnson, J. R., 1980. Trace element and isotopic evidence for magma mixing in alkalic and transitional basalts near the East Pacific Rise at 8°N. In Rosendahl, B. R., Hekinian, R., et al., Init. Repts. DSDP, 54: Washington (U.S. Govt. Printing Office), 63-70.
- Bougault, H., Joron, J. L., and Treuil, M., 1980. The primordial chondritic nature and large-scale heterogeneities in the mantle: evidence from high and low partition coefficient elements in oceanic basalts. *Philos. Trans. R. Soc. London, Ser. A*, 297:203-213.
- Bougault, H., and Treuil, M., 1980. Mid-Atlantic Ridge: zero-age geochemical variations between Azores and 22°N. *Nature*, 286: 209-212.
- Bougault, H., Treuil, M., and Joron, J. L., 1979. Trace elements in basalts from 23°N and 36°N in the Atlantic Ocean: fractional crystallization, partial melting, and heterogeneity of the Upper Mantle. *In* Melson, W. G., Rabinowitz, P. D., et al., *Init. Repts. DSDP*, 45: Washington (U.S. Govt. Printing Office), 493-506.
- Clague, D. A., and Bunch, T. E., 1976. Formation of ferrobasalt at East Pacific midocean spreading centers. J. Geophys. Res., 81: 4247-4256.
- DePaolo, D. J., and Wasserburg, G. J., 1976. Nd isotopic variations and petrogenetic models. *Geophys. Res. Lett.*, 3:249-252.
- Floyd, P. A., and Tarney, J., 1979. First-order alteration chemistry of Leg 49 basement rocks. In Luyendyk, B. P., Cann, J. R., et al., Init. Repts. DSDP, 49: Washington (U.S. Govt. Printing Office), 693-708.
- Frey, F. A., Green, D. H., and Ray, S. D., 1978. Integrated models of basalt petrogenesis. J. Petrol., 19:463-513.
- Hart, S. R., 1971. K, Rb, Cs, Sr and Ba contents and Sr isotope ratios of ocean floor basalts. *Philos. Trans. R. Soc. London, Ser. A*, 268:573-587.
- Hart S. R., Erlank, A. J., and Kable, E. J. D., 1974. Sea floor basalt alteration: some chemical and Sr isotopic effects. *Contrib. Miner*al. Petrol., 44:219–230.
- Hart, S. R., Schilling, J.-G., and Powell, J. L., 1973. Basalts from Iceland and along the Reykjanes Ridge: Sr isotope geochemistry. *Nature Phys. Sci.*, 246:104–107.
- Humphris, S. E., Thompson, R. N., Gibson, I. L., and Marriner, G. F., 1980. Comparison of geochemistry of basalts from the East Pacific Rise, OCP Ridge and Siqueiros Fracture Zone, Deep Sea Drilling Project Leg 54. *In* Rosendahl, B. R., Hekinian, R., et al., *Init. Repts. DSDP*, 54: Washington (U.S. Govt. Printing Office), 635-650.
- Langmuir, C. H., Bender J. F., Bence, A. E., Hanson, G. N., and Taylor, S. R., 1977. Petrogenesis of basalts from the FAMOUS area: Mid-Atlantic Ridge. *Earth Planet. Sci. Lett.*, 36:133-156.
- Leake, B. E., Hendry, G. L., Kemp, A., Plant, A. G., Harvey, P. K., Wilson, J. R., Coats, J. S., Aucott, J. W., Lünel, T., and Howarth, R. J., 1969. The chemical analysis of rock powders by automatic X-ray fluorescence. *Chem. Geol.*, 5:7-86.
- Lonsdale, P., and Klitgord, K. D., 1978. Structure and tectonic history of the eastern Panama Basin. Geol. Soc. Am. Bull., 89: 981-999.
- Luddon, J. N., and Thompson, G., 1979. An evaluation of the behavior of the rare earth elements during the weathering of sea-floor basalt. *Earth Planet. Sci. Lett.*, 43:85-92.
- Marsh, N. G., Saunders, A. D., Tarney, J., and Dick, H. J. B., 1980. Geochemistry of basalts from the Shikoku and Daito Basins, Deep Sea Drilling Project Leg 58. In Klein, G. deV., Kobayashi, K., et al., Init. Repts. DSDP, 58: Washington (U.S. Govt. Printing Office), 805-842.
- Mattey, D. P., Marsh, N. G., and Tarney, J., 1980. The geochemistry, mineralogy, and petrology of basalts from the West Philippine and Parece Vela Basins and from the Palau-Kyushu and West Mariana Ridges, Deep Sea Drilling Project Leg 59. In Kroenke, L., Scott, R., et al., Init. Repts. DSDP, 59: Washington (U.S. Govt. Printing Office), 753-800.

- Mattey, D. P., and Muir, I. D., 1980. Geochemistry and mineralogy of basalts from the Galapagos Spreading Center, Deep Sea Drilling Project Leg 54. In Rosendahl, B. R., Hekinian, R., et al., Init. Repts. DSDP, 54: Washington (U.S. Govt. Printing Office), 755-772.
- Mitchell, W. S., and Aumento, F., 1977. Uranium in oceanic rocks: DSDP Leg 37. Can. J. Earth Sci., 14:794-808.
- Natland, J. H. and Melson, W. G., 1980. Compositions of basaltic glasses from the East Pacific Rise and Siqueiros Fracture Zone, Near 9°N. In Rosendahl, B. R., Hekinian, R., et al., Init. Repts. DSDP, 54: Washington (U.S. Govt. Printing Office), 705-724.
- O'Hara, M. J., 1977. Geochemical evolution during fractional crystallization of a periodically refilled magma chamber. *Nature*, 266: 503-507.
- O'Nions, R. K., Evensen, N. M., and Hamilton, P. J., 1980. Differentiation and evolution of the mantle. *Philos. Trans. R. Soc. Lon*don, Ser. A, 297:479-493.
- O'Nions, R. K., Hamilton, P. J., and Evensen, N. M., 1977. Variations in ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr ratios in oceanic basalts. *Earth Planet. Sci. Lett.*, 34:13-22.
- Pankhurst, R. J., 1977. Open system crystal fractionation and incompatible element variation in basalts. *Nature*, 268:36–38.
- Pearce, J. A., and Cann, J. R., 1971. Ophiolite origin investigated by discriminent analysis using Ti, Zr and Y. Earth Planet. Sci. Lett., 12:339-349.
- Pearce, J. A., and Norry, M. J., 1979. Petrogenetic implications of Ti, Zr, Y, and Nb variations in volcanic rocks. *Contrib. Mineral. Petrol.*, 69:33-47.
- Pritchard, R. G., Cann, J. R., and Wood, D. A., 1979. Low-temperature alteration of oceanic basalts, DSDP Leg 49. In Luyendyk, B. P., Cann, J. R., et al., Init. Repts. DSDP, 49: Washington (U.S. Govt. Printing Office), 709-714.
- Reynolds, R. C., Jr., 1967. Estimation of mass absorption coefficients by Compton scattering: improvements and extensions of the method. Am. Mineral., 52:1493-1502.
- Rhodes, J. M., Blanchard, D. P., Dungan, M. A., Rodgers, K. V., and Brannon, J. C., 1979. Chemistry of Leg 45 basalts. *In Melson*, W. G., Rabinowitz, P. D., et al., *Init. Repts. DSDP*, 45: Washington (U.S. Govt. Printing Office), 447-460.
- Rosendahl, B. R., Hekinian, R., et al., 1980. Init. Repts. DSDP, 54: Washington (U.S. Govt. Printing Office).
- Saunders, A. D., in press. The Gulf of California: geochemistry of basalts recovered during Leg 65 of the Deep Sea Drilling Project. In Lewis, B. T. R., Robinson, P., et al., Init. Repts. DSDP, 65: Washington (U.S. Govt. Printing Office).
- Saunders, A. D., Fornari, D. J., Joron, J. L., Tarney, J., and Treuil, M. in press. Geochemistry of basic igneous rocks recovered from the Gulf of California: Deep Sea Drilling Project Leg 64. *In Cur*ray, J. R., Moore, D. G., et al., *Init. Repts. DSDP*, 64, Pt. 2: Washington (U.S. Govt. Printing Office).
- Saunders, A. D., Tarney, J., Marsh, N. G., and Wood, D. A., 1980. Ophiolites as ocean crust or marginal basin crust: a geochemical approach. Proc. Int. Ophiolite Conf., Nicosia, Cyprus, pp. 193-204.
- Schilling, J.-G., 1973. Iceland mantle plume: geochemical evidence along Rekjanes Ridge. Nature, 242:565–571.
- Schilling, J.-G., Anderson, R. N., and Vogt, P., 1976. Rare earth, Fe and Ti variations along the Galapagos spreading centre, and their relationship to the Galapagos mantle plume. *Nature*, 261:108-113.
- Sun, S.-S., Nesbitt, R. W., and Sharaskin, A. Ya., 1979. Geochemical characteristics of mid-ocean ridge basalts. *Earth Planet. Sci. Lett.*, 44:119-138.
- Tarney, J., Saunders, A. D., Mattey, D. P., Wood, D. A., and Marsh, N. G., 1981. Geochemical aspects of back-arc spreading in the Scotia Sea and western Pacific. *Philos. Trans. R. Soc. London,* Ser. A, 300:263-285.
- Tarney, J., Saunders, A. D., Weaver, S. D., Donnellan, N. C. B., and Hendry, G. L., 1979. Minor-element geochemistry of basalts from Leg 49, North Atlantic Ocean. *In* Luyendyk, B. P, Cann, J. R., et al., *Init. Repts. DSDP*, 49: Washington (U.S. Govt. Printing Office), 657-691.
- Tarney, J., Wood, D. A., Saunders, A. D., Cann, J. R., and Varet, J., 1980. Nature of mantle heterogeneity in the North Atlantic: evi-

dence from deep sea drilling. Philos. Trans. R. Soc. London, Ser. A, 297:179-202.

- Thompson, R. N., and Humphris, S. E., 1980. Silicate mineralogy of basalts from the East Pacific Rise, OCP Ridge, and Siqueiros Fracture Zone: Deep Sea Drilling Project, Leg 54. In Rosendahl, B. R., Hekinian, R., et al., Init. Repts. DSDP, 54: Washington (U.S. Govt. Printing Office), 651–670.
- van Andel, Tj. H., Heath, G. R., et al., 1973. Init. Repts. DSDP, 16: Washington (U.S. Govt. Printing Office).
- Vogt, P. R. 1979. Amplitudes of oceanic magnetic anomalies and the chemistry of oceanic crust: synthesis and review of 'magnetic telechemistry.' Can J. Earth. Sci., 16:2236–2262.
- Vogt, P. R., and Johnson, G. L., 1973. Magnetic telechemistry of oceanic crust? Nature, 245:373-375.

- White, W. M., Schilling, J.-G., and Hart, S. R., 1976. Evidence of the Azores mantle plume from strontium isotope geochemistry of the Central North Atlantic. *Nature*, 263:659–663.
- Wood, D. A., 1979. Dynamic partial melting: its application to the petrogeneses of basalts erupted in Iceland, the Faeroe Islands, the Isle of Skye (Scotland) and the Troodos Massif (Cyprus). Geochim. Cosmochim. Acta, 43:1031-1046.
- Wood, D. A., Joron, J.-L., Treuil, M., Norry, M. J., and Tarney, J., 1979. Elemental and Sr isotope variations in basic lavas from Iceland and the surrounding ocean floor: The nature of mantle source in homogeneities. *Contrib. Mineral. Petrol.*, 70:319-339.
- Wood, D. A. Tarney, J., Varet, J., Saunders, A. D., Bougault, H., Joron, J. L., Treuil, M., and Cann, J. R., 1979. Geochemistry of basalts drilled in the North Atlantic by IPOD Leg 49: implications for mantle heterogeneity. *Earth Planet. Sci. Lett.*, 42:77–97.