38. RARE EARTH ABUNDANCES IN DSDP SITES 332, 334, AND 335, AND INFERENCES ON THE AZORES MANTLE BLOB ACTIVITY WITH TIME

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ABSTRACT

Rare earth (RE) abundances for 33 lavas ranging from picrites to differentitated basalts are reported from Sites 332, 334, and 335. Remarkably similar V-shaped relative RE fractionation patterns were observed for Holes 332A, 332B, and Site 334, with an [La/Sm]E.F. (enrichment factors) averaging 1.21 and ranging only by ± 0.22 for one standard deviation, yet with an absolute level of RE pattern enrichment ranging from 15 to $20 \times$ to as low as $4 \times$ chondrites (i.e., a factor of ~5). In contrast, uniform and light RE depleted patterns were observed throughout Site 335, with absolute variations occurring only over a factor of 1.5.

Basalts from Site 335 are typical of normal mid-ocean ridge segments and regimes and appear to be derived from the lowvelocity layer depleted in large ionic lithophile elements (depleted low velocity layer, DLVL-derived), whereas basalts and picrites from Holes 332A, 332B, and Site 334 appear to be derived from a two-component mantle mixture (DLVL, and the Azores Mantle "Blob" enriched in light RE).

Patterns with the lowest absolute enrichments in Holes 332A, 332B, and Site 334 require unusually large degrees of melting for noncumulate lavas, additional crystal accumulation at shallow depth for highly porphyritic cumulate lavas, and a relatively large amount of olivine in the mantle source. Presence of abundant spinel and unusually low FeO*/FeO*+MgO and high Cr content relative to similar lavas from the Mid-Atlantic Ridge (MAR) (40° to 30°N) are consistent with this interpretation.

Secular variation of the $[La/Sm]_{E,F}$ from 13 m.y.B.P. until present is shown to reflect an increase in the flux intensity of the Azores Mantle "Blob" and of its extent of overflow along the MAR axis.

INTRODUCTION

Mid-ocean ridges can be subdivided into three types of segments based on rare earth (RE) abundance patterns in basalts erupted along their axis (Schilling, 1973a, 1975a, b; Schilling et al., 1974). These are:

1) Ridge segments over rising mantle currents (blobs or plumes) which by compression produce tholeiitic volcanism enriched in light RE, large ionic lithophile elements (LILE), and radiogenic Sr. These are produced at a rate independent of the rate of lithospheric plate divergence above;

2) Normal ridge segments, where tholeiitic basalt is passively derived from an asthenosphere strongly depleted in light RE, LILE, and radiogenic Sr. Here volcanism is occurring at a rate directly proportional to the rate of the lithospheric plate divergence above; and

3) Transitional segments where the two types of mantle appear to interact to a variable extent depending on the flux of the mantle blob (or plume) and rate of plate divergence (Schilling, 1973a, 1975a).

Lavas with a wider spectrum of compositions have been noted along ridge segments over plumes and of transitional type. The cause seems to be the independence of the rate of mantle plume upwelling from the rate of plate divergence above. As a result, excessive amounts of magma are generated, which tend to stagnate near the base of the crust until the next generation of cracks occurs by spreading, and segregation of melt seems to occur over a wider range of depths than usually occurs beneath normal mid-ocean ridges (Sleep, 1974; Schilling, 1975a).

On the basis of RE profiles from basalts dredged along the Mid-Atlantic Ridge (MAR), Schilling (1975a) has shown that the MAR area chosen by the French-American Mid-Ocean Undersea Study (FAMOUS), and Leg 37 are located on and across a transitional ridge segment.

In this contribution we report on the RE pattern variation of lavas cored at Holes 332A, 332B and Sites 334 and 335. The results should offer a unique opportunity to monitor possible secular variations, and thereby the flux intensity of the Azores Blob and its overflow along the ridge axis, and/or MAR spreading rate variations with time. The approach has been demonstrated for the Faeroe-Iceland-MAR system (Schilling and Noe-Nygaard, 1974), but this time the monitoring is across a transitional segment south of the Azores.

RESULTS

Concentrations for nine rare earths, Na, Fe, Sc, Co and Cr, all obtained by a rapid nondestructive instrumental neutron activation analysis technique, are given in Chapters 2, 4, and 5 (this volume), and Figure 1a-c shows the RE fractionation patterns obtained.

Accuracy and precision of the routine RE technique of analysis can be estimated from the JB-1 average for the four irradiations and one sigma (Table 1). Results for basalt samples with RE enrichment below 10x chondrites should have somewhat lower precision due to lower count rates. This is readily observed from the increasing irregularity in low RE enrichment patterns in Figure 1.

Samples were prepared for analysis by carefully breaking cores into small fragments to avoid altered patches or small calcite veinlets whenever present. The freshest fragments were then ground in an agate mortar.

Finally, three samples (332A-8-2, 2-15 cm; 332A-40-2, 26-33 cm; and 332B-35-2, 51-58 cm) are rocks chosen as standards for cross-laboratory comparisons (see other authors). Major element analyses were also obtained on the same powder batch in our laboratory, and these results are reported and compared in Table 1 of Wright (this volume). Major elements on some samples marked "c" were obtained by electron microprobe X-ray analyses on fused beads of the same rock powders by Sigurdsson (this volume).

DISCUSSION

Hole 332A

Sample 8-2, 2-15 cm is a feldspar phyric basalt. It is slightly light RE enriched. [La/Sm] EF is 1.48 and the



Figure 1a. Rare earth abundance enrichments relative to chondrites as a function of their atomic number.

general RE level of enrichment is about 15× chondrites (Figure 1a). Its RE pattern is comparable to basalt from FAMOUS for time zero as illustrated on an [La/Sm]_{E.F.} versus FeO*/FeO*+MgO diagram (Figure 2).

Sample 40-2, 26-33 cm is a highly porphyritic plagioclase, augite, and olivine phyric basalt. The relative RE pattern is very similar to that for the feldspar phyric basalt at 122.55 meters depth, but its general level of enrichment is only half as much as 8-2, 2-15, i.e., 7×.

Concentrations of Rare-Earths, Co, Cr, and Sc in Standard Sample JB-1 by Instrumental Neutron Activation Analysis ^a							
	1	2	3	4	Average	JB-1 Recommended ^C	Chondritesd
La	42.4	39.8	42.9	39.7	41.2 ±2.1	36	0.30
Ce	70.1	73.9	77.4	82.3	75.9 ±4.5	67	0.84
Nd	27.6	30.7		32.7	30.3 ±2.1	25	0.58
Sm	5.9	5.5	5.7	5.2	5.6 ±0.3	4.8	0.21
Eu	1.5	1.5	1.8	1.7	1.6 ± 0.1	1.5	0.074
Tb	1.2	1.0		1.3	1.2 ± 0.1	0.5	0.049
Yb	2.3	1.9	2.6	1.8	2.1 ± 0.3	2.1	0.18
Lu	0.29	0.31	0.26	0.29	0.29 ±0.0	2 0.31	0.025
Co	38	36		36	37 ±1.0	39	
Cr	479	456		438	458 ± 25	417	
Sc	29	27		27	28 ±1.0	26	

TARLE 1

^aConcentrations in ppm. Analyses are based on prepared standard solutions.

^bJB-1 standards analyses with Leg 37 irradiated samples (four separate irradiations) and average ±1 S. D.

^cFlanagan (1973).

^dChondrite values used in this laboratory for calculating Enrichment Factors (E. F.)



Figure 1b. Rare earth abundance enrichments relative to chondrites as a function of their atomic number.



Figure 1b. (Continued).

chondrites. It also has a slight positive Eu-anomaly suggesting accumulation of feldspar phenocrysts. Both the low level of enrichment and the small positive Eu anomaly suggest that this rock is probably a cumulate lava.



Figure 2. Variation of FeO*/FeO*+MgO wt % ratio against chondrite-normalized La/Sm ratio in some basalts from Holes 332B and 332A. Major element data are taken mostly from Sigurdsson (this volume) and three standard rock analyses shown in Wright (this volume). Also shown for comparison are latitudinal variations along the present MAR axis from dredged pillow basalts (Schilling, 1975a). Interpretation of this diagram in terms of partial melting, fractional crystallization, and mantle mixing is given in Schilling (1975a). FeO* stands for total iron expressed as FeO wt %.

Hole 332B

RE analyses were obtained at 24 different levels and thus cannot be discussed individually here. Figure 1b shows the RE patterns grouped together for similar depths and arranged in order of increasing depth from top to bottom. In general the relative pattern of RE fractionation is very similar throughout Hole 332B. The RE patterns tend to be slightly V-shaped and vary mostly from slightly light RE-enriched to nearly chondritic; whereas the heavy RE tend to increase slightly with increasing atomic number (or decreasing ionic size). The [La/Sm]_{E.F.} maximum range is 0.91-1.6, and the average is 1.21 ± 0.22 for 1 S.D., and thus is very uniform despite the fact that the absolute level of RE enrichments varies by as much as a factor of 4 to 5, and that the lavas vary rather widely in texture, mineralogy, and chemistry, ranging from Mg-rich picrites to aphyric and highly porphyritic basalts often rich in plagioclase and olivine and to a lesser extent clinopyroxene (see Sigurdsson, this volume). Figure 2 further shows the remarkable uniformity of the [La/Sm]_{FF} ratio. The [La/Sm]_{EF} variation appears to be independent of the FeO*/FeO* + MgO ratio, which ranges widely in these lavas (0.35-0.6). Figure 2 shows that relative to the RE profile along the present MAR axis, the [La/Sm]_{E.F.} in Hole 332B is slightly lower than basalt from the FAMOUS area, but overlaps with patterns found further south along the MAR axis, between 34°-36°N (Schilling, 1975a). Figure 2 also shows a lower range of FeO*/FeO* + MgO values of Hole 332B basalts relative to dredged

basalts from MAR axis (Schilling, 1975a), whether or not picrites are included or excluded from the comparison.

The surprising characteristic of Hole 332B which needs emphasis is the large variation in the overall absolute level of enrichment of the RE patterns which range from $3.5 \times$ to $15-20 \times$ chondrites. Generally, RE patterns in mid-ocean ridge basalts range $10 \times$ to $20 \times$ chondrites, or greater, regardless of whether the basalts are from normal ridge segments, light RE depleted and DLVL-derived, or from shallow platforms, light RE enriched and mantle plume-derived. Mid-ocean ridge basalts with overall RE pattern enrichments less than 10× chondrites are usually confined to picrites, of cumulate or noncumulate origin, such as, for example, picrites from DSDP Sites 14 and 18 in the South Atlantic (Frey et al., 1974; Schilling, 1975b); or Al2O3-richpicrites from MAR, 33°30'N, TR 123-4D (Schilling, 1975a); or MAR gabbros (Masuda and Jibiki, 1973; Schubert, 1972). Detailed scrutiny of RE patterns and related mineralogy, petrography, and bulk chemistry of these rocks (Sigurdsson, this volume) indicates that indeed dark brown spinel-bearing picrites (cumulate or noncumulate types) have the lowest total RE content and FeO*/FeO*+MgO ratios (Figure 2), and the highest Cr content (for example, low RE enrichment of picrites at 533 and 590 m depth in Hole 332B in Figure 1b). It should be noted, however, that the lowest absolute RE enrichment patterns for Hole 332B are not all from picrites. This appears also to be the case for some porphyritic lavas of probable cumulate nature (see, for example, 150-220 m depth in Hole 332B (in Fig. 1b), which is composed of feldspar-phyric basalts). This point is also apparent on a Cr versus [Sm] EF diagram (Figure 3), in which the [Sm] E.F. is used as an indicator of overall RE pattern enrichment. In general, Cr content in Hole 332B decreases rapidly with increasing [Sm] E.F. Picrites are richest in Cr and lowest in [Sm] EF, but the feldspar-phyric lavas of 150-220 meters depth are low in both [Sm] EF and Cr content as well.

Site 335

Rocks from six distinct levels were analyzed and the RE patterns obtained are shown in Figure 1a. In marked contrast to Holes 332A, 332B and Site 334, basalts from Site 335 have light RE depleted patterns typical of basalts erupted along normal mid-ocean ridges. The absolute level of RE enrichment also varies comparatively little throughout Site 335; suggesting much more uniform dynamic conditions of formation for these basalts and derivation from the DLVL in the asthenosphere (Schilling, 1971, 1975b).

CONCLUSIONS

RE Pattern Characteristics

The most striking RE characteristics of Leg 37 basalts are:

1) Remarkably similar V-shaped relative RE fractionation patterns, constant $[La/Sm]_{E,F}$ but lack of significant Eu anomalies at Sites 332 and 334, despite



Figure 3. Variation of Cr content versus Sm enrichment factor relative to chondrites for Hole 332B lavas analyzed in this study. Note the inverse relationship between Cr and Sm, except for plagioclase feldspar phyric basalt between the 150-204 meter depth of the drilled core. The highest Cr content are found in Mg-rich-spinelbearing picrites.

large textural, mineralogical, and bulk chemistry variations for lavas ranging from picrites to differentiated basalts; and large variations of the absolute level of enrichment of the RE pattern ranging from about $4\times$ to $15-20\times$ chondrites.

The RE patterns with the lowest enrichments in Holes 332A and 332B are the most unusual and require special explanation. They can be attributed to significantly larger degrees of partial melting of peridotite in the case of spinel-bearing picrites of a noncumulate nature. This seems to be so because in the case of above 20% partial melting of spinel or plagioclase peridotites the enrichment of overall RE group can decrease rapidly with increasing melting without appreciably changing the $[La/Sm]_{E.F.}$, since at this stage RE partitioning is mostly controlled by olivine and to a lesser extent orthopyroxene (see fig. 9 in Schilling, 1975b). The low FeO*/FeO* + MgO range, high Cr content, and abundance of spinels in picrites and basalts of a noncumulate origin with low total RE content are also consistent with larger degrees of melting. In addition, accumulation of phenocrysts of olivine and plagioclase, which do not affect the light RE significantly (Schilling, 1971, 1973b), and possibly some clinopyroxene, might also be required in the case of some highly porphyritic rocks of a cumulate nature.

Finally, variation in the amount of olivine originally present in the mantle source might also have to be considered.

Further qualitative and quantitative estimates of the extents of partial melting, mineralogical composition of the mantle source, and accumulation of phenocrysts by fractional cyrstallization need to be modeled for each rock individually, and in conjunction with other petrographic, mineralogic, and bulk chemical data. Such a task is beyond the scope of this preliminary report.

2) The RE patterns at Site 335 are in marked contrast to Sites 332, and 334 by being light RE depleted and very uniform throughout.

RE Secular Variations and Evidence on the Azores Mantle Plume Activity

Inferences can be obtained from the nature of the relative RE pattern variations of Leg 37 profiles across the transitional MAR segment, southwest of the Azores Mantle Blob. Schilling's binary Blob-DLVL mixing model (Schilling, 1973a, 1975a; Schilling and Noe-Nygaard, 1974) assumes the rate of spreading to be independent of the vertical mantle blob flux. Binary mantle mixing conditions beneath the ridge axis depend on the intensity variation of these two independent rates. Mixing appears to occur prior to or during mantle partial melting probably by adiabatic decompression of diapirs while rising beneath the Azores and the MAR axis (Schilling, 1975a). Figure 4a shows the variation of the [La/Sm]_{E.F} with distance (or time) across the MAR. A noticeable and statistically meaningful decrease of the $[La/Sm]_{E,F}$, occurs from FAMOUS (time zero) to Sites 332 and 334, which form a plateau (3.5-8.9 m.y.B.P.), to Site 335 (13 m.y.B.P.) which shows low values typical of normal mid-ocean ridge basalts. The error bars show the maximum [La/Sm] EF. observed at each site, which reflect variations due to differences in the degree of melting, extent of fractional crystallization and mixing of magmas during eruptions. The general $[La/Sm]_{E,F}$ variation with time (or distance) can thus only be attributed to secular mantle source variations.

In terms of the binary Azores Mantle Blob-DLVL mixing model which has been found to be applicable along the present MAR axis south of the Azores, the $[La/Sm]_{E.F.}$ can then be used to calculate the mixing proportions (Z) of the two component mantles. The equation for binary mixing is:

$$Z = \frac{(R_B - R_A)}{R_M (n - 1) - (nR_A - R_B)}$$
(1)

where: R_A , R_B , and R_M are the La/Sm ratio of the Azores Mantle Blob, the DLVL asthenosphere source, and a mixture of both components, respectively; $n=C_A/C_B$ is the ratio of the Sm concentrations in component mantle A and B; and Z is the mass ratio of component mantles A/A+B, $(0 \le Z \le 1)$. Rigorously,

 R_{A} , R_{B} , R_{M} , and *n* are unknown, but the values for tholeiitic basalts derived from these mantle sources, if produced by degrees of partial melting $y \leq 20\%$, are for all practical purposes identical to their source (Schilling, 1975a, b). R_A , R_B , and *n* are estimated from the RE profile along the MAR at the present time (Schilling, 1975a), and are equal to 2.45, 0.525, and 1.19, respectively; and for R_M , average La/Sm values shown in Figure 4c, for FAMOUS, Site 332, 334, and 335 are used to calculate Z using Equation 1. The Azores Mantle Blob contribution to the mixture (Z), and its variation with time (or distance) is shown in Figure 4c. According to the model, the increase of Z with time until present can be attributed either to an increase of the flux intensity of the Azores Blob and/or the deceleration in spreading rate from the past to present. Independent evidence of either of these two possibilities is therefore required. The spreading rate based on magnetic anomalies appears to have been constant (1.17 cm/yr) for the last 9 m.y. at least (Figure 4b). Therefore the increase in Z during this time (9 to 0 m.y.B.P.) can only be accounted for by an increase in the Azores Mantle Blob intensity. Z is equal to zero at Site 335 (13 m.y.B.P.). This in turn indicates that the influence of the Azores Mantle Blob overflow could not have reached Site 335 latitude at this time, thus again suggesting a lower flux of the Azores Mantle Blob 13 m.y.B.P. It therefore appears that at 13 m.y.B.P. the Azores Mantle Blob flux was of lower intensity, and its overflow along the MAR did not extend as far as presently observed on the MAR axis (Schilling, 1975a). The fact that Site 335 is slightly north of the spreading flow line with respect to FAMOUS is consistent with this proposal. Because of the lack of direct drilling evidence at the latitude of the Azores platform for this particular time, uncertainties remain as to whether the Azores Mantle Blob at this time had not reached the earth's surface, or simply was of lower intensity.

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Figure 4. Secular variation of: (a) La/Sm ratio normalized to chondrites; error bars are for maximum variations observed for Holes 332A and 332B and Sites 335, and dredged basalts from FAMOUS area (Schilling, 1975a). (b) Half spreading rates; solid-dashed line from Leg 37 data (this report); dotted line from Pitman and Talwani (1972). (c) Relative mass proportions Z of Azores Mantle Blob component to binary mantle mixture from which lava of Sites 332A, and 334, and 335, and dredged basalts from FAMOUS area are derived. The other mantle source end member component is the low-velocity layer depleted in light RE and large ionic lithophile elements (DLVL). Pure end-member mantle components for present MAR axis are marked by heavy crosses. See also text and Schilling (1973a, 1974, 1975a, b) for explanation of the model.

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