

## 5. PETROLOGY AND ISOTOPE CHARACTERISTICS (H, O, S, Sr, AND Nd) OF BASALTS FROM OCEAN DRILLING PROGRAM HOLE 504B, LEG 111, COSTA RICA RIFT<sup>1</sup>

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### ABSTRACT

Petrography and isotope geochemical characteristics of H, O, S, Sr, and Nd have been described for basalts recovered from Hole 504B during Leg 111 of the Ocean Drilling Program. The petrographic and chemical features of the recovered basalts are similar to those obtained previously (DSDP Legs 69, 70, and 83); they can be divided into phyrlic (plagioclase-rich) and aphyric (plagioclase- and clinopyroxene-rich) basalts and show low abundances of TiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, and Sr. This indicates that the basalts belong to Group D, comprising the majority of the upper section of the Hole 504B. The diopside-rich nature of the clinopyroxene phenocrysts and Ca-rich nature of the plagioclase phenocrysts are also consistent with the preceding statement. The Sr and Nd isotope systematics (average <sup>87</sup>Sr/<sup>86</sup>Sr = 0.70267 ± 0.00007 and average <sup>143</sup>Nd/<sup>144</sup>Nd = 0.513157 ± 0.000041) indicate that the magma sources are isotopically heterogeneous, although the analyzed samples represent only the lowermost 200-m section of Hole 504B.

The rocks were subjected to moderate hydrothermal alteration throughout the section recovered during Leg 111. Alteration is limited to interstices, microfractures, and grain boundaries of the primary minerals, forming chlorite, actinolite, talc, smectite, quartz, sphene, and pyrite. In harmony with the moderate alteration, the following alteration-sensitive parameters show rather limited ranges of variation: H<sub>2</sub>O = 1.1 ± 0.2 wt%, δD = -38‰ ± 4‰, δ<sup>18</sup>O = 5.4‰ ± 0.3‰, total S = 562 ± 181 ppm, and δ<sup>34</sup>S = 0.8‰ ± 0.3‰. Based on these data, it was estimated that the hydrothermal fluids had δD and δ<sup>18</sup>O values only slightly higher than those of seawater, the water/rock ratios were as low as 0.02–0.2, and the temperature of alteration was 300°–400°C. Sulfur exists predominantly as pyrite and in minor quantities as chalcopyrite. No primary monosulfide was detected. This and the δ<sup>34</sup>S values of pyrite (δ<sup>34</sup>S = 0.8‰) suggest that primary pyrrhotite was almost completely oxidized to pyrite by reaction with hydrothermal fluids containing very little sulfate.

### INTRODUCTION

The basalt samples recovered from Hole 504B during Leg 111 of the Ocean Drilling Program (ODP) represent the deepest section of the oceanic crust ever drilled. Studies of these basalts will reveal the *in-situ* petrological structure and geochemical characteristics of rock units in the deep oceanic crust near the Galapagos Spreading Center. Mid-oceanic ridge basalts (MORB) are currently believed to be derived from picritic primary magmas, which are generated at pressures from 10 to 15 kbar and change their compositions to one along the olivine/plagioclase/clinopyroxene liquidus boundary at shallow depths during ascent (e.g., Shibata and Thompson, 1986). The Hole 504B basalt samples recovered during Leg 111, together with those from the previous Deep Sea Drilling Project (DSDP) Legs 69, 70, and 83, could give further insight into the magmatic processes at a typical diverging plate boundary.

Knowledge of the depth of seawater penetration into the oceanic crust and the physicochemical conditions under which the oceanic crust is altered by interaction with the penetrating seawater forms a framework for our understanding of the bulk geochemistry of the oceanic crust subducting at converging plate boundaries. The rocks recovered from Hole 504B during DSDP

Legs 69, 70, and 83, to a maximum depth of 1350 m below seafloor (mbsf), are variously altered by the circulating seawater at low to hydrothermal temperatures (Alt et al., 1986a, 1986b; Barrett and Friedrichsen, 1982; Friedrichsen, 1985; Kawahata and Furuta, 1985; Kawahata et al., 1987). It is thus a matter of interest to know to what depth and to what extent alteration persists in the basalts drilled from Hole 504B during Leg 111. Such alteration is best understood by the mineralogical, chemical, and isotopic variations of the rocks. In the present paper, we report the preliminary results of our study on the petrography and whole-rock variations of hydrogen, oxygen, sulfur, strontium, and neodymium isotope ratios of the Leg 111 massive basalts that are free from visible veins and fractures.

### ANALYTICAL METHODS

#### Sample Selection

Sub-bottom depths of the Hole 504B rocks recovered during Leg 111 range from 1352.8 to 1562.3 mbsf. Ten representative specimens were selected at an even distribution throughout the cored interval. The samples are massive and devoid of apparent veins or fractures in hand sample. Each of the 10 specimens was trimmed for any dirt, washed with distilled water, and dried. A thin section of each specimen was prepared for petrographic and electron microprobe analyses. The remaining portion of each specimen was then pulverized for chemical and isotopic analyses, which were performed on a whole-rock basis.

#### Whole-Rock Chemistry

The powdered samples were decomposed by a mixture of HNO<sub>3</sub>, HClO<sub>4</sub>, and HF in sealed teflon bombs. After decomposition, Na and K contents were measured by atomic absorption spectrophotometry. Ca, Mg, Al, Ti, Fe (as total Fe), Mn, and other minor elements were determined with inductively coupled plasma emission spectrophotometry. Silica content was determined colorimetrically with the molybdenum yellow method after Na<sub>2</sub>CO<sub>3</sub> fusion on a separate aliquot of the sample.

<sup>1</sup> Becker, K., Sakai, H., et al., 1989. *Proc. ODP, Sci. Results*, 111: College Station, TX (Ocean Drilling Program).

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## Mineral Analysis

Mineral analysis was made using a three-channel JEOL X-ray microprobe analyzer at an accelerating voltage of 15 kV and a sample current of 0.01–0.02  $\mu\text{A}$ . The correction procedure was that of Bence and Albee (1968) with the alpha factors of Nakamura and Kushiro (1970).

## Hydrogen, Oxygen, and Sulfur Isotope Analyses

Hydrogen was quantitatively extracted as  $\text{H}_2\text{O}$  from a sample by inductive heating to 1300°C in vacuum after absorbed water was removed at 200°C for at least 2 hr (Suzuoki and Epstein, 1976). The extracted  $\text{H}_2\text{O}$  was quantitatively converted to  $\text{H}_2$  over heated uranium, which was manometrically measured to give the  $\text{H}_2\text{O}$  content and analyzed with a mass spectrometer to determine the D/H ratio.

Oxygen was extracted from samples with the  $\text{BrF}_5$  method (Clayton and Mayeda, 1963) and converted to  $\text{CO}_2$  for isotopic measurement.

Sulfur was extracted by decomposing the samples in vacuum with a strong phosphoric acid solution containing  $\text{Sn}^{2+}$  ions (Ueda and Sakai, 1983). With this method, sulfur in sulfide and sulfate in the samples are recovered as  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , respectively. The  $\text{H}_2\text{S}$  was converted to  $\text{SO}_2$  with  $\text{CuO}$ . Sulfur contents were worked out from manometric determination of the  $\text{SO}_2$  gases. The sulfur isotope measurements were made only for the sulfide sulfur because of the small sulfate sulfur content of the samples.

Isotopic results are expressed in a conventional  $\delta$ -notation with respect to the V-SMOW standard for hydrogen and oxygen and to the Canyon Diablo troilite for sulfur. Analytical accuracies are  $\pm 0.1\text{‰}$  for  $\delta^{18}\text{O}$ ,  $\pm 0.2\text{‰}$  for  $\delta^{34}\text{S}$ , and  $\pm 1.0\text{‰}$  for  $\delta\text{D}$ . We obtained  $\delta^{18}\text{O} = 9.65\text{‰}$  for the NBS-28 quartz reference sample and  $\delta\text{D} = -58.8\text{‰}$  for the NBS-30 biotite reference sample.

## Strontium and Neodymium Isotope Analyses

Rock powders were dissolved in a mixture of 40% HF, 65%  $\text{HNO}_3$ , and 30% HCl in a sealed teflon bomb. Separation chemistry and mass spectrometry were followed by the procedures described in Kagami et al. (1982, 1987). The  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were normalized using  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ , respectively. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the reference samples NBS-987 and JB-1A are  $0.710243 \pm 0.000017$  (2 sigma, 5 analyses) and  $0.704089 \pm 0.000011$  (2 sigma, single analysis), respectively. The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of the reference samples BCR-1, JB-1A, and JB-1 are  $0.512638 \pm 0.000005$  (18 analyses),  $0.512784 \pm 0.000020$  (single analysis), and  $0.512786 \pm 0.000015$  (single analysis), respectively (Kagami et al., 1987). Mean relative experimental errors at the 2 sigma level are 0.003% and 0.004% for Sr and Nd isotopic ratios, respectively. Values of  $\epsilon_{\text{Sr}}$  and  $\epsilon_{\text{Nd}}$  were reported using the bulk Earth parameters  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{present}} = 0.7045$  and  $^{143}\text{Nd}/^{144}\text{Nd}_{\text{present}} = 0.51264$ .

## PETROGRAPHY AND MINERAL CHEMISTRY

The Leg 111 Shipboard Scientific Party (1988) indicated that the lithologic characters of basalts recovered from Hole 504B are essentially the same as those described from the lowermost section of the hole cored during Leg 83, and hence, the basalts recovered represent the continuation of the sheeted dike zone first recognized during Leg 83 (Anderson et al., 1982). The Leg 111 basalts occur predominantly as massive units. In addition, a small number of dikes were also identified by the presence of the chilled intrusive contacts. The exact mode of emplacement is not known for the basalts occurring as massive units, although several lines of evidence strongly support their origin as the interiors of large dikes (Adamson, 1985). The basalts of this study can be divided into two petrographic groups: aphyric and phyrlic basalts. For consistency, we adopted the classification scheme for basalts employed by the Leg 83 petrologists in the following petrographic description (Kempton et al., 1985).

The aphyric basalts (Samples 111-504B-147R-1, 73–77 cm [Piece 8C], and 111-504B-154R-1, 97–102 cm [Piece 6A]) are medium grained (0.1–2 mm), contain less than 1% crystals that qualify as phenocrysts, and are characterized by a subophitic to intersertal texture. Euhedral to subhedral plagioclase and subhedral to anhedral, equant clinopyroxene are the main primary constituents, forming more than 80% of these samples (Table 1).

Slightly larger clinopyroxene crystals tend to enclose subhedral plagioclase lathes subophitically at their marginal zones. In addition to these two major minerals, the samples contain minor amounts of olivine, Fe-Ti oxides, and quartz as primary constituents. The olivine is, however, completely altered to one or more phyllosilicates and occurs only as pseudomorphs that preserve euhedral to subhedral olivine morphologies. In general, quartz occurs interstitially between plagioclase lathes and clinopyroxene crystals, and it formed in close association with or occurs in vermicular intergrowth with sodic plagioclase. The sodic plagioclase and quartz are heavily charged with hairlike microlites (probably actinolite) and Fe-Ti oxides. Textural relations suggest that the quartz and sodic plagioclase probably formed together with hairlike microlites and Fe-Ti oxides through late-stage deuteric processes, but at present we cannot completely rule out the possibility that they are the products of low-temperature seawater alteration.

The rest of the basalt samples chosen for our study are sparsely or moderately phyrlic (<5% phenocrysts) and contain phenocryst assemblages composed of olivine, plagioclase, and/or clinopyroxene, although the olivine phenocrysts are totally altered to one or more phyllosilicates (see Table 1). A few equant, brown spinel grains (0.05 mm in diameter) are noted as inclusions in plagioclase phenocrysts in Samples 111-504B-143R-1, 46–48 cm (Piece 9), and 111-504B-153R-1, 4–6 cm (Piece 2). Plagioclase is the most abundant, ubiquitous phenocryst phase in the phyrlic basalts, forming up to 3% of the rock in this mode. The plagioclase phenocrysts or microphenocrysts are typically subhedral, with the long axis ranging from 1 to 3 mm. Large plagioclase crystals rarely have cavities filled with cryptocrystalline brownish material or devitrified melt. Clinopyroxene occurs as a phenocryst phase in all but two of the eight phyrlic basalts examined. The clinopyroxene phenocrysts form up to 2% of the rock, with the grain size ranging from less than 0.5 to 5 mm along the c-axis. Some of the clinopyroxene phenocrysts subophitically embay plagioclase lathes that are similar in size and morphology to those occurring in the groundmass. In most cases, these phenocryst or microphenocryst phases, including pseudomorphs after olivine, occur as single crystals, but glomerocrystic aggregates were commonly found in samples with a cryptocrystalline or fine-grained groundmass. The glomerocrystic clumps usually consist of several plagioclase crystals commonly clustering together with olivine and/or clinopyroxene.

Groundmass textures for phyrlic basalts with a medium-grained groundmass (Samples 111-504B-145R-1, 50–52 cm [Piece 8A], 111-504B-148R-1, 43–45 cm [Piece 6A], 111-504B-153R-1, 4–6 cm [Piece 2], and 111-504B-159R-1, 46–48 cm [Piece 8]) are generally similar to those described for the aphyric basalts, and need not be repeated here. Samples 111-504B-160R-1, 16–17 cm (Piece 3), and 111-504B-165R-1, 26–27 cm (Piece 3B), are characterized by a fine-grained groundmass with an intergranular to intersertal texture. In these two samples, the groundmass clinopyroxene occurs as anhedral, equant crystals in intergranular or very rarely subophitic relationships with interlocking subhedral plagioclase lathes. We also commonly observed interstitial pockets composed of vermicular sodic plagioclase and quartz both heavily charged with tiny opaque grains and hairlike microlites. Neither fresh olivines nor olivine pseudomorphs were observed in the groundmass. Groundmass textures for Samples 111-504B-143R-1, 46–48 cm (Piece 9), and 111-504B-169R-1, 116–118 cm (Piece 22), are partly subvolcanic with fine-grained, sheaf or plumose clinopyroxenes and slender plagioclase prisms. Skeletal crystals that typically develop in the glassy, chilled selvage of abyssal basalt pillows were not seen in these samples.

Modal analyses indicate that the Leg 111 basalt samples are moderately to extensively altered, with modal proportions of secondary minerals ranging from 7% to 36% of the rock (Table 1).

**Table 1. Modal compositions of basalts from Hole 504B, Leg 111.**

	143R-1, 46-48 cm (Piece 9) 1359.6	145R-1, 50-52 cm (Piece 8A) 1378.3	147R-1, 73-77 cm (Piece 8C) 1397.4	148R-1, 43-45 cm (Piece 6A) 1407.2	153R-1, 4-6 cm (Piece 2) 1445.3	154R-1, 97-102 cm (Piece 6A) 1454.3	159R-1, 46-48 cm (Piece 8) 1488.1	160R-1, 16-17 cm (Piece 3) 1494.7	165R-1, 26-27 cm (Piece 3B) 1529.5	169R-1, 116-118 cm (Piece 22) 1548.7
Depth (mbsf)										
Sample no.	6	11	20	25	37	42	48	49	59	64
<sup>a</sup> Rock type	OP	OPC	A	PC	P	A	OPC	PC	OPC	PC
Clinopyroxene	36.9	35.6	37.6	42.2	35.3	37.2	36.8	37.8	32.8	22.3
Plagioclase	37.9	42.2	45.7	45.1	50.0	52.2	47.4	48.0	46.8	33.1
Quartz	0.9	0.3	0.3	0.8	0.2	0.5	0.4	0.1	0.3	—
Spinel	tr	—	—	—	tr	—	—	—	—	—
Fe-Ti oxide	5.7	3.4	3.1	4.4	1.5	2.3	3.5	2.6	4.5	8.3
Total fresh	80.5	81.5	86.7	92.5	87.0	92.2	88.1	88.5	84.4	63.7
Clays	15.9	5.1	4.6	2.0	7.1	4.2	2.8	4.2	6.0	32.7
Chlorite	1.3	1.4	4.7	3.1	1.7	1.6	4.1	1.7	3.0	1.1
Talc	1.5	5.6	1.2	0.2	0.3	0.5	0.4	—	0.4	0.1
Actinolite	0.3	5.8	2.4	1.7	3.8	1.4	3.2	5.3	6.0	2.1
Quartz	—	—	—	—	—	—	0.2	—	—	—
Sphene	—	—	—	—	—	—	0.7	0.1	—	0.1
Sulfides	0.5	0.6	0.4	0.5	0.1	0.1	0.5	0.2	0.2	0.2
Total altered	19.5	18.5	13.3	7.5	13.0	7.8	11.9	11.5	15.6	36.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Note: tr = trace.

<sup>a</sup> OP = olivine-plagioclase-phyric basalt; OPC = olivine-plagioclase-clinopyroxene-phyric basalt; PC = plagioclase-clinopyroxene-phyric basalt; P = plagioclase-phyric basalt; A = aphyric basalt.

The secondary minerals observed under the microscope include chlorite, actinolite, talc, smectite, quartz, sphene, and sulfide minerals (mostly pyrite). Neither zeolite group minerals nor albite were positively identified in our examination of the samples. Epidote and prehnite are not present, either. In most cases, alteration apparently took place in parts of the interstitial fine-grained or cryptocrystalline materials and along microfractures, cleavages, and grain boundaries of primary minerals. In the samples with a medium-grained groundmass, the secondary minerals are thus generally confined to brownish or dark green clots, with irregular outlines and up to 0.5 mm in diameter in sporadic distribution throughout the samples. On the other hand, alteration is generally slight in the remaining part of the samples, where primary minerals are conspicuously fresh. The brownish green clots are usually composed of brownish green smectite and chlorite with lesser amount of actinolite. It is noteworthy that the clinopyroxene appears to be more susceptible to alteration processes than the plagioclase; thus, clinopyroxene crystals commonly are partly replaced by sheaflike bundles of actinolite, but in contrast, plagioclase alteration is restricted only to the formation of chlorite and/or smectite along microfractures and cracks. As noted previously, olivine is completely altered to one or more phyllosilicates. The pseudomorphs after olivine are generally composed of either (1) brown smectite, (2) brown smectite + talc + magnetite, or (3) talc + magnetite. Some of the pseudomorphs show zonal structures with brown smectite at the center and talc plus magnetite in the marginal zone, and vice versa.

Representative microprobe analyses of clinopyroxenes are listed in Table 2, and all the pyroxene analyses obtained are plotted in the conventional pyroxene quadrilateral (Fig. 1). No Ca-poor pyroxene was observed in any of the samples analyzed. The pyroxenes are mostly augites, and there is an overall, wide variation in composition. The cores of pyroxene phenocrysts, however, show a rather limited range of composition and are plotted in the region of endiopsidite in the pyroxene quadrilateral (Fig. 1A), which probably implies that the samples were derived from magmas with similar, if not the same, FeO/MgO ratios.

These phenocrystic pyroxenes are strongly zoned; e.g., a single pyroxene phenocryst shows an increase in FeO from 5.03 wt% at the core to 25.11 wt% at the rim, accompanied by decreases in MgO and CaO. This iron increase in the compositional zonation is also accompanied by a slight enrichment in titanium and depletion in aluminum. Such trends in the compositional zonation were also, though less extensively, observed in the groundmass pyroxenes. They do not exhibit a noticeable increase in Ti plus Al abundance, however, in comparison with the phenocrystic pyroxenes, which is a feature known from many other groundmass clinopyroxenes from abyssal basalts (e.g., Dungan and Rhodes, 1978). The Ti plus Al abundances observed in the Hole 504B phenocrystic, as well as the groundmass, pyroxenes fall in the range of those for gabbros dredged from the ocean floor (e.g., Shibata et al., 1979; Elthon, 1987). The chemical characteristics of the Leg 111 clinopyroxenes are generally similar to those of the clinopyroxenes obtained during Leg 83 from the same hole (Kempton et al., 1985).

Representative microprobe analyses of plagioclase are listed in Table 3. The anorthite contents of plagioclase observed as phenocrysts, microphenocrysts, and groundmass grains of the Leg 111 samples from Hole 504B vary greatly, ranging from An<sub>90</sub> to An<sub>49</sub> (Fig. 2). Plagioclase phenocrysts commonly have a relatively homogeneous, broad core of An<sub>90-80</sub>, with an oscillatory zoned, more sodic rim in which we observed a few thin zones with compositions as calcic as or more calcic than that of the core. Groundmass plagioclases are generally normally zoned. Kempton et al. (1985) noted that plagioclase compositions from the Leg 83 recovery of Hole 504B are distinctive in their relatively high An content (up to 90 mol%). Natland et al. (1983) reported anorthite contents of as high as An<sub>94</sub> for plagioclase from the upper portion of Hole 504B. The Ca-rich nature of plagioclases from the Hole 504B basalts cored during the previous DSDP legs apparently persists in the Leg 111 plagioclases. Figure 2 shows the relationship between the An content and the Mg/(Mg + Fe) ratio in Leg 111 phenocryst and groundmass plagioclases. There is a regular, positive correlation between An

**Table 2. Microprobe analyses of clinopyroxene from Hole 504B, Leg 111.**

Analysis no. <sup>a</sup>	143R-1, 46–48 cm (Piece 9)		145-1, 50–52 cm (Piece 8A)		153R-1, 4–6 cm (Piece 2)		154R-1, 97–102 cm (Piece 6A)		160R-1, 16–17 cm (Piece 3)	169R-1, 116–118 cm (Piece 22)
	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	51.25	50.87	52.20	50.28	52.00	48.81	51.76	50.25	50.63	52.25
TiO <sub>2</sub>	0.98	1.04	0.32	1.06	0.59	0.85	0.44	0.90	0.76	0.28
Al <sub>2</sub> O <sub>3</sub>	4.66	1.91	2.58	1.88	2.47	1.15	3.43	1.39	2.84	3.02
Cr <sub>2</sub> O <sub>3</sub>	0.28	0.02	0.69	0.03	0.01	0.06	0.36	0.05	0.00	1.48
<sup>b</sup> FeO*	6.92	17.90	4.66	18.46	8.59	26.23	6.37	18.93	11.97	4.52
MnO	0.15	0.49	0.11	0.50	0.27	0.77	0.17	0.49	0.34	0.13
NiO	0.01	0.01	0.03	0.05	0.00	0.04	0.02	0.02	0.03	0.00
MgO	15.01	12.56	18.14	13.49	17.53	7.09	17.82	12.82	15.66	17.96
CaO	21.22	15.57	20.63	14.18	18.32	15.07	19.18	14.66	16.80	20.76
Na <sub>2</sub> O	0.23	0.29	0.18	0.23	0.22	0.20	0.18	0.23	0.24	0.19
Total	100.71	100.66	99.54	100.16	100.00	100.27	99.73	99.74	99.27	100.59

Cations calculated on the basis of 6 oxygens

Si	1.877	1.934	1.914	1.922	1.918	1.945	1.900	1.937	1.907	1.899
Al	0.201	0.086	0.112	0.085	0.107	0.054	0.148	0.063	0.126	0.129
Ti	0.027	0.030	0.009	0.030	0.016	0.025	0.012	0.026	0.022	0.008
Cr	0.008	0.001	0.020	0.001	0.000	0.002	0.010	0.002	0.000	0.043
Mg	0.820	0.712	0.992	0.769	0.964	0.421	0.975	0.737	0.879	0.973
Ni	0.000	0.000	0.001	0.002	0.000	0.001	0.001	0.001	0.001	0.000
Fe <sup>2+</sup>	0.212	0.569	0.143	0.590	0.265	0.874	0.196	0.610	0.377	0.137
Mn	0.005	0.016	0.003	0.016	0.008	0.026	0.005	0.016	0.011	0.004
Ca	0.833	0.634	0.811	0.581	0.724	0.644	0.754	0.605	0.678	0.808
Na	0.016	0.021	0.013	0.017	0.016	0.015	0.013	0.017	0.018	0.013
Total	3.999	4.003	4.018	4.013	4.018	4.007	4.014	4.014	4.019	4.014
Mg	44.0	37.2	51.0	39.6	49.3	21.7	50.6	37.8	45.4	50.7
Fe	11.4	29.7	7.3	30.4	13.6	45.1	10.2	31.2	19.5	7.2
Ca	44.6	33.1	41.7	30.0	37.1	33.2	39.2	31.0	35.1	42.1

<sup>a</sup> 1 = core of groundmass grain; 2 = rim of grain in analysis no. 1; 3 = core of phenocryst grain with subophitic rim; 4 = rim of grain in analysis no. 3; 5 = core of subophitic groundmass grain; 6 = rim of grain in analysis no. 5; 7 = core of subophitic grain; 8 = rim of grain in analysis no. 7; 9 = core of groundmass grain; 10 = core of phenocryst grain.

<sup>b</sup> Total iron as FeO.

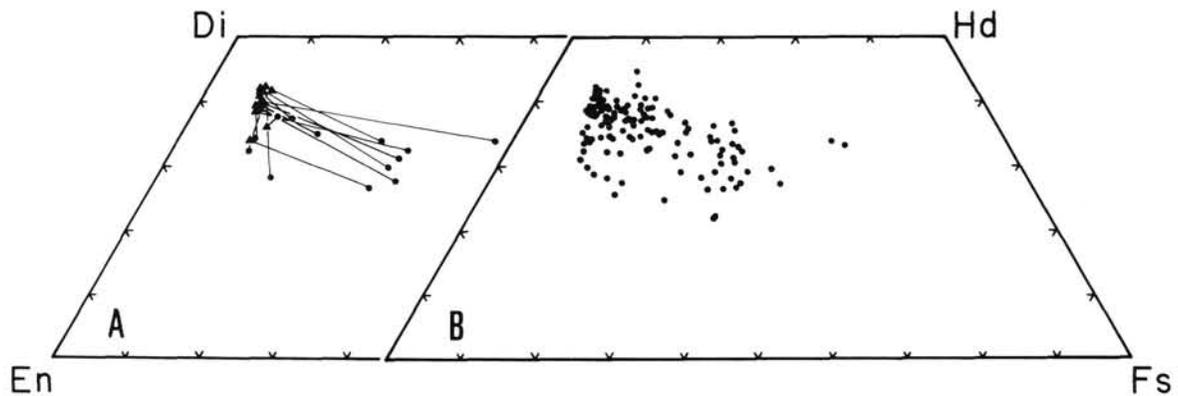


Figure 1. Pyroxene quadrilateral showing plots of the molecular proportions of clinopyroxenes from the Hole 504B basalts recovered during Leg 111. **A.** Clinopyroxene phenocryst compositions. Solid triangles indicate compositions of the phenocryst core; solid circles indicate those of the rim. Analyses obtained from the same grain are connected by a tie line. **B.** Compositions of phenocryst, microphenocryst, and groundmass clinopyroxenes.

content and Mg/(Mg + Fe) for plagioclases with less than An<sub>75</sub>. A similar relationship was observed for the Leg 83 plagioclases (Kempton et al., 1985).

### WHOLE-ROCK CHEMISTRY

The basalts obtained from Hole 504B during the previous DSDP Legs 69, 70, and 83 were classified into three distinct chemical groups: Groups M, D, and T (Autio and Rhodes, 1983; Kempton et al., 1985). The Group M basalts, including those of Kempton et al.'s (1985) Group M', are similar in major and

trace element abundances to those called Type I by Bryan et al. (1976) and are comparatively rare. They exhibit moderate FeO\*/MgO ratios (1.10) and moderate abundances of TiO<sub>2</sub> (1.3–1.4 wt%), Na<sub>2</sub>O (2.4–2.5 wt%), Y (30–31 ppm), Zr (103–104 ppm), and Nb (2–3 ppm). Autio and Rhodes (1983) and Kempton et al. (1985) indicated that the Group M basalts are multiply saturated and that substantial fractionation, involving olivine, plagioclase, and spinel, must have taken place. The majority of the Hole 504B basalts studied previously belongs to Group D (Table 4). These basalts, including those of Kempton et al.'s (1985)

**Table 3. Microprobe analyses of plagioclase from Hole 504B, Leg 111.**

Analysis no. <sup>a</sup>	143R-1, 46-48 cm (Piece 9)		145R-1, 50-52 cm (Piece 8A)	147R-1, 73-77 cm (Piece 8C)		148R-1, 43-45 cm (Piece 6A)	153R-1, 4-6 cm (Piece 2)	154R-1, 97-102 cm (Piece 6A)		165R-1, 26-27 cm (Piece 3B)	
	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub>	47.39	50.11	51.29	45.70	51.36	54.51	50.09	46.97	55.96	52.15	53.43
TiO <sub>2</sub>	0.07	0.03	0.03	0.02	0.06	0.04	0.04	0.00	0.05	0.00	0.06
Al <sub>2</sub> O <sub>3</sub>	32.91	30.33	29.09	33.48	29.54	27.20	30.65	32.30	26.57	28.78	27.86
<sup>b</sup> FeO*	0.07	0.28	0.62	0.35	0.66	0.95	0.47	0.42	0.89	0.74	1.06
MnO	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.04	0.06
MgO	0.13	0.28	0.26	0.17	0.24	0.14	0.32	0.28	0.09	0.24	0.17
CaO	17.98	15.81	14.32	18.50	14.19	11.62	15.85	17.36	10.54	13.91	12.67
Na <sub>2</sub> O	1.41	2.65	3.31	1.15	3.45	4.80	2.62	1.77	5.38	3.63	4.36
K <sub>2</sub> O	0.01	0.00	0.02	0.01	0.00	0.01	0.02	0.00	0.01	0.01	0.02
Total	99.97	99.49	98.95	99.38	99.50	99.27	100.07	99.10	99.49	99.50	99.69
Cations calculated on the basis of 8 oxygens											
Si	2.179	2.303	2.365	2.124	2.355	2.488	2.292	2.183	2.538	2.389	2.440
Al	1.784	1.643	1.581	1.834	1.596	1.463	1.653	1.769	1.421	1.554	1.499
Ti	0.002	0.001	0.001	0.001	0.002	0.001	0.001	0.000	0.002	0.000	0.002
Mg	0.009	0.019	0.018	0.012	0.016	0.010	0.022	0.019	0.006	0.016	0.012
Fe <sup>2+</sup>	0.003	0.011	0.024	0.014	0.025	0.036	0.018	0.016	0.034	0.028	0.040
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.002
Ca	0.886	0.779	0.707	0.921	0.697	0.568	0.777	0.864	0.512	0.683	0.620
Na	0.126	0.236	0.296	0.104	0.307	0.425	0.232	0.160	0.473	0.322	0.386
K	0.001	0.000	0.001	0.001	0.000	0.001	0.001	0.000	0.001	0.001	0.001
Total	4.990	4.992	4.993	5.011	4.998	4.992	4.996	5.011	4.987	4.995	5.002
Ca	87.5	76.7	70.4	89.8	69.4	57.1	76.9	84.4	51.9	67.9	61.6
Na	12.4	23.3	29.5	10.1	30.6	42.8	23.0	15.6	48.0	32.0	38.3
K	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.1
Mg/(Mg + Fe)	0.75	0.63	0.43	0.46	0.39	0.22	0.55	0.54	0.15	0.36	0.23

<sup>a</sup> 1 = core of euhedral phenocryst; 2 = rim of grain in analysis no. 1; 3 = core of groundmass plagioclase; 4 = core of subhedral phenocryst; 5 = rim of grain in analysis no. 4; 6 = core of groundmass plagioclase; 7 = core of a glomerocryst; 8 = core of plagioclase lath from aphyric basalt; 9 = rim of grain in analysis no. 8; 10 = core of groundmass plagioclase; 11 = rim of groundmass plagioclase.

<sup>b</sup> Total iron as FeO.

Group D', have low abundances of TiO<sub>2</sub> (0.71–1.2 wt%), Na<sub>2</sub>O (1.5–2.5 wt%), and K<sub>2</sub>O (<0.01–0.5 wt%), with extremely low abundances of Zr (34–60 ppm), Sr (47–94 ppm), Y (16–28 ppm), and Nb (<0.5–1.3 ppm). The Group T basalts, though minor in amounts, are similar to the Group D basalts in terms of abundances of moderately incompatible elements (e.g., TiO<sub>2</sub>, Na<sub>2</sub>O, Y, and Zr), but are enriched in highly incompatible elements such as La and Nb relative to the other magmaphile elements.

Major and trace element abundances of the Hole 504B basalts recovered during Leg 111 (Table 4) exhibit chemical characteristics similar to those of the Group D basalts described in the preceding, although these data alone do not permit us to distinguish between Group D and Group T unambiguously. Trace element data obtained by the Leg 111 shipboard scientists, however, indicate that 26 analyzed Leg 111 samples are depleted in Nb (<2 ppm) and Zr (<60 ppm) and, hence, belong to Group D (Shipboard Scientific Party, 1988). Thus, most of the petrologic inferences made for the Group D basalts by the previous investigators would also be applicable to our samples. None of the samples listed in Table 4 are considered primitive. These samples are moderately evolved, with FeO\*/MgO ratios of 0.90 to 1.36, and show a slightly scattered, limited range of distribution that defines a possible fractionation trend in various variation diagrams (e.g., as FeO\*/MgO increases TiO<sub>2</sub> and Na<sub>2</sub>O contents correspondingly increase whereas Al<sub>2</sub>O<sub>3</sub> and CaO contents decrease). Major and trace element chemistry of these samples is no doubt modified through low-temperature alteration processes.

### OXYGEN AND HYDROGEN ISOTOPIC VARIATIONS OF THE LEG 111 BASALTS

The Hole 504B basalts have been divided into three zones according to the mode of alteration (Alt et al., 1986a; Kawahata and Furuta, 1985): (1) oxic submarine weathering characterized by iddingsite, saponite, and iron oxide (upper pillow alteration zone or zone I, 274.5–550 mbsf); (2) suboxic to anoxic alteration at slightly warmer temperatures (lower pillow alteration zone or zone II, 550–890 mbsf); and (3) high-temperature hydrothermal metamorphism (transition zone and dike sections, 890–1350 mbsf). Kawahata et al. (1987) further subdivided the lowermost part into two zones, emphasizing the transition zone of hydrothermal alteration under greenschist facies conditions with extensive veining as zone III (890–1050 mbsf) and a zone of high-temperature hydrothermal alteration in the deeper sheeted dike portion as zone IV (>1050 mbsf). The basalt samples analyzed in this investigation represent the continuation of zone IV.

The results of oxygen and hydrogen isotopic analyses for the Leg 111 basalts, together with their water content, are given in Table 5 and shown as a function of depth below seafloor in Figure 3, which also shows the results given by Kawahata et al. (1987) for the Hole 504B samples recovered during previous DSDP legs. Fresh MORB samples have very low water contents (H<sub>2</sub>O<sup>+</sup>) of 0.2 to 0.4 wt%, with δD values of –70‰ to –80‰ (Craig and Lupton, 1976; Kyser and O'Neil, 1984). The rocks from zones I and II contain 0.4–0.8 wt% H<sub>2</sub>O<sup>+</sup>, with δD values ranging from –70‰ to –40‰, reflecting formation of low-

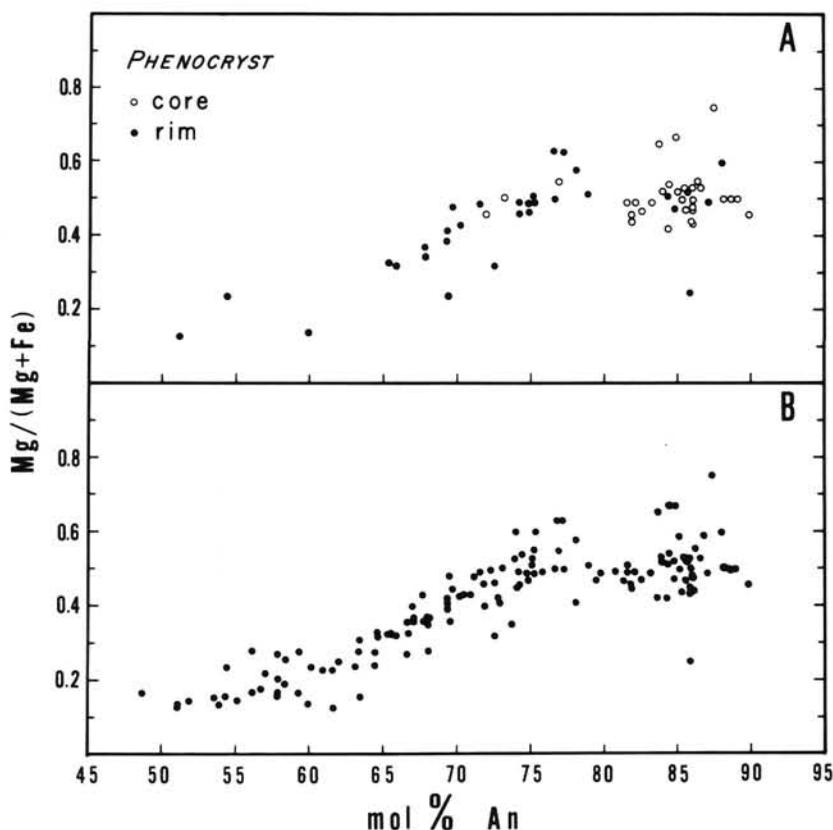


Figure 2. An vs. Mg/(Mg + Fe) in plagioclase from Leg 111 basalt samples. A. Plagioclase phenocrysts. B. Phenocryst, microphenocryst, and groundmass plagioclase.

temperature minerals like iddingsite, saponite, smectite, and iron oxide (Kawahata et al., 1987). In zone III, a conspicuous peak in the  $H_2O^+$  content of up to 5.3 wt% at about 1000 mbsf is associated with a cluster of high  $\delta D$  values ranging from  $-34\text{‰}$  to  $-25\text{‰}$  (average  $-32\text{‰}$ ). The large variation of the  $H_2O^+$  content and high  $\delta D$  values reflect variable and extensive alteration of pillow lavas and sheeted dikes with high permeability in zone III. The  $\delta D$  values are in good agreement with those reported for submarine greenstones (Satake and Matsuda, 1979; Stakes and O'Neil, 1982). In zone IV, where massive sheeted dikes are dominant, the water content decreases down to 1350 mbsf, but below this depth it becomes rather constant ( $1.1 \pm 0.2$  wt%). The  $\delta D$  values tend to become lower toward the bottom of the hole, but still show  $\delta D$  values typical of minerals hydrothermally altered under submarine conditions.

The most abundant hydrogen-bearing minerals in zone IV (Leg 111) are brownish green smectite, chlorite, talc, and actinolite, all developing as olivine pseudomorphs or along microfractures and boundaries of primary minerals. Smectite and chlorite contain more than 10 wt% water, whereas talc and actinolite contain less than 5 wt%. Taking the relative abundances of these minerals into account (Table 1), we thus infer that the whole-rock water content and hydrogen isotopic composition are mostly determined by those values of smectite and chlorite. Figure 4 is a plot of the whole-rock  $\delta D$  values of zone IV as a function of a reciprocal of the water content. The solid line in Figure 4 is the  $\delta D$  vs.  $1/H_2O$  relationship when fresh MORB with  $\delta D = -70\text{‰}$  and  $H_2O^+ = 0.2$  wt% is progressively hydrated with formation of chlorite having  $\delta D = -34\text{‰}$  and  $H_2O^+ = 13$  wt%. The value of  $\delta D_{chl} = -34\text{‰}$  was taken from a vein chlorite found in zone IV at 1222.6 mbsf (Sample 504B-123-1, 11–13 cm) (Kawahata et al., 1987). The two dashed lines

limit a range of possible  $\delta D$  values of chlorite in equilibrium with seawater at  $300^\circ\text{C}$ , where the equilibrium hydrogen isotope fractionation factor ( $1000 \ln \alpha$ ) between chlorite and water was taken to be  $-35 \pm 10$  (Taylor, 1974; Marumo et al., 1980). Most of the data points are above the "chloritization line." This is probably because either the hydrothermal fluids that reacted with the rocks had  $\delta D$  values slightly higher than that of seawater or alteration minerals such as chlorite and smectite were formed at temperatures higher than  $300^\circ\text{C}$ , although hydrogen isotope fractionation factors for the chlorite-water and smectite-water at hydrothermal temperatures have not been well defined yet. It is suggested from Figure 4 that the  $\delta D$  values of the alteration assemblages, extrapolated to  $H_2O^+ > 5$  wt%, are within  $-30\text{‰} \pm 5\text{‰}$ , almost the same range as that observed for the highly altered rocks in zone III (see Fig. 3). This leads to the inference that the  $\delta D$  values of the hydrothermal fluids responsible for alteration in zone IV of the Leg 111 basalts are not significantly different from those values in zones III and IV for the Leg 83 basalts (i.e.,  $\delta D_{fluid} = 3\text{‰} \pm 13\text{‰}$ ), although the temperatures of the hydrothermal fluids may have been somewhat higher than those estimated from fluid inclusion measurements of vein quartz ( $323^\circ\text{C}$  at 998.3 mbsf,  $315^\circ\text{C}$  at 1014.3 mbsf, and  $287^\circ\text{C}$  at 1200 mbsf; Kawahata et al., 1987).

The whole-rock  $\delta^{18}\text{O}$  values throughout Hole 504B (Fig. 3) show that the rocks in zones I and II are more enriched in  $^{18}\text{O}$  than typical fresh MORB ( $\delta^{18}\text{O} = 5.8\text{‰} \pm 0.3\text{‰}$ ; Taylor, 1968; Muehlenbachs and Clayton, 1972) and that the Leg 83 rocks in zones III and IV are hydrothermally highly altered with variable  $\delta^{18}\text{O}$  values ( $4.4\text{‰}$ – $7.0\text{‰}$ ). The  $\delta^{18}\text{O}$  values of the zone IV rocks recovered during Leg 111 range from  $4.9\text{‰}$  to  $5.7\text{‰}$  and are less variable in comparison with those from zone III, with an average ( $5.4\text{‰}$ ) only slightly lower than the value for the fresh

**Table 4. Chemical composition of basalt from Hole 504B, Leg 111, compared with Legs 69, 70, 83 and the Kane Fracture Zone.**

	143R-1, 46-48 cm (Piece 9)	145R-1, 50-52 cm (Piece 8A)	147R-1, 73-77 cm (Piece 8C)	148R-1, 43-45 cm (Piece 6A)	153R-1, 4-6 cm (Piece 2)	154R-1, 97-102 cm (Piece 6A)	159R-1, 46-48 cm (Piece 8)	160R-1, 16-17 cm (Piece 3)	165R-1, 26-27 cm (Piece 3B)	169R-1, 116-118 cm (Piece 22)	JB-1A <sup>a</sup> (R)	JB-1A <sup>b</sup> (GSJ)	Leg 111 basalts <sup>c</sup>	Legs 69 and 70: Group D basalts <sup>d</sup>	Leg 83: Group D' basalts <sup>e</sup>	Kane Fracture Zone, Mid-Atlantic Ridge <sup>f</sup>
Major elements (wt%)																
SiO <sub>2</sub>	48.3	48.7	47.8	49.3	47.3	51.2	51.0	49.6	50.3	47.6	52.1	52.16	49.11	50.4	49.9	49.99
TiO <sub>2</sub>	0.82	0.79	0.89	1.03	0.88	1.01	0.67	1.11	1.00	0.91	1.27	1.30	0.91	0.92	0.92	1.50
Al <sub>2</sub> O <sub>3</sub>	16.93	14.81	15.19	13.57	15.42	14.85	13.93	14.36	15.27	14.87	14.40	14.51	14.92	15.9	15.5	15.95
<sup>8</sup> FeO*	9.21	8.93	8.83	10.30	8.79	9.88	10.93	10.84	9.64	10.07	8.19	8.19	9.74	8.88	9.09	9.62
MnO	0.15	0.15	0.07	0.16	0.07	0.17	0.17	0.19	0.08	0.15	0.14	0.15	0.14	0.16	0.19	0.17
MgO	8.87	9.88	8.34	7.58	8.54	8.24	8.16	8.07	7.64	8.52	7.72	7.75	8.38	8.4	8.6	8.12
CaO	13.27	12.87	12.78	11.46	12.80	12.42	12.41	12.25	12.24	12.88	9.06	9.23	12.54	12.5	13.0	11.46
Na <sub>2</sub> O	1.66	1.52	1.97	1.89	1.93	1.95	1.96	1.98	1.73	1.62	2.72	2.74	1.82	2.0	—	2.55
K <sub>2</sub> O	0.01	0.01	0.01	0.01	0.03	0.02	0.01	0.01	0.02	0.01	1.35	1.46	0.01	0.11	0.02	0.14
Total	99.22	97.66	95.88	95.30	95.76	99.74	99.24	98.41	97.92	96.63	96.95	97.49				
Trace elements (ppm)																
												(JB-1) <sup>b</sup>				
Sr	49	42	54	47	39	51	48	51	28	40	449	435	45	64	55	131
Cr	408	607	464	146	310	303	88	161	119	360	408	405	297	359	336	287
Co	117	103	129	153	82	149	126	128	74	126	74	38.4	119	—	—	45
Ni	133	155	117	71	85	98	64	80	48	117	137	139	97	117	117	129
Cu	91	85	88	75	78	93	81	84	41	538	56	56	125 <sup>h(80)</sup>	—	—	68
FeO*/MgO	1.04	0.90	1.06	1.36	1.03	1.20	1.34	1.34	1.26	1.18			1.16	1.06	1.06	1.18

Note: Dash indicates no analysis.

<sup>a</sup> GSJ standard analyzed together with the Leg 111 samples.

<sup>b</sup> Recommended values for the GSJ standards JB-1 and JB-1A.

<sup>c</sup> Average values of 10 samples of Leg 111 basalts (this study).

<sup>d</sup> Average values of 61 samples (Autio and Rhodes, 1983).

<sup>e</sup> Average values of 56 samples (Kempton et al., 1985).

<sup>f</sup> Average values of 52 samples (Bryan et al., 1981).

<sup>g</sup> Total iron as FeO.

<sup>h</sup> Average value without Sample 111-504B-169R-1, 116-118 cm (Piece 22).

**Table 5. Hydrogen, oxygen, and sulfur isotope analyses of basalts from Hole 504B, Leg 111.**

Sample no.	Core, section, interval (cm), piece	Rock type <sup>a</sup>	Degree of alteration (%)	H <sub>2</sub> O <sup>+</sup> (wt%)	δD (‰)	δ <sup>18</sup> O (‰)	Sulfide as sulfur (ppm)	Sulfate as sulfur (ppm)	δ <sup>34</sup> S of sulfide sulfur (‰)
6	143R-1, 46-48, 9	OP	19.5	1.30	-31.5	5.0	576	9	0.7
11	145R-1, 50-52, 8A	OPC	18.5	1.09	-38.6	5.3	521	9	1.4
20	147R-1, 73-77, 8C	A	13.3	0.93	-40.2	5.6	650	6	1.0
25	148R-1, 43-45, 6A	PC	7.5	1.00	-45.2	5.7	900	14	0.2
37	153R-1, 4-6, 2	P	13.0	1.39	-34.6	5.6	258	1	1.0
42	154R-1, 97-102, 6A	A	7.8	0.97	-37.7	5.5	575	5	0.8
48	159R-1, 46-48, 8	OPC	11.9	0.97	-41.4	5.7	767	3	0.5
49	160R-1, 16-17, 3	PC	11.5	1.10	-37.8	5.3	487	6	0.8
59	165R-1, 26-27, 3B	OPC	15.6	0.91	-35.7	5.0	483	2	0.7
64	169R-1, 116-118, 22	PC	36.3	1.43	-39.0	4.9	404	3	0.4
Average			15.4	1.11	-38.2	5.4	562	6	0.8
1 sigma			8.3	0.19	3.8	0.3	181	4	0.3

<sup>a</sup> OP = olivine-plagioclase-phyric basalt; OPC = olivine-plagioclase-clinopyroxene-phyric basalt; PC = plagioclase-clinopyroxene-phyric basalt; P = plagioclase-phyric basalt; A = aphyric basalt.

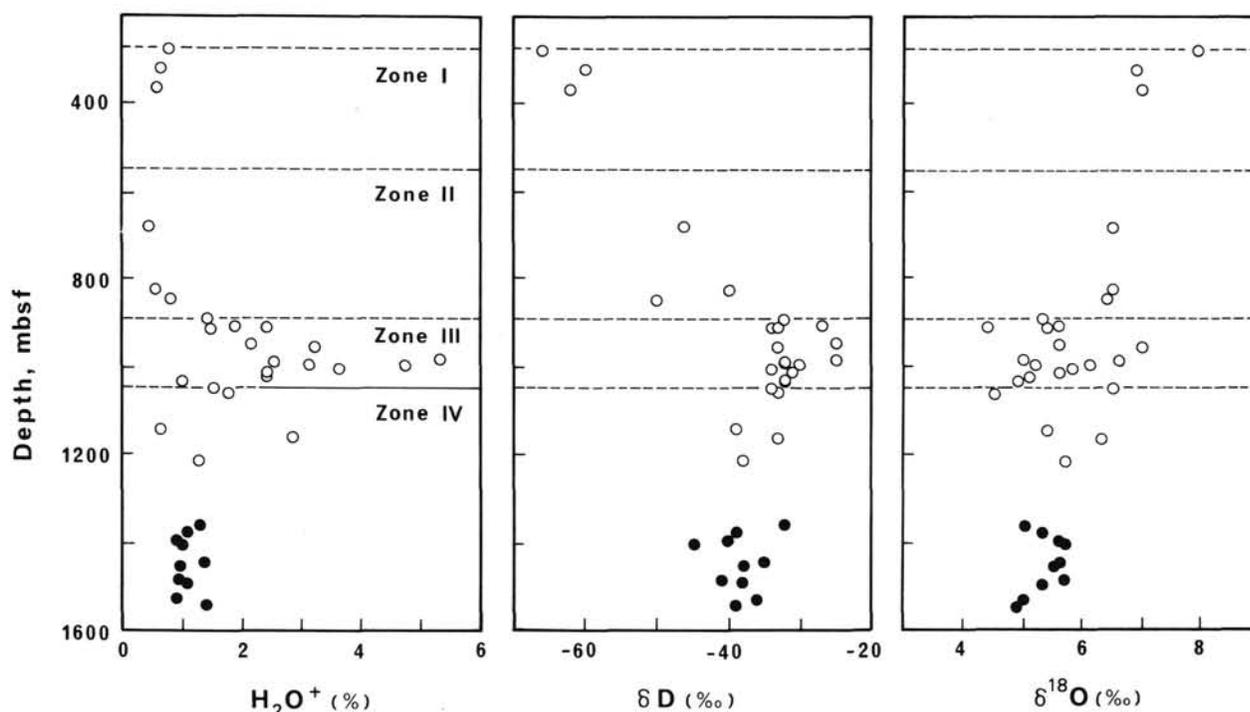


Figure 3. Water content,  $\delta D$ , and  $\delta^{18}O$  values of Leg 111 basalts (solid circles) plotted as a function of depth. The data for the upper rocks (open circles) are from Kawahata et al. (1987). Zone I = oxic weathering; zone II = suboxic to anoxic alteration; zone III = extensive hydrothermal alteration in the pillow/dike transition; and zone IV = hydrothermal alteration of sheeted dikes (Kawahata et al., 1987).

MORB. The  $\delta^{18}O$  values in Table 5 and a general isotopic trend depicted in Figure 3 are in good agreement with those given by Alt et al. (1986b), Friedrichsen (1985), and Barrett and Friedrichsen (1982) for the Hole 504B basalts obtained in the previous legs.

Figure 5 shows the variation in  $\delta^{18}O$  of zone IV Leg 111 samples as a function of percentage alteration and the rock type. The decrease in  $\delta^{18}O$  of the whole rocks is apparently related to the extent of alteration, but not to the textural rock types (Table 5). Assuming that the alteration minerals were in oxygen isotope equilibrium with hydrothermal fluids at 300°C and that the unaltered part retained the original value of  $\delta^{18}O_{MORB} = 5.8\text{‰}$ , we can calculate the whole-rock  $\delta^{18}O$  values in terms of the relative proportions of alteration minerals to the primary minerals and mineral-water fractionation factors. The fractionation factors

are not well known for the minerals found in the alteration assemblage, so that only a rough approximation is made through regression equations compiled by Cole et al. (1987) for smectite, chlorite, talc, actinolite, and sphene. The calculated whole-rock  $\delta^{18}O$  values are in reasonable agreement with the measured values when the  $\delta^{18}O_{fluid}$  is taken to be between 0 and 3‰. The relatively low  $\delta^{18}O$  values of Samples 111-504B-143R-1, 46-48 cm (Piece 9) (5.0‰), 111-504B-160R-1, 16-17 cm (Piece 3) (5.0‰), and 111-504B-169R-1, 116-118 cm (Piece 22) (4.9‰) may indicate the presence of hydrothermal fluids with temperatures as high as 400°C.

The  $\delta^{18}O$  values of the altered portion of the samples can be estimated from a material-balance calculation based on the assumptions that the fresh portion retains the original value of  $\delta^{18}O = 5.8\text{‰}$  and that the percentage of alteration determined

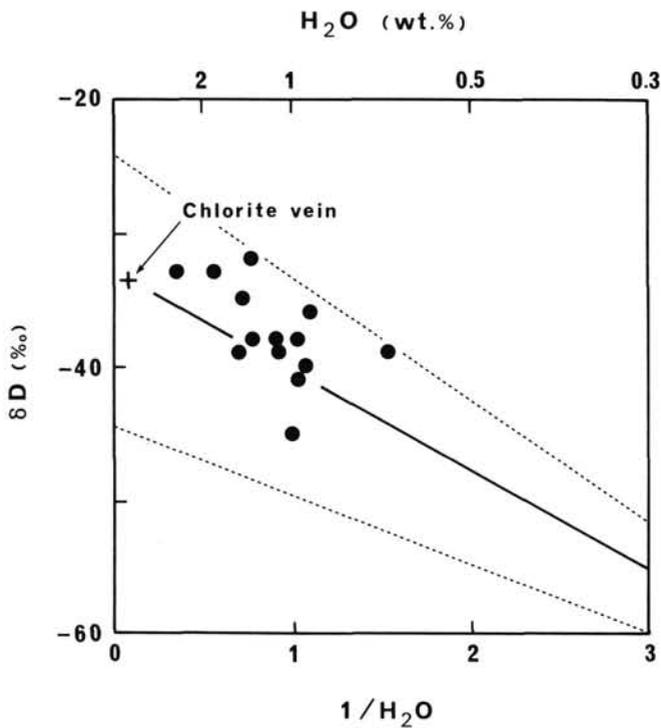


Figure 4. The whole-rock  $\delta D$  values of zone IV rocks (this study; Kawahata et al., 1987) plotted against the reciprocal of water content. A straight line represents the relationship of fresh MORB ( $\delta D = -70\text{‰}$  and  $H_2O = 0.2 \text{ wt}\%$ ) progressively hydrated with the formation of chlorite ( $\delta D = -34\text{‰}$  and  $H_2O = 13 \text{ wt}\%$ ; see text). The two dashed lines limit a range of possible  $\delta D$  values of chlorite in equilibrium with seawater at  $300^\circ\text{C}$ .

on a microscopic scale approximates that actually occurring on a bulk sample scale. The calculated  $\delta^{18}\text{O}$  values range from  $0.7\text{‰}$  to  $5.0\text{‰}$ , with an average of  $3.0\text{‰}$ . The  $\delta^{18}\text{O}_{\text{alt}}$  values tend to be higher with increasing predominance of chlorite and talc. This is somewhat strange, because their mineral-water oxygen

isotope fractionation factors are rather small in the temperature interval between  $300^\circ$  and  $400^\circ\text{C}$ , which indicates that the fluid was more enriched in  $^{18}\text{O}$  during alteration in the zone IV Leg 111 rocks than estimated either locally or regionally. This suggestion is consistent with the high  $\delta^{18}\text{O}$  values ( $5\text{‰}$ – $7\text{‰}$ ) of vein minerals (chlorite and mixed-layer clays) from the same zone (H. Masuda, unpubl. data).

The oxygen isotope composition of the rocks that have interacted with hydrothermal fluids can be related to water/rock ratios, the  $\delta^{18}\text{O}$  values of the interacting fluids, and the oxygen isotope fractionation factors between the rocks and fluids (Taylor, 1977). On the assumption that the  $\delta^{18}\text{O}$  values of fluids and unaltered basalts are 0 and  $+5.8\text{‰}$ , respectively, and that a basalt-water fractionation is approximated by that given in Cole et al. (1987), the maximum  $\delta^{18}\text{O}_{\text{alt}}$  value of  $5\text{‰}$  may be attained when the water/rock ratio is higher than 0.2 (in weight) at  $300^\circ\text{C}$ . Water/rock ratios as great as 2 and temperatures as high as  $420^\circ\text{C}$  are required for the lowest  $\delta^{18}\text{O}_{\text{alt}}$  value of  $1.5\text{‰}$  (excluding an exceptionally low value of  $0.7\text{‰}$ ). Kawahata et al. (1987) estimated a water/rock ratio of 1.6 for zone III. This value, however, should be taken as the maximum, because the rocks from zone III exhibit very high degrees of alteration. The water/rock ratios described here refer to the weight ratios of fluids to "completely reacted" rocks. The extent to which the rocks examined here are altered is about 15% on the average. Therefore, the "actual" water/rock ratios should be smaller than those previously stated by a factor of up to 10, namely in the range of 0.02 to 0.2.

#### SULFUR CONCENTRATIONS AND ISOTOPIC VARIATIONS

Microscopic observations of ore minerals reveal that the sulfide mineralogy is essentially the same for all of the samples. Sulfide minerals are mostly pyrite with trace amounts of chalcopyrite. Pyrite occurs as irregular grains up to 0.3 mm in size, dispersed in the more extensively altered part of the basalts. The pyrite grains are usually associated with small particles of chalcopyrite ( $<0.02 \text{ mm}$  in size) at or near the rims of the grains. Chalcopyrite occurs also as discrete tiny grains ( $<0.001 \text{ mm}$  in size) in silicate matrices. Only a single occurrence of pyrrhotite was found as a tiny inclusion in a pyrite grain from Sample 111-

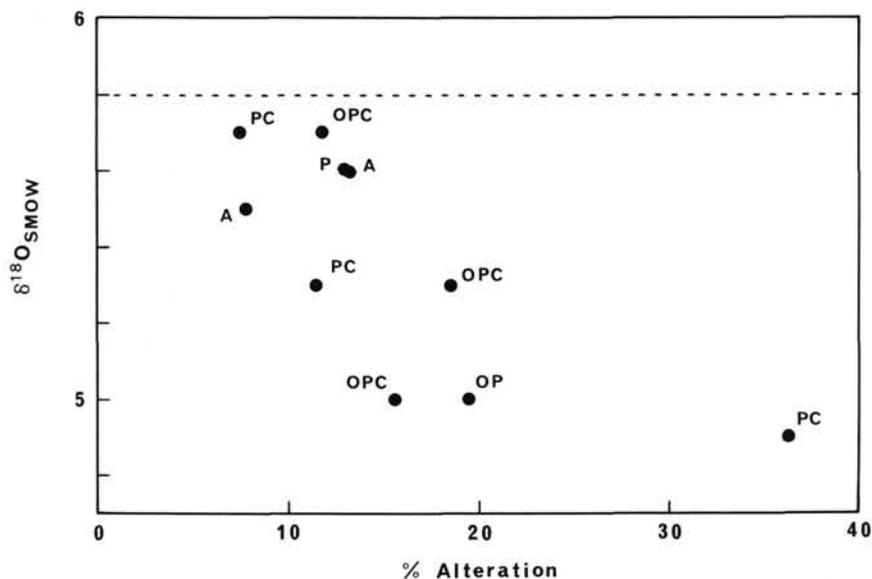


Figure 5. The whole-rock  $\delta^{18}\text{O}$  vs. percentage of alteration as determined by modal analysis for Leg 111 basalts (see Table 1 for rock type abbreviations).

504B-143R-1, 46–48 cm (Piece 9). No other sulfide minerals were detected.

The measured concentrations and isotope compositions of sulfur are given in Table 5. The concentrations of sulfide sulfur range from 258 to 900 ppm. The concentrations of sulfate sulfur are very low, ranging from 1 to 14 ppm, forming only 0.4% to 1.7% of the total sulfur. The  $\delta^{34}\text{S}$  values of sulfide sulfur exhibit a very narrow spread, ranging from +0.2‰ to +1.4‰, with an average of +0.7‰.

The sulfur content of the basalts from the anoxic alteration zone (zone II) is highly variable (20 to 2490 ppm) (Belyi et al., 1983; Hubberten, 1983). In comparison with the basalts in zone II, the sulfur concentration of the Leg 111 basalts is not as variable. The average for the Leg 111 samples is 562 ppm, close to the average value of 650 ppm calculated by Belyi et al. (1983) for the unaltered basalts from the anoxic alteration zone. Although the sulfur contents of the Leg 111 samples are similar to those of the zone II samples, there is a significant difference between them in terms of the sulfur species present. In our samples, sulfur comes almost exclusively from pyrite, whereas chemical analyses of shallow samples indicated the presence of sulfur as monosulfide, pyrite, and sulfate as well (Belyi et al., 1983; Hubberten, 1983). Distler et al. (1983) described the occurrence of primary sulfides from zone II as globules consisting of single-phase sulfide solid solutions (iron-nickel and iron-copper) and as multiphase sulfide aggregates commonly consisting of pyrrhotite, pentlandite, chalcopyrite, cubanite, and magnetite. The occurrence of anhydrite in veins was also reported from various horizons of Hole 504B (Alt et al., 1983, 1985; H. Masuda, pers. comm., 1988). Both the mode of occurrence and sulfur isotope ratios of the anhydrite suggest that it is secondary in origin (Alt et al., 1983, 1985).

A considerable fraction (>5%) of sulfur exists as sulfate in most fresh ocean floor basalts (Sakai et al., 1984). Thus, the almost complete absence of sulfate sulfur as well as of monosulfide sulfur in the Leg 111 samples indicates that the primary sulfur species in the basalts were almost completely lost during the hydrothermal alteration. Figure 6 shows a plot of the total sulfur concentration as a function of  $\text{H}_2\text{O}^+$  content. Although there is a large scatter of data in Figure 6, the total sulfur concentration tends to decrease as alteration proceeds, and the total sulfur concentration extrapolated to  $\text{H}_2\text{O}^+ = 0.4$  wt% is >1000 ppm, which is typical for submarine basalts from the Galapagos

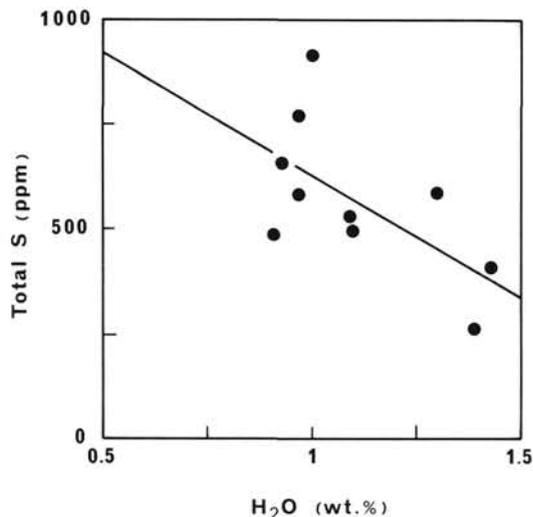


Figure 6. Relationship between the total sulfur and water contents of Leg 111 basalts. The line is the least-squares fit.

Ridge (Sakai et al., 1984). Sulfate sulfur may have either been dissolved away into the hydrothermal fluids or originally been very small in concentration. Monosulfide sulfur would have been oxidized to form pyrite or partially oxidized to form sulfate ions.

The isotopic compositions of sulfide sulfur studied in this investigation show a very narrow variation. The average value of +0.7‰ for the Leg 111 samples is very close to the  $\delta^{34}\text{S}$  values of fresh basalt glasses from the nearby Galapagos Ridge (+0.4‰ and +0.5‰) and other fresh ocean floor basalt glasses (+0.3‰  $\pm$  0.5‰) (Sakai et al., 1984). In contrast, the sulfides from zone II have highly variable  $\delta^{34}\text{S}$  values ranging from -11.9‰ to +10.3‰ (Belyi et al., 1983; Hubberten, 1983). To explain the large variation observed, decomposition by oxidation of primary sulfides to form sulfite or thiosulfate ions was postulated. The sulfite and/or thiosulfate ions thus formed were then disproportionated to pyrite and sulfate with a large isotope fractionation (Field et al., 1976; Belyi et al., 1983).

Honnorez et al. (1985) obtained  $\delta^{34}\text{S}$  values of +2.9‰ to +5.0‰ for pyrite from the stockwork sulfide veins drilled at 910–928 mbsf in Hole 504B on Leg 83. They interpreted the increase in  $\delta^{34}\text{S}$  values relative to ocean floor basalts as incorporation of sulfide derived from the reduction of seawater sulfate.

The  $\delta^{34}\text{S}$  values of pyrites studied herein apparently indicate that such a disproportionation accompanied by a large isotope fractionation is not applicable to the Leg 111 samples. The close similarity in  $\delta^{34}\text{S}$  values to those of fresh ocean floor basalts, especially when the total sulfur concentrations are high (Fig. 7), suggests that the primary sulfur was converted to the secondary pyrite without a large isotope fractionation. The formation of pyrite from the primary monosulfides (mainly pyrrhotite) is an oxidation reaction. The possible reaction that is responsible for the pyrrhotite-pyrite conversion may be



Loss of  $\text{H}_2\text{S}$  would lower the sulfur content of the altered basalts without giving rise to a large change in the isotopic compositions (Ohmoto and Rye, 1979). The aforementioned reaction would produce a mineral assemblage of pyrite-magnetite-quartz, which was a typical run product of the experimental fayalite-seawater interaction (Shanks et al., 1981). The following pyrite-pyrrhotite conversion reaction has been proposed by Shanks

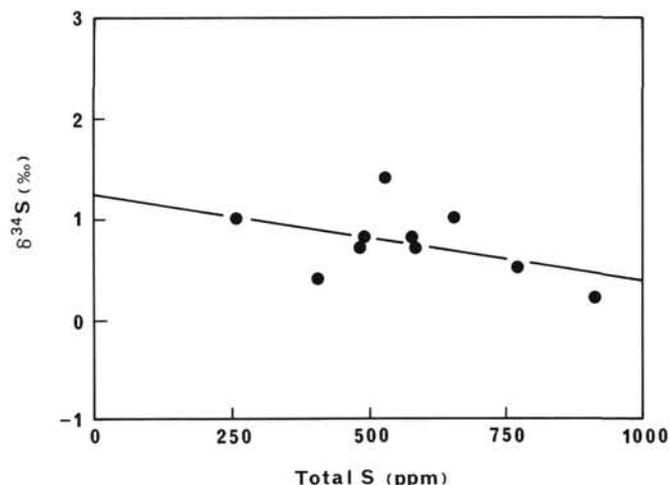
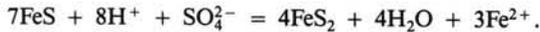


Figure 7. Sulfur isotopic ratios plotted as a function of total sulfur concentration for Leg 111 basalts. The line is the least-squares regression of the data.

and Seyfried (1987), assuming that seawater-derived sulfate is the required oxidizing agent:



This reaction successfully explains the slight but distinct enrichment in  $^{34}\text{S}$  of the stockwork pyrite from Hole 504B (Honnorez et al., 1985) as well as sulfides from ocean floor massive sulfide deposits (e.g., the East Pacific Rise at  $21^\circ\text{N}$ —Styrt et al., 1981; Juan de Fuca Ridge—Shanks and Seyfried, 1987; Galapagos Rift at  $86^\circ\text{W}$ —Skirrow and Coleman, 1982). The latter reaction might be applicable also to the Leg 111 case, if the ratio of sulfide-sulfur to sulfate-sulfur is close to or larger than 7 in basaltic magmas and if both sulfur forms are remobilized with hydrothermal fluids that are more oxidative than in the magmas.

### VARIATIONS IN STRONTIUM AND NEODYMIUM ISOTOPE RATIOS

The strontium and neodymium isotopic analyses of the Leg 111 basalts from Hole 504B are given in Table 6. The variation in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for the Leg 111 section is shown in Figure 8 along with previously reported data (Kawahata et al., 1987). In contrast to the variation in zone III and the uppermost part of zone IV, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the deeper part of zone IV (Leg 111) are uniform and very close to those reported for fresh MORB (i.e.,  $0.70265 \pm 0.00020$ ; Hart, 1976). These data indicate that the basalts are little affected by hydrothermal alteration, in agreement with observations of mineralogy,  $\text{H}_2\text{O}^+$  content,  $\delta\text{D}$ , and  $\delta^{18}\text{O}$  variations discussed in the previous sections.

The Sr and Nd isotopic ratios of basalts from Hole 504B are plotted in Figure 9 and compared to those from the East Pacific Rise, East Pacific Rise small seamounts, and Galapagos Islands (Zindler et al., 1984). The data from the Galapagos Spreading Center reported by Verma et al. (1983) are also shown in Figure 9. Zindler et al. (1984) ascribed the scatter of the Sr and Nd isotopic ratios of rocks from the East Pacific Rise small seamounts to mantle heterogeneity. White and Hofmann (1978) suggested that the larger scatter for the Galapagos Islands was due to mixing of two magmas derived from two different mantle sources with isotopically distinct features. Subsequently, White (1979) indicated that much of the scatter resulted from weathering effects on Sr isotopic ratios. Verma et al. (1983) explained the scatter of the isotopic data from the Galapagos Spreading Center by mixing of the MORB source and Galapagos plume.

The basalts from Hole 504B are quite similar to those from the East Pacific Rise but are significantly different from those from the Galapagos Islands with respect to Sr and Nd isotopic compositions. The systematic variations of the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of the Hole 504B basalts may be interpreted to represent either hydrothermal alteration after emplacement

**Table 6. Strontium and neodymium isotopic analyses of basalts from Hole 504B, Leg 111.**

Sample no.	Core, section, interval (cm), piece	$^{87}\text{Sr}/^{86}\text{Sr}$	$\epsilon_{\text{Sr}}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$\epsilon_{\text{Nd}}$
6	143R-1, 46-48, 9	0.70270 (2)	-25.6	0.513128 (19)	9.54
11	145R-1, 50-52, 8A	0.70261 (2)	-26.8	0.513211 (27)	11.14
20	147R-1, 73-77, 8C	0.70264 (2)	-26.4	0.513112 (22)	9.21
25	148R-1, 43-45, 6A	0.70261 (2)	-26.9	0.513132 (27)	9.60
37	153R-1, 4-6, 2	0.70271 (2)	-25.4	0.513137 (29)	9.69
42	154R-1, 97-102, 6A	0.70274 (2)	-25.0	0.513130 (21)	9.56
48	159R-1, 46-48, 8	0.70258 (3)	-27.3	0.513212 (24)	11.16
49	160R-1, 16-17, 3	0.70272 (5)	-25.3	0.513195 (27)	10.83
59	165R-1, 26-27, 3B	0.70261 (2)	-26.8	0.513200 (27)	10.92
64	169R-1, 116-118, 22	0.70281 (2)	-24.0	0.513117 (18)	9.30

Note: Numbers in parentheses represent an analytical reproducibility in terms of 2 sigma, referring to the last digits.

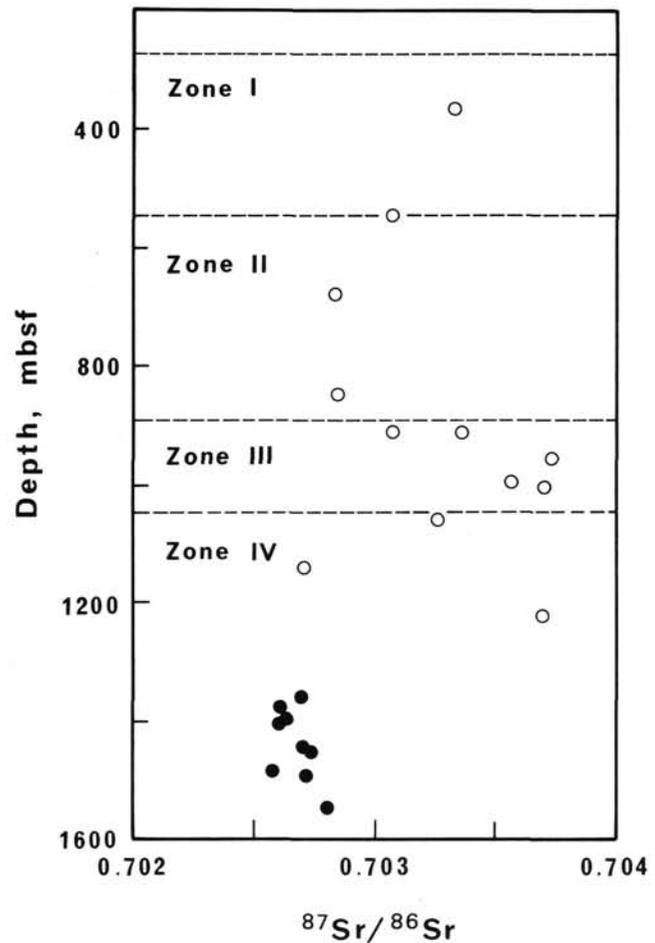


Figure 8. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (solid circles) of the Leg 111 basalts plotted against depth. Open circles are data from Kawahata et al. (1987) shown for comparison.

or existence of two magmas generated at distinct sources with different isotopic ratios, that is, heterogeneity in the mantle source. We examine these possibilities in the following.

Varying degrees of hydrothermal alteration may be invoked to explain the systematic isotopic variation, because Sample 111-504B-169R-1, 116-118 cm (Piece 22), which has the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and the lowest  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio, was subjected to intense alteration (Table 1). Basalt-seawater interaction is known to raise the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of basalt, as seen in Figure 8, but the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios usually remain almost unchanged because of very low concentration of Nd in seawater (namely 2-3 pg/g; Piepgras and Wasserburg, 1980).

Interaction with hydrothermal fluids that have reacted with pelagic clays with  $^{87}\text{Sr}/^{86}\text{Sr} = 0.70917$  and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.51247$  (Goldstein and O'Nions, 1981) or those reacted with a mantle plume at Galapagos with  $^{87}\text{Sr}/^{86}\text{Sr} = 0.704$  and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.51282$  (Verma et al., 1983) might be a possible cause for the isotopic variations observed in the Hole 504B basalts if the fluids had a moderately high Nd concentration. However, Nd concentrations ranging from 20 to 336 pg/g with  $\epsilon_{\text{Nd}} = -3$  (or  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512486$ ) were reported for hydrothermal fluids from  $21^\circ\text{N}$  on the East Pacific Rise (Piepgras and Wasserburg, 1985). The preceding Nd concentrations are 6-100 times larger than that of seawater, but still much lower than that of basalts from the East Pacific Rise and the East Pacific Rise small seamounts (i.e., 6-33 ppm; Zindler et al., 1984). If a maximum

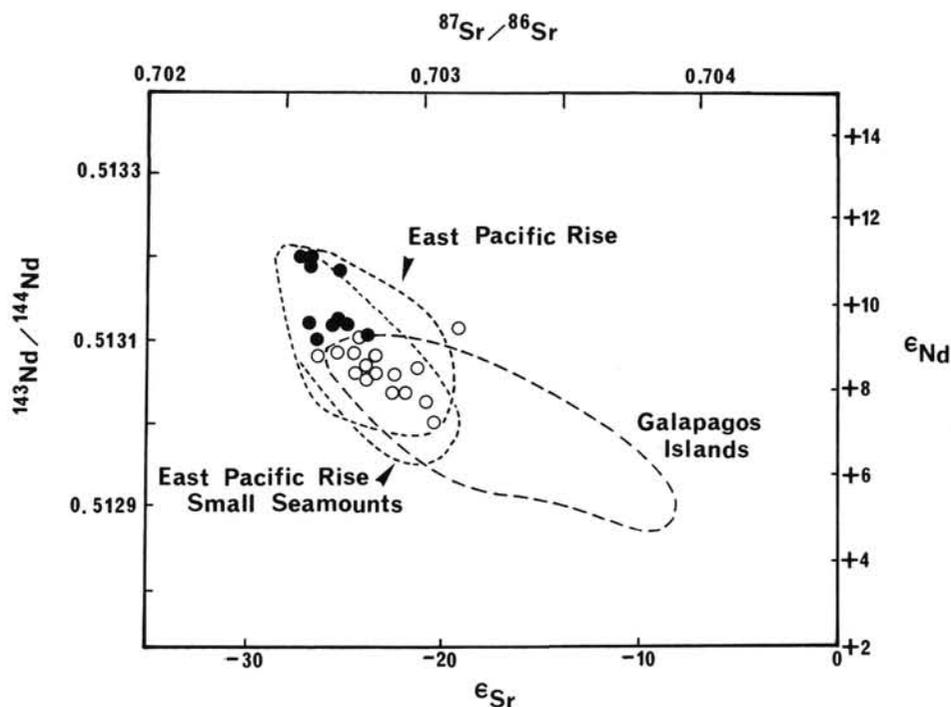


Figure 9. Sr-Nd isotopic correlation for the Leg 111 basalts (solid circles) and related rocks. The regions for the East Pacific Rise, East Pacific Rise small seamounts, and Galapagos Islands are from Zindler et al. (1984). Open circles represent basalts from the Galapagos Spreading Center (Verma et al., 1983).

solubility of Nd in hydrothermal fluids is assumed to be 300 pg/g and  $^{143}\text{Nd}/^{144}\text{Nd}$  is equal to 0.51247, very high water/rock ratios of about 4000 are required to change the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of basalt from 0.51321 (Sample 111-504B-159R-1, 46–48 cm [Piece 8]) to 0.51312 (Sample 111-504B-169R-1, 116–118 cm [Piece 22]). This value contradicts sharply with the low water/rock ratios of 0.02–0.2 based on the oxygen isotopic balance. Therefore, hydrothermal alteration is highly unlikely as a cause of the observed Nd and Sr isotopic variations in the Hole 504B basalts.

The Nd isotopic data of the Leg 111 basalts from Hole 504B indicate that the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios can be divided into two groups, with group averages of 0.51313 and 0.51320, respectively (Fig. 9). There is no intermediate group. The ratios of the first group are close to the highest ones of the Galapagos Spreading Center basalts, whereas those of the latter group agree with the highest values of rocks from the East Pacific Rise and the East Pacific Rise small seamounts. This suggests that each group represents a distinct magma derived from a different mantle source without mixing. The variations in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios within each group and those between the two groups may also indicate a small-scale mantle heterogeneity.

### SUMMARY AND CONCLUSIONS

The basalts recovered from Hole 504B during Leg 111 occur predominantly as the massive units that probably represent the interiors of large dikes. The basalt samples chosen for our study can be divided into aphyric and phyric basalts. In the aphyric basalts plagioclase and clinopyroxene are the main primary constituents (> 80 vol%), and olivine, Fe-Ti oxide, and quartz are minor constituents. Phenocrysts of the phyric basalts consist of abundant plagioclase with lesser amounts of clinopyroxene and olivine, although the olivine is completely altered to phyllosilicates. Plagioclases and clinopyroxenes remain rather fresh.

The chemical features are essentially similar to those of the Group D basalts that comprise the majority of rocks recovered

during the previous DSDP Legs 69, 70, and 83. The Leg 111 basalts are characterized by low abundances of  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and some minor elements such as Zr, Sr, Y, and Nb. The phenocrystic clinopyroxenes are strongly zoned and show a wide range of compositional zonation, but the core compositions are limited in the range of endiopside, implying that the Leg 111 basalts were derived from magmas with similar  $\text{FeO}^*/\text{MgO}$  ratios. Plagioclase crystals also show a wide chemical variation from  $\text{An}_{90}$  to  $\text{An}_{49}$ , but the cores, in general, are rich in the An component. The Ca-rich nature of the plagioclases is in common with that observed in the previously studied Hole 504B plagioclases.

The Leg 111 basalts are moderately altered, typically in parts of interstitial fine-grained materials and along microfractures and grain boundaries of primary minerals. The secondary minerals are chlorite, actinolite, talc, smectite, quartz, sphene, and pyrite. The extent of alteration on a whole-rock basis is rather uniform throughout the entire Leg 111 section, as shown by the limited ranges of water content,  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{34}\text{S}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  values. The alteration occurred at temperatures of 300°–400°C under very low water/rock ratios (< 0.2). The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of the hydrothermal fluids responsible for the alteration are close to or slightly greater than those of seawater.

During alteration, primary sulfide (pyrrhotite) was exclusively remobilized to form the secondary pyrite in one part and to dissolve into fluids in the other. The  $\delta^{34}\text{S}$  values of pyrite are very close to those of fresh submarine basalt glasses, indicating that almost no isotopic fractionation nor incorporation of seawater sulfate took place during the pyritization process. The low-sulfate nature of the hydrothermal fluids is consistent with the idea that the deeper sheeted dike portion of the Hole 504B served as a feeder zone for the fluids in which sulfate ions had been lost during passage through the recharge zone.

The Sr and Nd isotopic compositions of the studied basalts are indistinguishable from those of typical fresh MORB, again implying low seawater/rock ratios during alteration. However,

the Nd isotopic compositions are split into two groups, suggesting isotopic heterogeneity in their magma sources.

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