12. ABUNDANCES OF RARE EARTHS AND OTHER TRACE ELEMENTS LEG 46 BASALTS (DSDP)

R. Emmermann and H. Puchelt, Institut für Petrographie und Geochemie der Universität (T.H.) Karlsruhe, Germany

ABSTRACT

On a total of 25 basalt samples drilled in Hole 396B (Leg 46) the rare earth elements La, Ce, Sm, Nd, Eu, Tb, Dy, Yb, and Lu and the trace elements Li, F, Sc, V, Cr, Ni, Zn, Sr, and Hf have been determined by INAA and AAS. The data obtained indicate that there are no large-scale differences between basalts from different lithologic units met in this hole. However, minor differences do exist, which are especially pronounced in case of the REE.

All basalts analyzed are LREE depleted and exhibit smooth distribution patterns. Basalts from Lithologic Unit 4 differ from those of the other units by a very low overall enrichment of the REE compared to chondrite. The average concentrations of Sc, V, Zn, and Hf are also lowest in this unit, whereas Cr and Ni are highest. The differences are in keeping with petrographic features and can be explained by the special mineralogical composition of these basalts. According to the RE abundances and the concentrations of the other trace elements all rocks investigated can be classified as "typical" mid-ocean ridge basalts. The basaltic magmas are derived from a LREE depleted mantle source; it is assumed, that these magmas have not undergone any large-scale differentiation after their formation.

INTRODUCTION

A 255-meter-thick section of basalt, basaltic breccia, gravel, and sand was drilled in Hole 396B during Leg 46. The hole is located about 160 km east of the Mid-Atlantic Ridge (at 22°59.1'N and 43°30.9'W) on magnetic anomaly 5A (13 m.y.). The basement rocks, overlain by 150 meters of sediments, were subdivided into eight lithologic units by the shipboard scientific staff (Dmitriev, Heirtzler et al., 1976).

Units 1 and 2 (150.5-235.5 m) consist of sparsely phyric pillow basalts with less than 1 per cent phenocrysts of olivine and plagioclase in equal amounts. Unit 3 is a sparsely phyric basalt flow (less than 1% olivine and plagioclase phenocrysts) with a thickness of 8.5 meters. Unit 4 (243.0-315.0 m) represents a highly phyric pillow basalt sequence with phenocrysts of plagioclase (10.4 to 20.4%) and olivine (1.3 to 6.0%). Units 5 through 8 (Cores 23 to 33) comprise a sequence of pillow basalt, sand, and gravel.

Forty-one samples of the basalts were analyzed on shipboard by XRF for all major oxides except Na₂O and the trace elements Zr, Sr, Ni, and Cr; additionally, H₂O and CO₂ were determined using a CHN-analyzer. On the basis of these analyses, all rocks can be classified as typical oceanic tholeiites, with only limited chemical variation. The ranges of variation for the major oxides (given on a dry weight basis) are: SiO₂ = 49-51%; TiO₂ = 0.9-1.7%; A1₂O₃ = 15-18%; FeO (total Fe) = 7.4-10.4%; MgO = 7-9%; CaO = 10.8-12.8%; K₂O = 0.1-0.35%. For the trace elements the following limits were found: Zr = 60-130 ppm; Sr = 110-170 ppm; Ni = 110-160 ppm; and Cr = 250-370 ppm.

Despite this small variability, four major chemical units could be established using TiO₂ as the most effective single discriminant. Unit A (Cores 4 to 15) corresponds to lithologic Units 1, 2, and 3; and Unit B (Cores 16 to 22) to lithologic Unit 4. Unit C (Cores 23 to 32) represents the basaltic breccia, sand, and gravel sequence, and Unit D (Core 32, Section 1, 60 cm through Core 33) consists of pillow basalts. From step-like chemical changes between the units and a relative homogeneity within each unit, it was concluded that these chemically defined units represent discrete magma batches (Dmitriev, Heirtzler, et al., 1976).

On the basis of the shipboard results, 25 basalt samples, representative of the entire compositional spectrum, were selected by us for the determination of further trace elements. We were chiefly concerned with analysis of the rare earths (REE) La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, and Lu, because abundances of these elements (a) provide a rather specific mean for characterizing basalts and in discriminating between the various types, and (b) may also yield some information on the processes involved in generation of basaltic magma. In addition to rare earths, the concentrations of Li, F, Sc, V, Cr, Ni, Zn, Sr, and Hf were determined.

The purpose of this paper is to provide additional data for the chemical characterization of the basalts, to investigate downhole variation of the basaltic profile, and to evaluate, if possible, the petrogenetic processes responsible for generation of the basalt types sampled.

ANALYTICAL METHODS, PRECISION AND ACCURACY

The rare earths La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, and Lu, and the elements Sc, Cr, and Hf were determined by instrumental neutron activation analysis (INAA). The analytical procedure is shown in a flow diagram in Figure 1. Before analysis, the material was ground in an agate mortar



Figure 1. Flow diagram of INAA determinations.

to a grain size of less than 100 μ m and dried at 105°C for five hours. Two reactor irradiations were carried out with each of the investigated samples. An irradiation of one day enables determination of all elements with half-lives of more than one and one-half days. For this purpose, about 100 mg of sample material is packed into Al-capsules and irradiated together with single element standards (Puchelt, et al., 1976) in modified Harwell cans at a thermal neutron flux of 8×10^{13} n/cm²s in the research reactor FR-2 in Karlsruhe. After a cooling time of six to eight days, the sample material is unpacked and weighed into special sample holders. The first measurement allows all elements with half-lives up to 18 days to be determined with good precision. A further cooling time of three weeks improves the detection limit of elements with a decay time longer than 18 days.

The short-lived isotopes of Sm, Eu, and Dy are determined by a one-minute irradiation in the pneumatic tube. Samples of 50 to 80 mg are weighed for this purpose in capsules of polyethylene of the highest purity. In this case also irradiation is performed simultaneously with the respective single element standards. The best results for these elements are obtained after a cooling time of one hour (Dy) or one day (Sm, Eu).

For measurement of the δ spectra, a coaxial Ge(Li) detector with a resolution of 2.3 keV at 1.33 MeV and an effeciency 10 per cent, and a high purity planar Ge-detector with an effective area of 200 mm², 7 mm thickness, and a resolution of 540 eV at 122 KeV is available. Both detectors are connected to multichannel analyzers (Nuclear Data 2200 and Canberra 8100), which are equipped with 4096 channels and 100-MHz ADC's, and are coupled to a HP 2100 computer. Evaluation of the spectra and computation of element concentrations are performed by our computer program GAMMA (Puchelt, et al., 1976). The elements Li, V, Cr, Ni, Zn, and Sr were determined in highly concentrated solutions (10 grams of sample per liter) by atomic absorption spectrometry (Varian VAAG and Perkin-Elmer 303). For the determination of fluoride, a fluoride-specific ion electrode (Orion 94-09) was used. The analyses were performed without separation of aluminum following the procedure described by Ingram (1970).

The precision of the methods used was tested by replicate measurements of selected samples; the accuracy was always checked by carrying samples of the international reference rocks BCR-1, AGV-1, GSP-1, BR, and BM through the whole procedure along with each series of Leg 46 samples. The values obtained by us for BCR-1 are given in Table 1 in comparison to the recommended values (Flanagan, 1973). This table also includes our data for the interlaboratory "standards" 1, 2, and 3 (Leg 46 basalts), which were distributed among the laboratories involved in the analyses of Leg 46 samples (see Kirkpatrick, this volume). The precision (2σ in relative percent) for the elements analyzed within the concentration range of these "standards" is given in the last colume of Table 1; it varies between 5 per cent for Sc and Tb and 20 per cent for Ce, Nd, and Hf.

RESULTS

The abundances of the 18 trace elements determined in the basalts from Hole 396B are summarized in Table 2. The

TABLE 1 Analytical Results (in ppm) for BCR-1 and the Three Leg 46 Interlaboratory "Standards"

Element	BCF	R-1	Leg 4	6 "Standa			
	This Work	Flanagan (1973)	No. 1	No. 2	No. 3	Precision 20 (relative %)	
Li	12	12.8	11	7	13	10	
F	453	470	181	164	150	10	
Sc	32	33	38.5	39.7	31.8	5	
V	400	399	244	193	156	15	
Cr	18	17.6	343	301	369	10	
Ni	15	15.8	158	133	120	10	
Zn	114	120	56	66	50	10	
Sr	335	330	125	143	110	10	
La	27	26	2.6	4.0	2.4	10	
Ce	50	53.9	9.5	11.6	6.7	10	
Nd	31	29.0	7.8	11.9	7.4	10	
Sm	6.5	6.6	3.4	4.1	2.4	15	
Eu	1.90	1.94	1.15	1.39	0.83	10	
Tb	1.4	1.0	0.87	0.96	0.60	5	
Dy	5.6	6.3	5.5	6.7	3.5	15	
Yb	3.6	3.4	2.8	3.2	2.2	10	
Lu	0.52	0.55	0.50	0.57	0.38	10	
Hf	5.1	4.7	2.5	2.9	1.5	20	

 TABLE 2

 Concentrations (in ppm) of 18 Trace Elements in Leg 46 Basalts

Sample (Interval in cm)	Sub-basement Depth (m)	Lithologic Unit	Li	F	Sc	v	Cr	Ni	Zn	Sr	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu	Ht
4.1 90.97	2.20	1	10	140	27	220	227	1.12	60	122		0.6	0.0	2.2	1.22	0.07	6.2	24	0.65	2.0
6 2 97 02	10.00	1	10	140	37	220	327	142	68	132	3.4	9.5	9.9	5.5	1.22	0.87	0.3	3.6	0.65	2.0
3-2, 07-93	10.99	1		140	37	260	312	142	59	124	3.8	9.9	9.4	3.9	1.19	0.94	5.1	3.4	0.54	1.8
7-1, 25-50	24.28	1	11	200	38	260	330	149	72	134	4.9	11.4	9.3	3.5	1.20	0.89	5.9	3.7	0.64	1.9
7-1,60-62	25.26	1	25	290	36	170	315	151	76	118	2.7	9.5	9.8	3.6	1.21	0.92	5.7	3.6	0.55	2.4
7-2, 107-113	30.99	1	13	170	38	295	335	147	62	132	3.1	9.4	10.0	3.7	1.15	0.84	5.7	3.4	0.63	2.0
8-1, 128-135	38.29	1	14	160	39	385	301	139	75	142	4.1	11.5	10.1	3.9	1.28	0.99	5.9	3.9	0.57	2.3
9-1, 75-80	44.62	1	14	150	40	375	299	136	68	143	3.3	11.3	10.0	4.2	1.23	1.14	6.4	4.0	0.75	2.7
11-1, 104-108	62.78	1	13	200	38	360	298	149	70	137	4.1	10.4	9.4	3.7	1.16	0.87	6.5	3.6	0.65	2.0
11-2, 27-33	63.68	1	29	230	38	305	294	126	80	140	3.2	9.6	8.7	3.6	1.18	0.82	6.3	3.6	0.53	2.1
14-1, 121-127	77.91	2	27	300	38	305	279	153	61	154	4.7	12.8	10.8	4.2	1.39	1.00	6.9	4.1	0.65	2.4
15-1, 116-120	87.07	3	31	210	38	260	290	151	68	157	4.9	13.0	11.2	4.2	1.32	0.90	6.6	3.7	0.62	2.5
15-2, 111-115	87.89	3	7	160	38	320	289	142	73	148	4.4	13.1	11.8	4.1	1.30	1.01	6.7	3.8	0.66	2.5
15-4, 13-20	90.69	3	7	160	38	320	282	149	66	148	3.9	10.6	9.7	3.9	1.30	1.02	6.2	3.9	0.62	2.4
15-4, 132-141	92.29	3	8	180	37	305	282	145	76	152	4 1	10.3	9.6	39	1 34	0.92	63	3.8	0.67	25
16-1, 97-102	97.08	4	13	200	31	260	315	145	58	135	24	7.4	7.2	26	0.98	0.76	49	28	0.44	20
16-4.63-68	110.02	4	15	130	34	250	309	136	73	134	3.1	89	7.8	3.0	1.04	0.75	4.2	2.9	0.52	1.9
16-5, 34-36	113.75	4	26	240	32	220	310	130	25	139	2.0	0.9	7.4	2.7	0.00	0.66	10	2.9	0.40	1.6
20-1. 35-42	136.45	4	13	180	32	295	308	134	61	144	2.9	6.5	8.5	3.1	1.00	0.67	4.5	2.5	0.49	1.6
20-3, 21-27	139.82	4	25	200	28	277	312	153	49	127	2.4	6.7	7.2	2.2	0.99	0.66	4.5	2.5	0.40	2.0
21-1 3-10	145.78	4	11	170	32	220	256	151	50	122	2.4	2.2	1,5	2.2	0.00	0.00	4.0	2.5	0.37	2.0
21-1 102-110	150.53	4	12	120	21	250	242	151	30	133	2.0	1.2	0.5	2.4	0.96	0.70	4.5	2.5	0.49	2.1
22.2 8.12	157.88	4	12	160	20	105	245	100	41	129	2.0	0.4	1.2	2.2	0.80	0.07	4.0	2.5	0.40	1.4
22-2, 0-12	163 21	4	15	120	29	105	343	165	54	121	1.8	6.2	6.9	1.9	0.82	0.60	5.0	2.4	0.35	1.3
22 1 11 12	227.00	4	12	120	30	220	337	108	46	128	2.2	6.6	6.8	2.0	0.81	0.55	4.1	2.2	0.43	1.1
32-1, 11-13	237.09	7	13	280	35	260	329	139	61	161	4.0	10.0	9.0	2.7	1.10	0.76	5.6	3.1	0.62	2.0
32-1, 39-02	241.43	1	20	270	56	540	2/6	143	72	142	5.0	12.5	11.6	3.7	1.33	0.99	7.0	3.9	0.61	2.6

numbering of the samples is according to standard DSDP procedure (i.e., Core No., Section No., interval in cm). For each sample sub-bottom depth is also given along with its stratigraphic position.

In addition to presentation of the REE data in tabular form, the chondrite-normalized REE abundances are shown graphically (Figures 2-5). For the normalization procedure the following chondrite values (in ppm) were used: La = 0.315; Ce = 0.813; Nd = 0.5966; Sm = 0.1917; Eu = 0.07216; Tb = 0.049; Dy = 0.325; Yb = 0.2075; and Lu = 0.03225 (Masuda, 1975). In describing the REE characteristics of basalts, several parameters are of interest. As a measure of the degree of fractionation of the light rare earths (LREE) the ratio La/Sm (normalized to chondrite) is used and referred to as La/Sm e.f. For typical mid-ocean ridge basalts (MORB) this value is below unity; that is, the normalized distribution patterns are LREE-depleted. To characterize the fractionation of the heavy rare earths (HREE) a similar ratio, Sm/Yb e.f., can be used. Often the HREE are almost unfractionated; that is, they exhibit chondritic patterns. Therefore, the Yb e.f. provides a reasonable measure for the overall enrichment of the HREE. A characteristic feature in the REE distribution curve of some basalts is the occurrence of a positive or negative Eu anomaly (Puchelt and Emmermann, 1977). These anomalies are expressed by a value Eu*, which is the ratio of the normalized Eu value of the sample to the interpolated Eu value obtained when the adjacent REE are connected by a smooth distribution curve.

The chondrite-normalized REE patterns of the investigated basalts are given in Figures 2 through 5, which correspond to the four major lithologic groups encountered in the hole. In order to show the relationship of the patterns with depths, sub-bottom depth for each sample is given. As can be seen from these figures, the basalts analyzed exhibit in general very similar REE distributions. All samples are LREE-depleted, the La/Sm e.f. varying between 0.44 and 0.94. Only one sample (uppermost in Figure 3) shows an almost unfractionated pattern with a very slight linear increase in the concentrations from La to Lu and an overall

REE enrichment of about 18 compared to chondrite. Minor differences exist in the shape of the curves and in the enrichment factors. Most samples are more or less unfractionated for the HREE. In some cases a maximum is found for the intermediate REE (Sm-Tb); Tb to Lu showing a decrease. Significant anomalous behavior of Eu cannot be observed. In all cases, the Eu values found are on or very close to the distribution curve constructed as a smooth regression line.

As far as the REE level is concerned, there is an obvious difference between the samples of lithologic Unit 4 and the other units. Basalts from Unit 4 are, in general, characterized by the lowest REE abundances. The La values are only 5 to 10 times the chondritic value, whereas in all other units the La enrichment is between 9 and 17. The HREE enrichment level of Unit 4 shows a variation from 11 to 17 as compared to 18 to 24 of the other units. The similarity of the other lithologic units and marked differences between these and Unit 4 is also evident in Table 3, which gives the averages of all elements determined.

Among the other trace elements determined, Sc is probably most pertinent in distinguishing between the different units. It shows a very limited variation in all lithologic units, and its concentrations in Unit 4 are much lower as compared to the other units. The same is true for Hf; however, the scatter of Hf (except in Unit 3) is much larger. Unit 4 is also distinguishable from the other units with regard to the average V, Cr, and Zn concentrations (Table 3). The Cr content is highest in basalts of Unit 4, whereas V and Zn are lowest. The Sr abundances deviate from this general picture. They are lowest in Unit 4 but surprisingly enough are similar to the Sr concentrations found in Units 1 and 2, whereas Units 3 and 5 through 8 have higher average values. Fluorine and especially lithium show relatively large variations. Furthermore, the average Li values of different units are similar.

A comparison of the present data with the average composition of "abyssal oceanic tholeiites" (last column in Table 3) as given by Wedepohl (1975) shows that the Leg 46 basalts in their REE, Cr, and V contents are very close to the



Figure 2. Chondrite-normalized REE patterns of Leg 46 basalts (lithologic Units 1 and 2).

abyssal oceanic tholeiite of Wedepohl. The dissimilarity in case of the other trace elements may be due to the fact that too few analyses are available for averaging.

DISCUSSION

The REE and other trace element data indicate that there are no large-scale differences between the basalts from different lithologic units of Hole 396B. However, minor differences do exist, and these are especially marked in case



Figure 3. Chondrite-normalized REE patterns of Leg 46 basalts (lithologic Unit 3).

of the REE. When the data set is closely scrutinized, lithologic Unit 4 stands out, whereas the other units are very similar in composition. This is also in keeping with the major element chemistry (Dmitriev, Heirtzler, et al., 1976) and can be related to the rather specific petrographic features of this basalt sequence. It might be recalled here that Unit 4 consists of highly phyric pillow basalts which contain up to 20 per cent phenocrysts of plagioclase and up to 6 per cent phenocrysts of olivine. Additionally, microphenocrysts of spinel occur in small amounts.

This mineralogical composition directly reflects the trace element abundances. The overall low concentration of REE in Unit 4 is due to the fact that early phases of plagioclase and olivine hardly concentrate any appreciable amount of REE, and as such, their presence in larger concentrations in any subsequent liquid would result in dilution of REE, when whole rock analysis of the liquid and crystal cumulates together is made. On the other hand, the concentration of olivine will cause an enrichment of Ni, and the occurrence of spinelmicrophenocrysts is responsible for the observed Cr enrichment. The significantly lower concentration of Sc can be attributed to a smaller amount of clinopyroxene in this unit, which is the major Sc carrier.

The trace element data thus support the view that the basalt sequence of Hole 396B was built up by the extrusion of several compositionally slightly different magma batches. The general depletion of the LREE in all samples can only be explained if these magmas are derived from a LREE-depleted mantle source. Furthermore, the absence of any considerable degree of variation in the shape of the REE distribution curves, as well as the absence of Eu anomalies, may indicate that these magmas have not undergone any large-scale differentiation after their generation.

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Figure 4. Chondrite-normalized REE patterns of Leg 46 basalts (lithologic Unit 4).



Figure 5. Chondrite-normalized REE patterns of Leg 46 basalts (lithologic Unit 7).

 TABLE 3

 Average Chemical Composition (in ppm) of the Five Lithologic

 Units of Hole 396B (Leg 46)

		Litholog			
Element	1 and 2	3	4	5	Abyssal Oceanic Tholeiite
Li	16	14	15	17	8
F	198	178	169	275	No value
Sc	37.9	37.8	31.0	34.5	52 (?)
V	294	301	242	300	303
Cr	309	286	328	303	298
Ni	143	147	152	141	119
Zn	69	71	51	67	84
Sr	136	151	133	152	121
La	3.7	4.3	2.5	4.5	3.8
Ce	10.5	11.8	7.2	11.3	12.4
Nd	9.7	10.6	7.5	10.3	10.7
Sm	3.8	4.0	2.5	3.2	3.7
Eu	1.22	1.32	0.93	1.23	1.3
Tb	0.93	0.96	0.67	0.88	0.8
Dy	6.1	6.5	4.6	6.3	6.2
Yb	3.7	3.8	2.6	3.5	2.9
Lu	0.62	0.64	0.45	0.62	0.52
Hf	2.2	2.5	1.7	2.3	No value

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