7. REE, Ba, AND Sr ABUNDANCES AND Sr, Nd, AND Ce ISOTOPIC RATIOS IN HOLE 504B BASALTS, ODP LEG 111, COSTA RICA RIFT¹

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ABSTRACT

Abundances of rare earth elements (REE), Ba, and Sr and isotopic ratios of Sr, Nd, and Ce were determined for six samples of basalts drilled at Hole 504B on Leg 111 of the Ocean Drilling Program. Analyses found that these basalts are the most depleted in Sr, Ba, and light REE among mid-ocean ridge basalts (MORB); Ba depletion is especially notable. On the other hand, Sr, Nd, and Ce isotopic ratios for basalts from Hole 504B are within the range of typical MORB values.

INTRODUCTION

Studies of rare earth element (REE) abundances and Nd and Sr isotopic ratios of mid-ocean ridge basalts (MORB) contribute to our understanding of the formation of these rocks and the geochemical nature of the mantle from which MORB is derived. Recently, tracing of Ce isotopes based on the decay of ¹³⁸La to ¹³⁸Ce has been applied to studies of the petrogenesis and evolution of the Earth's crust and mantle (Tanaka and Masuda, 1982; Tanaka et al., 1987, 1988; Dickin, 1987a, 1987b, 1988; Dickin et al., 1987). Coupling analysis of the La-Ce system with the Sm-Nd system should be significant because both pairs belong to the rare earth group. In this chapter we report REE, Sr, and Ba abundances and isotopic ratios of Sr and Nd in Hole 504B basalts, recovered during Ocean Drilling Program (ODP) Leg 111 investigations of the Costa Rica Rift. The Ce isotopic ratio is reported for one sample.

Hole 504B, of Deep Sea Drilling Project (DSDP) Legs 69, 70, and 83 and ODP Leg 111, is the deepest section of basement drilled in the ocean crust, in 5.9-Ma crust about 200 km south of the Costa Rica Rift. Hole 504B basalts are known to be the most depleted among MORB in incompatible elements such as Th, Ta, Na, Sr, and light REE; however, basalts moderately enriched in the incompatible elements—a different magma type were also recovered (Autio and Rhodes, 1983; Marsh et al., 1983; Etoubleau et al., 1983; Kempton et al., 1985; Tual et al., 1985; Emmermann, 1985). Leg 111 deepened Hole 504B by 212.3 m, to a total depth of 1562.3 m below seafloor (mbsf) or 1287.8 m into basement. New data for trace element abundances and isotopic ratios from this section of Hole 504B will help clarify the geochemical nature of the deepest recovery of MORB.

METHODS

Six samples from Hole 504B were analyzed; descriptions of Samples 111-504B-143R-1, 22-24 cm, 111-504B-145R-2, 62-64 cm, 111-504B-148R-1, 83-88 cm, 111-504B-150R-1, 122-123 cm, 111-504B-163R-2, 29-31 cm, and 111-504B-169R-1, 102-105 cm, are in Table 1. The rocks recovered from Hole 504B during Leg 111 are aphyric or sparsely to highly phyric, fine- to medium-grained olivine tholeiitic basalts. Most are slightly altered.

After acid decomposition of the samples, REE, Ba, and Sr were separated from major elements by an AG50W-X8 resin column in HCl me-

Table 1.	Descriptions	of samples	analyzed,	Hole 504B,
Leg 111	(Shipboard Sci	ientific Par	ty, 1988).	

Core, section, interval (cm)	Description		
143R-1, 22-24	Moderately plagioclase-olivine-clinopyroxene phyric basalt		
145R-2, 62-64	Moderately clinopyroxene-plagioclase-olivine phyric basalt		
148R-1, 83-88	Moderately plagioclase-clinopyroxene-olivine phyric basalt		
150R-1, 122-123	Sparsely olivine-clinopyroxene-plagioclase phyric basalt		
163R-2, 29-31	Moderately plagioclase-olivine-clinopyroxene phyric basalt		
169R-1, 102-105	Moderately clinopyroxene-olivine-plagioclase phyric basalt		

dia. Ce and Nd for isotopic analysis were separated using an AG5OW-X8 resin column with α -hydroxy-isobutyric acid. REE, Sr, and Ba abundances were determined on a JEOL JMS-05RB mass spectrometer by the isotope dilution method. Isotopic compositions of Sr and Nd were measured on a VG 354 mass spectrometer using three and five Faraday collectors, respectively. Ce isotopic composition was measured on a VG 54-38 double-focusing mass spectrometer. The measured isotopic ratios of Sr, Nd, and Ce were normalized against 86 Sr/ 88 Sr = 0.1194, 146 Nd/ 144 Nd = 0.7219, and 136 Ce/ 142 Ce = 0.01688, respectively. Details of our Ce isotope measurement are described elsewhere (Makishima et al., 1987).

Isotopic ratios were measured for the standard salts as follows: ⁸⁷Sr/ ⁸⁶Sr ratio for NBS987 Sr standard was 0.71019 \pm 4 (2 σ_m); ¹⁴³Nd/¹⁴⁴Nd ratios for La Jolla Nd standard and for Johnson Matthey Nd₂O₃ (JMC32l, batch no. S.810931A) were 0.511823 \pm 16 and 0.511080 \pm 12, respectively; and ¹³⁸Ce/¹⁴²Ce ratio for Johnson Matthey CeO₂ (JMC304) was 0.0225775 \pm 14. Our ¹⁴³Nd/¹⁴⁴Nd ratios for both La Jolla standard and Johnson Matthey Nd₂O₃ exhibit slightly lower values than those reported by O'Nions et al. (1977), Jahn et al. (1980), Lugmair et al. (1983), and Bell and Blenkinsop (1987) (Table 2).

In plotting chondrite-normalized REE, Sr, and Ba abundances, a linear scale as well as a logarithmic scale was used for the ordinate axis, following Shimizu et al.'s (1980) strategy for distinguishing REE patterns of abyssal tholeiites. Masuda (1979) explained the advantage and theoretical significance of linear scale plotting for solid-type igneous rocks or potentially for the conjugate relationship between the solid-and liquid-type rocks, based on the model originally presented by Masuda and Matsui (1966) and further developed by Masuda. In Masuda's (1979) model, the basic evolutionary framework for the REE patterns of whole-rock samples of common igneous rocks is determined by the solidification process, starting from melt with a chondritic REE abundance ratio as a linear bulk-partition coefficient function. Thus, for incipient solid-phase REE patterns, using a linear scale for the vertical axis is advantageous in demonstrating rectilinearity, whereas a logarithmic scale is significant for plotting liquid-type material systems.

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

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Table 2. Comparison of ¹⁴³Nd/¹⁴⁴Nd ratios for Nd standard salts.

	La Jolla standard	JMC 321 Nd ₂ O ₃	
This study	$0.511823\ \pm\ 0.000016$	0.511080 ± 0.000012	
Lugmair et al. (1983)	0.511858 ± 0.000004		
Bell and Blenkinsop (1987)	0.51186 ± 0.00002		
O'Nions et al. (1977)		0.51112 ± 0.00003	
Jahn et al. (1980)		0.511137 ± 0.000008	

Note: Errors are $2\sigma_{\rm m}$. The ¹⁴³Nd/¹⁴⁴Nd ratio by Lugmair et al. (1983) was normalized against ¹⁴⁸Nd/¹⁴⁴Nd = 0.241572, and the ¹⁴⁶Nd/¹⁴⁴Nd correspondingly obtained was 0.721878 \pm 0.000007 for the La Jolla Nd standard. The Nd isotopic ratios from O'Nions et al. (1977), Jahn et al. (1980), Bell and Blenkinsop (1987), and this study were normalized against ¹⁴⁶Nd/ ¹⁴⁴Nd = 0.7219.

RESULTS AND DISCUSSION

REE, Ba, and Sr Abundances

REE, Sr, and Ba abundances for four samples are listed in Table 3 and presented on chondrite-normalized patterns (Masuda-Coryell plot; Masuda, 1962; Coryell et al., 1963) in Figure 1. The depletion of Ba (0.70-0.89 ppm) is remarkable. Ba abundance in oceanic tholeiitic basalts ranges from several to several hundred parts per million and averages 14.5 ppm in Puchelt's (1972) list of Ba concentration in terrestrial rocks. Similar typical Ba abundances of 12.2 ppm for Type I MORB and 55 ppm for Type II MORB are reported by the Basaltic Volcanism Study Project (1981). In comparison to Bryan et al.'s (1976) classification, Type I corresponds to basalt erupted along the "normal" topographic section of mid-ocean ridges and Type II corresponds to basalt produced at elevated sections of mid-ocean ridges adjacent to volcanic platforms associated with oceanic islands. Sr abundances in the Hole 504B basalts are also low (54-61 ppm), but are not as depleted as Ba abundances. Faure (1986) reported Sr abundances ranging from 96 to 154 ppm for oceanic tholeiites from the Pacific Ocean. The average Sr concentrations summarized by the Basaltic Volcanism Study Project (1981) are 127 and 105 ppm for Type I and Type II MORB, respectively.

 $(La/Sm)_N$ values around 0.3 for Hole 504B samples (Table 3) are lower than the 0.4-0.7 values of MORB from the corresponding normal ridge segment (Sun et al., 1979), suggesting

Table 3. REE, Ba, and Sr abundances (ppm) in Hole 504B basalts.

	Sample				
Element	143R-1, 22-24 cm	145R-2, 62-64 cm	148R-1, 83-88 cm	163R-2 29-31 cm	Normalizing value ^a
La	1.177	1.023	1.23	1.086	0.378
Ce	4.59	3.98	4.97	4.44	0.976
Nd	5.44	4.71	5.98	5.36	0.716
Sm	2.27	1.95	2.39	2.25	0.230
Eu	0.842	0.727	0.921	0.809	0.0866
Gd	3.51	2.95	3.73	3.35	0.311
Dy	4.51	3.79	4.74	4.36	0.390
Er	2.91	2.44	3.08	2.74	0.255
Yb	2.86	2.31	3.01	2.65	0.249
Lu	0.431	0.338	0.453	0.359	0.0387
Ba	0.887	0.695	0.768	0.705	4.21
Sr	56.5	54.4	59.7	61.3	11.1
Ratios betw	een chrondri	te-normalized	values		
(La/Sm) _N	0.316	0.319	0.313	0.294	
(Ce/Yb) _N	0.409	0.440	0.421	0.428	

^a Normalizing values for REE and Ba are from abundances of these elements in Leedey chondrite (Masuda et al., 1973; Nakamura and Masuda, 1973). The normalizing value for Sr, 11.1 ppm, is from Gopalan and Wetherill (1971). strong depletion of light REE in the Hole 504B basalts. Sr and Ba abundances increase with increasing $(La/Sm)_N$ values and the Hole 504B basalts fall in the lowest value ranges (Figs. 2 and 3).

The chondrite-normalized REE patterns of four samples from Hole 504B are similar to each other, with some variation of fine structures in heavy REE span (Fig. 4). Generally, La, Ce, and Nd plot along a straight line, but Ce has a positive deviation from a La-Ce-Nd regression line whereas La and Nd deviate in a negative direction. (From a theoretical viewpoint, these deviations indicate an expected slight curvature.) REE patterns of basalts from Holes 417A and 417D (DSDP Leg 51, the Bermuda Rise; Shimizu et al., 1980) have the same features as observed for the Hole 504B La-Ce-Nd span. In plots of Samples 111-504B-143R-1, 22-24 cm, and 111-504B-148R-1, 83-88 cm, Gd, Dy, Er, and Yb appear to fall along a straight horizontal line, whereas heavy REE for Samples 111-504B-145R-2, 62-64 cm, and 111-504B-163R-2, 29-31 cm, show slightly curved features with a maximum at Dy.

Sr, Nd, and Ce Isotopic Ratios

The isotopic ratios of Sr. Nd. and Ce listed in Table 4 are essentially unaffected by alteration. 87Sr/86Sr ratios for five samples from this study are between 0.7024 and 0.7028, with a mean of 0.70266. A similar value of 0.70266 was reported as a mean ⁸⁷Sr/⁸⁶Sr ratio for the Hole 504B basalts recovered from 330 to 560 m within basement during Legs 69 and 70 (Barret and Friedrichsen, 1982; Barret, 1983), which is almost identical to the average isotopic value of fresh MORB. On the other hand, Barret and Friedrichsen (1982) and Barret (1983) found higher ⁸⁷Sr/⁸⁶Sr ratios, with a mean of 0.70320, in samples from the upper 260-m interval within basement at Hole 504B, and they interpreted these higher ratios in terms of strontium-isotope alteration during basalt-seawater interaction. Furthermore, for the Hole 504B basalts in the 580-1075-m interval within basement (Leg 83), higher and scattered ⁸⁷Sr/⁸⁶Sr ratios between 0.7025 and 0.7068 and with a mean of 0.7038 were reported by Friedrichsen (1985). Based on strontium, oxygen, and hydrogen isotopic compositions, Friedrichsen (1985) suggested the existence of a seawater/crust interface, now at a depth of 620 m within basement, during high-temperature water-rock interactions. The 87Sr/86Sr ratios obtained from our investigation have an average value similar to that for fresh MORB, suggesting that basalts in the 1075-1287-m interval within basement have undergone little alteration.

The ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr ratios of the Hole 504B basalts are similar to those reported for oceanic basalts from the Pacific, including the East Pacific Rise and Juan de Fuca and Galapagos ridges (Fig. 5) (Cohen et al., 1980; White and Hofmann, 1982). The similarity of the ¹⁴³Nd/¹⁴⁴Nd and ¹³⁸Ce/ ¹⁴²Ce ratios of Sample 111-504B-143R-1, 22-24 cm, to MORB ratios from the Mid-Atlantic Ridge (22°59.14'N, 43°30.39'W, and 23°02.63'N, 45°01.05'W) and East Pacific Rise (12°52'S, 11°57'W) (Tanaka et al., 1987) is evident in Figure 6.

Although a limited number of isotopic ratios were determined in this study, the Sr, Nd, and Ce isotopic ratios for Hole 504B basalts are within the range of typical MORB values. With respect to the trace element abundances, however, high depletion of incompatible elements in the Hole 504B basalts is not typical of MORB.

Isotopic Evolution of Nd

The isotopic evolution of Nd from Hole 504B basalts and depleted mantle relative to chondritic uniform reservoir (CHUR) is shown in Figure 7. Present-day CHUR values are 143 Nd/ 144 Nd = 0.512638 and 147 Sm/ 144 Nd = 0.1966 (Wasserburg et al., 1981). Two sets of corresponding values for present-day de-



Figure 1. Chondrite-normalized (logarithmic scale) REE-Ba-Sr patterns of Hole 504B basalts (Samples 111-504B-143R-1, 22-24 cm, 111-504B-145R-2, 62-64 cm, 111-504B-148R-1, 83-88 cm, and 111-504B-163R-2, 29-31 cm). Normalizing values for REE and Ba are from abundances of these elements in Leedey chondrite (Masuda et al., 1973; Nakamura and Masuda, 1973). The normalizing value for Sr, 11.1 ppm, is from Gopalan and Wetherill (1971).

pleted mantle were chosen for average MORB; the first set of parameters for depleted mantle (DM-A) is ¹⁴³Nd/¹⁴⁴Nd = 0.5131 (ϵ_{Nd} = +9.0) and ¹⁴⁷Sm/¹⁴⁴Nd = 0.2238 (Hawkesworth and van Calsteren, 1984) and the second set (DM-B) is ¹⁴³Nd/¹⁴⁴Nd = 0.513153 (ϵ_{Nd} = +10.0) and ¹⁴⁷Sm/¹⁴⁴Nd = 0.225 (Liew and McCulloch, 1985).

One of the simplest interpretations of the Nd isotopic ratios of the Hole 504B basalts is that the basalts were generated from CHUR with the same Sm/Nd ratios as the samples at ages in the CHUR model of 1.4×10^9 to 1.7×10^9 yr (Table 5 and Fig. 7). Another, more likely interpretation is that these basalts were derived from depleted mantle sources with a Sm/Nd ratio close to average MORB and subsequently experienced further depletion in incompatible elements. Redepletion occurred between 200 and 600 Ma for DM-A, with ¹⁴³Nd/¹⁴⁴Nd = 0.5131 ($\epsilon_{Nd} = +9.0$) and ¹⁴⁷Sm/¹⁴⁴Nd = 0.2238 (Hawkesworth and van Calsteren, 1984), whereas redepletion is younger than 365 Ma for DM-B, with ¹⁴³Nd/¹⁴⁴Nd = 0.513153 ($\epsilon_{Nd} = +10.0$) and



Figure 2. $(La/Sm)_N$ vs. Ba concentration for MORB. Open circles = Legs 2 and 3, Atlantic Ocean floor (Frey et al., 1974); triangles = Mid-Atlantic and Mid-Indian ridges (Sun et al., 1979); crosses = Holes 417A and 417D and Mid-Atlantic Ridge (Shimizu et al., 1980); solid circles = Hole 504B (this study).



Figure 3. $(La/Sm)_N$ vs. Sr concentration for MORB. Symbols same as for Figure 2.

 147 Sm/ 144 Nd = 0.225 (Liew and McCulloch, 1985). In the latter case, the redepletion process may be related to a formation series of basalts. A probable mechanism would be a limited partial-melting event just prior to basalt formation (i.e., a precursory partial melting). For either scenario, the sources of the Hole 504B basalts were probably derived from depleted mantle and underwent further depletion in incompatible elements. This model would satisfactorily explain the isotopic and abundance data for the Hole 504B basalts of Sr, Nd, and Ce isotopic ratios

with typical values of MORB but with further depletion of incompatible elements.

CONCLUSIONS

The basalts from Hole 504B are the most depleted in Sr, Ba, and light REE among MORB. Strong depletion of REE is suggested by $(La/Sm)_N$ ratios around 0.3 in the Hole 504B basalts, which are lower than the corresponding values of 0.4–0.7 for MORB from normal ridge segments. Ba abundances are extremely low (0.7–0.9 ppm), but the isotopic ratios of Sr, Nd, and Ce for Hole 504B basalts are within the range of typical MORB ratios. These data are explained by a model of basalt formation from sources depleted in incompatible elements, such as average MORB, that underwent further depletion caused by a precursory episode of limited partial melting.

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Table 4. Sr, Nd, and Ce isotopic compositions in Hole 504B basalts.

Core, section, interval (cm)	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd	$(\epsilon_N)^a$	¹³⁸ Ce/ ¹⁴² Ce ^b
143R-1, 22-24		0.513141 ± 0.000006	(+9.8)	0.0225689 ± 0.0000036
145R-2, 62-64	0.70247 ± 0.00001	0.513102 ± 0.000007	(+9.1)	
148R-1, 83-88	0.70271 ± 0.00004	0.513115 + 0.000006	(+9.3)	
150R-1, 122-123	0.70257 ± 0.00002		()	-
163R-2, 29-31	0.70283 ± 0.00006	0.513187 ± 0.000005	(+10.7)	-
169R-1, 102-105	0.70272 ± 0.00001	—	()	—

Note: Errors are $2\sigma_m$. ^a $\epsilon_{Nd} = ([R_{sample} - R_{CHUR}]/R_{CHUR}) \times 10^4$; R = ¹⁴³Nd/¹⁴⁴Nd and (¹⁴³Nd/¹⁴⁴Nd)_{CHUR} = 0.512638.

^b Value recalculated by normalization of ¹³⁸Ce/¹⁴²Ce = 0.0225762 for JMC3O4 Ce standard (Makishima et al., 1987).



Figure 4. Chondrite-normalized (linear scale) REE patterns of Hole 504B basalts (Samples 111-504B-143R-1, 22-24 cm, 111-504B-145R-2, 62-64 cm, 111-504B-148R-1, 83-88 cm, and 111-504B-163R-2, 29-31 cm).



Figure 5. ¹⁴³Nd/¹⁴⁴Nd vs. ⁸⁷Sr/⁸⁶Sr for Pacific Ocean MORB. Squares = Juan de Fuca Ridge, Galapagos Ridge, and East Pacific Rise (Cohen et al., 1980); triangles = East Pacific Rise (White and Hofmann, 1982); solid circles = Hole 504B (this study). The line shows the trend for MORB.



Figure 6. ¹⁴³Nd/¹⁴⁴Nd vs. ¹³⁸Ce/¹⁴²Ce for MORB. Solid circle = Hole 504B basalt (this study); open circle = basalt from East Pacific Rise (12°52'S, 110°57'W; Tanaka et al., 1987); open triangles = basalts from Mid-Atlantic Ridge (22°59.14'N, 43°30.90'W and 23°02.63'N, 45°01.05′W; Tanaka et al., 1987). $\epsilon = ([R_{sample} - R_{CHUR}]/R_{CHUR}) \times 10^4$, where R_{sample} is the sample isotopic ratios ¹⁴³Nd/¹⁴⁴Nd or ¹³⁸Ce/ 142Ce and R_{CHUR} is chondritic uniform reservoir. Present-day values of $(^{143}Nd/^{144}Nd)_{CHUR}$ and $(^{138}Ce/^{142}Ce)_{CHUR}$ are 0.512638 (Wasserburg et al., 1981) and 0.0225722 (Shimizu et al., 1984, 1988), respectively.



Figure 7. Isotopic evolution of Nd in average MORB (dashed lines) and Hole 504B basalts (solid lines) (see text and Table 5). Depleted mantle A (DM-A) has present-day values of ¹⁴³Nd/¹⁴⁴Nd = 0.5131 (ϵ_{Nd} = +9.0) and ¹⁴⁷Sm/¹⁴⁴Nd = 0.2238 (Hawkesworth and van Calsteren, 1984). Depleted mantle B (DM-B) has present-day values of ¹⁴³Nd/¹⁴⁴Nd = 0.513153 (ϵ_{Nd} = +10.0) and ¹⁴⁷Sm/¹⁴⁴Nd = 0.225 (Liew and McCul-loch, 1985). CHUR (horizontal line) present-day values are ¹⁴³Nd/¹⁴⁴Nd = 0.512638 and ¹⁴⁷Sm/¹⁴⁴Nd = 0.1966 (Wasserburg et al., 1981). $\epsilon_{Nd}(T) = ([R_{sample}(T) - R_{CHUR}(T)]/R_{CHUR}(T)) \times 10^4$; R(T) = ¹⁴³Nd/ ¹⁴⁴Nd at time T. Figure 7. Isotopic evolution of Nd in average MORB (dashed lines) and

Table 5. Nd model ages for chondritic uniform reservoir (CHUR) and depleted mantle (DM-A and DM-B).

Core, section, interval (cm)	CHUR ^a	DM-A ^b	DM-B ^c
143R-1, 22-24	1.47×10^{9}	0.409×10^{9}	0.129×10^{9}
145R-2, 62-64	1.41×10^{9}	0.212×10^{9}	
148R-1, 83-88	1.72×10^{9}	0.424×10^{9}	-
163R-2, 29-31	1.55×10^{9}	0.618×10^{9}	0.365×10^9

Note: In calculating Nd model ages, the Nd isotopic ratios of the Hole 504B basalts are corrected by normalization of $^{143}\rm Nd/^{144}\rm Nd=0.511858$ for the La Jolla Nd standard.

- λ_{α}^{147} Sm = 6.54 × 10⁻¹²/yr. ^a Present-day parameters: ¹⁴³Nd/¹⁴⁴Nd = 0.512638 and ¹⁴⁷Sm/¹⁴⁴Nd = 0.1966 (Wasserburg et al., 1981). ^b Present-day parameters: ¹⁴³Nd/¹⁴⁴Nd = 0.5131 (ϵ_{Nd} = +9.0) and ¹⁴⁷Sm/¹⁴⁴Nd = 0.2238 (Hawkesworth and van Calsteren, 1984).
- c Present-day parameters: $^{143}Nd/^{144}Nd = 0.513153$ ($\epsilon_{Nd} = +10.0$) and $^{147}Sm/^{144}Nd = 0.225$ (Liew and McCulloch, 1985).