

40. RARE-EARTH ELEMENT GEOCHEMISTRY OF MARIANA FORE-ARC VOLCANICS: DEEP SEA DRILLING PROJECT SITE 458 AND HOLE 459B¹

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ABSTRACT

Volcanic basement rocks cored at Site 458 and Hole 459B in the Mariana fore-arc were analyzed for rare-earth elements. Samples recovered from the sites represent two petrologic and chemical groups: orthopyroxene-bearing, plagioclase-poor lavas (high-Mg bronzite andesites)—similar to “boninite”—which occur in the upper part of Site 458, and plagioclase-clinopyroxene basalts of arc tholeiite type, which occur in the lower part of Site 458 and at Hole 459B. Least fractionated, high-Mg bronzite andesite samples have rare-earth element (REE) abundances within the range 2–6 × chondrites, and arc tholeiite samples have REE abundances in the range 4–20 × chondrites. All samples analyzed have REE distributions which are relatively light REE (LREE)-depleted; high-Mg bronzite andesites have $(La/Yb)_N = 0.50–0.83$, and arc tholeiites have $(La/Yb)_N = 0.35–0.70$. For the greater number of samples, the high-Mg bronzite andesites are relatively less LREE-depleted than the arc tholeiites, despite higher $MgO/(MgO + \Sigma FeO)$, Cr and Ni abundances. The difference in relative REE distribution between the two volcanic groups is believed to reflect source characteristics.

The data suggest that a shift or compositional modification of the volcanic source material for the Mariana fore-arc occurred with the initiation of the high-Mg bronzite andesite volcanism. This may have been related to an influx of H_2O , which is important in the generation of high SiO_2 -high MgO liquids, into the sub-arc mantle. Compared with “boninite” type lavas from other areas, the Site 458 samples have similar low REE abundances, but are the only specimens which are relatively LREE-depleted. The Site 458 samples may therefore represent an “end member” in the two-stage depletion-enrichment process which has been proposed to account for the variable LREE content of these rocks. The low REE abundances found in many of the Site 458 samples also confirm the tendency of island arc volcanics to have lower REE contents than MORB.

INTRODUCTION

On Leg 60, basement volcanics of Eocene to early Oligocene age were cored at two sites in the Mariana fore-arc region—Site 458 (17°52'N, 146°56'E) and Hole 459B (17°52'N, 147°18'E). Because of their age and proximity to the Mariana Trench, volcanic rocks recovered from the fore-arc sites are likely to represent the earliest phase of Mariana arc volcanism, predating the opening of the Parece Vela Basin and Mariana Trough (Mrozowski and Hayes, 1980; Hussong and Fryer, 1980). The chemical and petrologic features of these lavas are therefore important in developing models for magma evolution in the primitive Mariana arc.

The igneous sections recovered from Site 458 and Hole 459B consisted of several petrographically and structurally distinct units (Fig. 1; site chapters, this volume). A major petrographic division within the sections is the occurrence of plagioclase-poor, magnesian orthopyroxene-bearing lavas in the upper part of Site 458, with more typical plagioclase-clinopyroxene basalts in the lower part of Site 458 and at Hole 459B. The orthopyroxene-bearing lavas (high-Mg bronzite andesites) are similar to bronzite andesites occurring in association with “boninite,” a high- SiO_2 , high-MgO, low- TiO_2 , plagioclase-free volcanic rock first identified in the Bonin Islands, Izu-Mariana arc (Petersen, 1891;

Kuroda and Shiraki, 1975). Other “boninite”-like lavas have been identified among samples dredged from the Mariana Trench near Guam (Dietrich et al., 1978) and on Cape Vogel, Papua-New Guinea (Dallwitz et al., 1966; Dallwitz, 1968). On the basis of chemical composition, high-Mg bronzite andesites from Site 458 and samples from the Mariana Trench and Cape Vogel are members of the “boninite series” as defined by Meijer (in press).

The objectives of this rare-earth element (REE) abundance study were twofold: (1) to provide data for these key trace elements that can be integrated with other geochemical, petrographic, and petrologic data in order to evaluate petrogenetic models for igneous processes occurring early in the history of the Mariana arc, and (2) to compare the “boninite series” lavas in the upper part of Site 458 with rocks of this compositional type from other locales. A characteristic of REE abundances in “boninite series” lavas is relative enrichment of the light REE [$(La/Sm)_N > 1$], in spite of an overall incompatible-element-depleted (e.g., $TiO_2 < 0.4\%$, $Sm < 6 \times$ chondrites) character (Hickey and Frey, 1979).

ANALYTICAL TECHNIQUE

Samples were analyzed for REE using a radiochemical neutron activation procedure. Powdered rock samples of 200 mg each were irradiated for 8 hours at a flux of $\sim 5 \times 10^{13}$ neutrons/cm² s. Standards used were either USGS standard rocks (BCR-1) or synthetic standards prepared by evaporating a calibrated REE solu-

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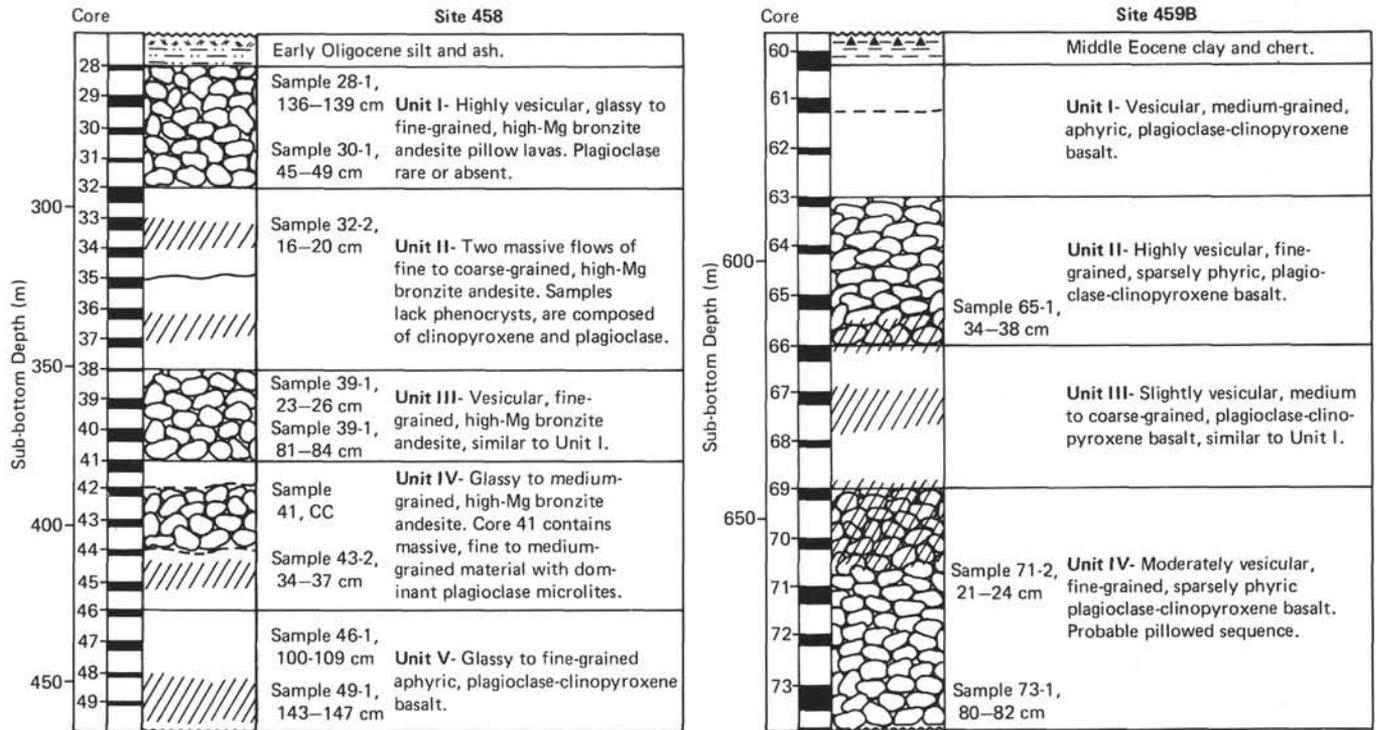


Figure 1. Igneous section at Site 458 and Hole 459B, showing location of samples analyzed for REE (site chapters, this volume; Meijer and Anthony, this volume).

tion on Specpure SiO_2 . After cooling for three to four days, samples and standards were "spiked" with aliquots of ^{144}Ce and ^{169}Yb tracer solution, and dissolved by HF-HClO_4 digestion. Chemical separation of REE was accomplished in two steps. Activity from Al, Si, Na, Fe, and some Cr was removed by elution with $2N$ HNO_3 on 1-cm (i.d.) ion-exchange columns containing 20-cm Bio Rad AG 50-X8 (100–200 mesh) resin. REE and Sc were recovered by elution with $6N$ HNO_3 . Sc was removed from samples, after evaporation and redissolution in $9N$ HCl , by solvent extraction with tri-*n*-butyl-phosphate. The inorganic fractions from this step were counted for REE gamma activity.

Chemical yields were determined by comparison of peak areas for ^{144}Ce and ^{169}Yb with a pure tracer solution, after correction for the contribution of ^{169}Yb produced in samples and standards during irradiation. Yields were normally better than 90 percent, and fractionation of REE during the procedure (Ce yield – Yb yield) was 2 percent or less for the samples reported here.

Precision and accuracy of the technique can be estimated from duplicate analyses of USGS standard BCR-1 and Sample 458-32-2, 16–20 cm (Table 1). Deviation from the mean for these analyses is less than 3 percent, except for Nd, which is 4 percent in this sample. Concentrations obtained for BCR-1 are similar to values reported in the literature for analyses by neutron activation (Jacobs et al., 1977) and isotope dilution (Hooker et al., 1975).

Table 1. Average of duplicate analyses by RNAA, Site 458.

	USGS BCR-1	Sample 32-2, 16–20 cm
La	25.5 ± 0.2	0.820 ± 0.006
Ce	53.0 ± 0.4	2.28 ± 0.04
Nd	28.2 ± 0.8	1.82 ± 0.08
Sm	6.70 ± 0.06	0.622 ± 0.006
Eu	2.03 ± 0.01	0.251 ± 0.007
Tb	1.05 ± 0.01	0.172 ± 0.001
Yb	3.33 ± 0.06	0.797 ± 0.009
Lu	0.48 ± 0.01	0.127 ± 0.002

Site 458

This site is located in the Mariana fore-arc, approximately 90 km west of the Trench. The volcanic section cored has been divided into five lithologic units based on the petrography and physical properties of the rocks (see Fig. 1 for sections and sample locations). The upper units contain vesicular, magnesian orthopyroxene, and clinopyroxene-bearing basaltic andesites. Glassy samples from zones of pillow lava (Unit I and part of Unit IV) or thin flows (Unit III) contain essentially no plagioclase, and bear the greatest similarity to "boninite." In samples from coarser grained, massive zones in the upper part of the section (Unit II), plagioclase occurs intergrown with pyroxene in roughly equal amounts. Unit V and part of Unit IV contain vesicular, augite-plagi-

oclase basalts and basaltic andesites. The section is divided between Units III and IV by a change in magnetic polarity and inclination of the rocks. Alteration products within the section include clay, carbonate, and zeolites.

Units I, II, and III

REE abundances for samples from these units are shown in Figure 2. Samples 28-1, 136-139 cm, 30-1, 45-49 cm, and 39-1, 23-26 cm are relatively fresh, glassy, high-Mg bronzite andesites. Sample 32-2, 16-20 cm is from the massive, plagioclase-bearing portion of Unit II, and the interstitial glass is somewhat altered. Samples from Units I, II, and III have the highest $MgO/(MgO + \Sigma FeO)$ (0.50-0.66) and the highest compatible element contents (Ni: 56-101 ppm, Cr: 168-290 ppm) (Table 2; Wood et al., this volume), found in lavas from the two fore-arc sites. REE distributions in the four samples are essentially identical. Absolute abundances are extremely low, ranging from $2.5 \times$ chondrites in LREE to $4 \times$ chondrites in HREE, with $(La/Yb)_N$ (chondrite normalized) = 0.65-0.68. The patterns are almost linear, with only slight flattening toward the HREE (Fig. 2).

Sample 39-1, 81-84 cm was taken from an area of Section 39-1 which is highly fractured and veined with clay minerals, and was included for comparison with Sample 39-1, 23-26 cm. The former was found to be extensively altered (65% altered glass) compared with the

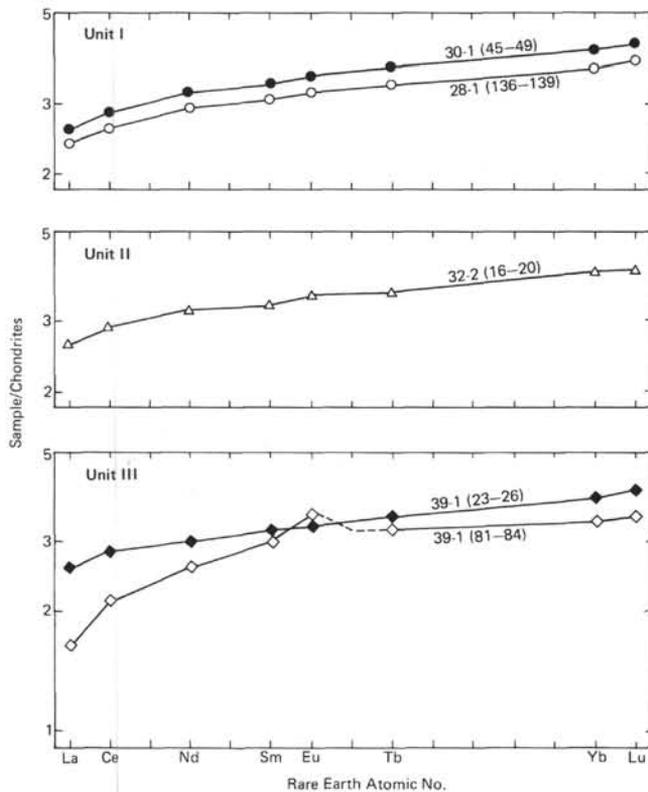


Figure 2. Chondrite-normalized (Leedey/1.20) REE abundances in samples from Site 458, Lithologic Units I, II, and III. Data from Table 2.

latter and with other samples from Units I, II, and III; it contains both pyroxene and plagioclase. The REE pattern for Sample 39-1, 81-84 cm is considerably more LREE-depleted than for the other samples described [$(La/Yb)_N = 0.50$], and it has a small positive Eu anomaly (Fig. 2).

Unit IV

This unit is separated from Units I, II, and III by a major change in the magnetic properties of the rocks; Units IV and V are, as a whole, more altered than Units I, II, and III. Unit IV contains both plagioclase-poor, high-Mg bronzite andesites, and plagioclase-clinopyroxene basalts. The uppermost part of the unit (Core 41) consists of massive, fine-grained plagioclase-rich material, with low $MgO/(MgO + \Sigma FeO)$ (0.43) and low Co (11 ppm) and Ni (11 ppm) contents, while Cores 42 through 45 have $MgO/(MgO + \Sigma FeO) = 0.53-0.55$, Ni = 65-82 ppm, and Cr = 157-176 ppm (Table 2; Wood et al., this volume). REE data for two samples from Unit IV are shown in Figure 3.

Sample 43-2, 34-37 cm is a glassy pillow fragment taken from the center of the unit, and is a plagioclase-free, two-pyroxene basaltic andesite. REE abundances in Sample 43-2, 34-37 cm range from $4 \times$ chondrites in LREE to $6 \times$ chondrites in HREE, with $(La/Yb)_N = 0.66$. Despite slightly higher REE abundances, the chondrite-normalized REE distribution is similar to that in samples from Units I, II, and III.

Sample 41, CC, from the upper, massive zone of Unit IV, is composed of 35 percent plagioclase microlites and 1 percent opaque oxides in a matrix of altered glass. REE abundances for Sample 41, CC range from $13 \times$ chondrites for LREE to $16 \times$ chondrites for HREE, with $(La/Yb)_N = 0.83$; therefore, this sample has the highest REE content and highest La/Yb ratio of the rocks studied from Units I through IV.

Unit V

This unit is composed of fine-grained, augite-plagioclase basalt, with some evidence of pillow structure in the upper and lower zones. In samples from Unit V, unlike Units I through IV, plagioclase is the dominant microphenocryst in glassy samples, while augite is subordinate, and Fe-Ti oxides are common. $MgO/(MgO + \Sigma FeO)$ values (0.44-0.53), and Cr (11-16 ppm) and (Ni 19-35 ppm) abundances are lower in this unit than in Units I through IV, except for Core 41, Unit IV (Table 2; Wood et al., this volume). TiO_2 contents in samples from Unit V range from 1.04 to 1.16 percent, and are approximately three times higher than in samples from Units I, II, and III (0.28-0.37%) and two times higher than in samples from Unit IV (0.49-0.58%), excluding Core 41, which has 1.13 percent TiO_2 . In addition, samples from Unit V have Ti/Zr ratios of 96-133, which are distinctly higher than those for all samples from Units I through IV (Ti/Zr = 50-72), including Core 41 (Table 2; Wood et al., this volume).

Sample 46-1, 100-109 cm is from the upper pillow zone of Unit V and is composed of 10 percent plagioclase

Table 2. Rare-earth element abundances and other geochemical features.

Sample (interval in cm)	Site 458									Hole 459B		
	Unit I		Unit II	Unit III		Unit IV		Unit V		Unit II	Unit IV	
	28-1, 136-139	30-1, 45-49	32-2, 16-20	39-1, 23-26	39-1, 81-84	41,CC 17-19	43-2, 34-37	46-1, 100-109	49-1, 143-147	65-1, 34-38	71-2, 21-24	73-1, 80-82
La	0.746	0.804	0.820	0.800	0.509	4.16	1.19	2.04	2.77	2.19	2.42	1.39
Ce	2.10	2.29	2.28	2.27	1.71	11.3	3.41	6.12	8.31	6.68	7.21	4.68
Nd	1.72	1.88	1.82	1.76	1.52	9.00	2.93	5.41	6.20	6.29	6.72	4.27
Sm	0.574	0.633	0.622	0.604	0.575	3.03	1.00	1.99	2.14	2.18	2.37	1.59
Eu	0.226	0.250	0.251	0.235	0.248	1.16	0.384	0.766	0.844	0.850	0.896	0.695
Tb	0.160	0.176	0.172	0.166	0.155	0.805	0.269	0.525	0.601	0.755	0.680	0.427
Yb	0.736	0.816	0.797	0.781	0.680	3.31	1.20	2.36	2.63	4.08	3.02	1.86
Lu	0.120	0.132	0.127	0.127	0.109	0.511	0.190	0.373	0.410	0.591	0.468	0.291
(La/Yb) _N ^a	0.67	0.65	0.68	0.68	0.50	0.83	0.66	0.57	0.70	0.35	0.53	0.49
Ti/Zr ^b	60	67	60	58	58	67	60	102	133	107	108	104
TiO ₂ ^b	0.28	0.30	0.30	0.28	0.28	1.13	0.51	1.16	1.04	1.21	1.14	1.14
MgO ^b	0.57	0.57	0.52	0.58	0.58	0.43	0.54	0.48	0.53	0.47	0.45	0.49
(MgO + ΣFeO)												
Ni ^b	74	81	59	71	71	11	82	28	19	24	11	20
Cr ^b	189	201	199	172	172	11	157	10	13	13	14	22
H ₂ O ⁺ ^c	2.52	2.01	0.85	2.06	2.49	1.57	2.43	2.18	2.73	2.98	0.95	2.80

^a Normalized to Leedy chondrite.

^b Data for samples from same core and section (Wood et al., this volume).

^c H₂O⁺ analyses performed on Perkin-Elmer Model 240B Elemental Analyzer, after drying at 110°C for 24 hours. CO₂ contents <0.3% for all samples.

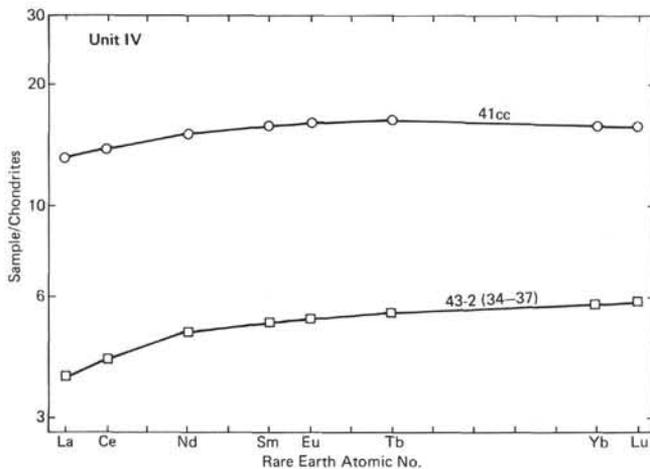


Figure 3. Chondrite-normalized REE abundances in samples from Site 458, Unit IV.

class microlites and microphenocrysts and minor clinopyroxene in a matrix of mostly fresh to palagonitized glass. REE abundances in this sample (Fig. 4) range from 6 × chondrites in LREE to 12 × chondrites in HREE, with (La/Yb)_N = 0.57. This pattern is more depleted in LREE relative to HREE than samples from Units I through IV, except for Sample 39-1, 81-84 cm.

Sample 49-1, 143-147 cm is from the lowest portion of Unit V, and is composed of 15-20 percent plagioclase microlites, minor clinopyroxene, and altered glass. Both glass and microlites in this sample are more altered than Sample 46-1, 100-109 cm. REE abundances in Sample 49-1, 143-147 cm (Fig. 4) range from 9 × chondrites in LREE to 13 × chondrites in HREE, with (La/Yb)_N = 0.70. This pattern, unlike that for Sample 46-1, 100-109 cm, is roughly parallel to REE patterns for samples from Units I through IV.

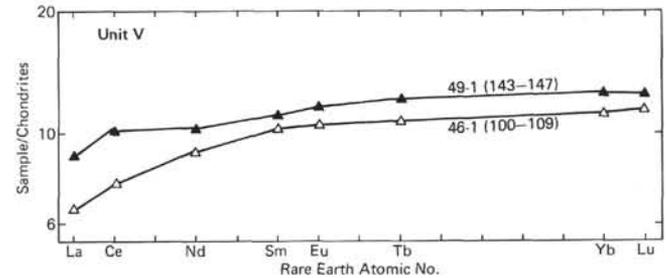


Figure 4. Chondrite-normalized REE abundances in samples from Site 458, Unit V.

Hole 459B

This hole is located approximately 40 km to the east of Site 458, immediately above the Trench slope break. The igneous section has been divided into four lithologic units, and consists of fine to coarse-grained, plagioclase-clinopyroxene basalts and basaltic andesites. Orthopyroxene-bearing lavas similar to Units I, II, and III at Site 458 were not found. Hole 459B lavas are similar to Unit V, Site 458 in MgO/(MgO + ΣFeO), Cr, and Ni abundances (Table 2; Wood et al., this volume). They also have Ti/Zr ratios of 89 to 117, similar to those for samples from Unit V, Site 458, but distinct from Ti/Zr ratios in Units I through IV of Site 458. Three samples from two units at Hole 459B containing fine-grained basalts were analyzed for REE.

Unit II

Sample 65-1, 34-38 cm was collected from the lower part of Unit II, and is a glassy pillow rind containing 5-10 percent plagioclase microlites and minor clinopyroxene granules. The glass is divitrified and palagonitized. REE abundances in this sample (Fig. 5) range from 7 × chondrites in LREE to 20 × chondrites in

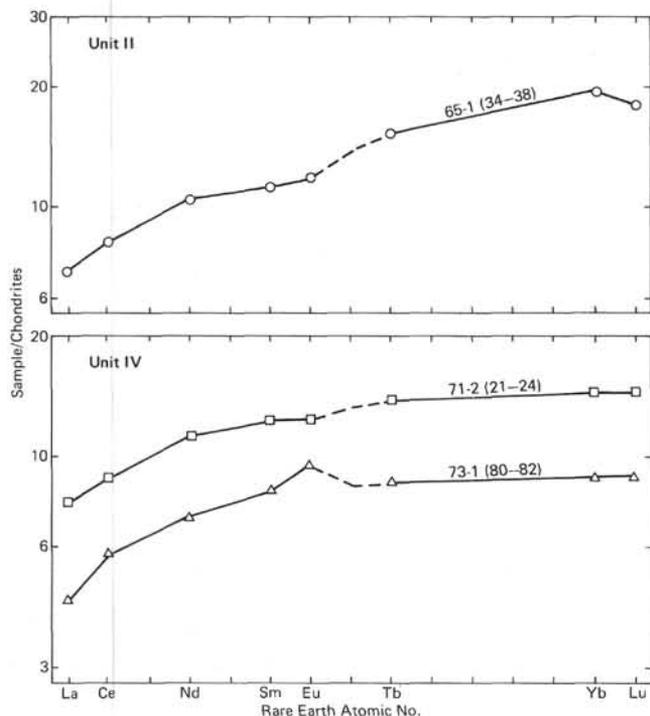


Figure 5. Chondrite-normalized REE abundances in samples from Hole 459B, Units II and IV.

HREE, with $(La/Yb)_N = 0.35$. The sample has a small negative Eu anomaly, which may be consistent with the occurrence of plagioclase as the primary phenocryst. The large relative depletion of LREE in Sample 65-1, 34-38 cm is greater than that of all other samples studied (Table 2).

Unit IV

Two samples from Unit IV were analyzed for REE. Sample 71-2, 21-24 cm is from the center of the unit, and contains 35 per cent plagioclase, as well as minor clinopyroxene and Fe-Ti oxides in a matrix of these minerals and devitrified glass. Clinopyroxene and interstitial glass are partially altered to clay. Sample 73-1, 80-82 cm is from the lowest portion of the unit, and is a glassy sample with dominant plagioclase and minor clinopyroxene.

REE abundances in Sample 71-2, 21-24 cm (Fig. 5) range from $8 \times$ chondrites for LREE to $15 \times$ chondrites for HREE, with $(La/Yb)_N = 0.53$, and in Sample 73-1, 80-82 cm from $4.5 \times$ chondrites in LREE to $9 \times$ chondrites in HREE, with $(La/Yb)_N = 0.49$. Both samples have small Eu anomalies, positive in Sample 73-1, 80-82 cm, and negative in Section 71-2. The REE patterns for these two samples are considerably different from that for Sample 65-1, 34-38 cm in Unit II of Hole 459B, but are similar to that for Sample 46-1, 100-109 cm in Unit V, Site 458 (Fig. 4).

DISCUSSION

In general, the REE characteristics of the samples studied are consistent with the lithologic unit divisions

based on petrography, physical properties of the rocks, and with other compositional differences within the two sections. The orthopyroxene-bearing samples from Units I, II, III, and IV, Site 458 [Samples 28-1, 136-139 cm; 30-1, 45-49 cm; 32-2, 16-20 cm; 39-1, 23-26 cm; and 43-2, 34-37 cm] have extremely similar REE patterns, with $(La/Yb)_N$ varying from 0.65 to 0.68, and absolute concentrations in the range 2 to $6 \times$ chondrites. These five samples correspond to units having Ti/Zr ratios less than 70. This, along with the presence of magnesian orthopyroxene and their low TiO_2 and REE abundances, relates them to the majority of "boninite series" volcanics which have been studied for trace elements (Sun and Nesbitt, 1978; Hickey and Frey, 1979).

Sample 39-1, 81-84 cm is more LREE-depleted than the other high-Mg bronzite andesites [$(La/Yb)_N = 0.50$], although its absolute HREE abundances are similar to those of Sample 39-1, 23-26 cm. Glass in this sample is considerably more altered than in the five samples described above, and it is possible that the difference in REE abundance is a secondary rather than primary feature. In this case REE, particularly LREE, which were concentrated in the glass relative to minerals during crystallization, may have been lost as the glass was altered. The positive Eu anomaly (Fig. 2) might be explained by the retention of Eu in plagioclase, as other REE were removed. H_2O analyses (Table 2) for samples from Units I through IV, which can also reflect relative extent of alteration, do not, however, indicate a significant difference between fresh-appearing samples and Sample 39-1, 81-84 cm. In general, H_2O contents for glass-rich samples from Site 458 and Hole 459B are very similar (2-3% H_2O), whether the glass is fresh-appearing or largely replaced by alteration products. Water contents correlate well with the crystallinity of individual samples; for example, Samples 32-2, 16-20 cm and 71-2, 21-24 cm, with less than 1 percent H_2O , contain more than 60 percent crystalline material. The presence of 2 to 3 percent H_2O in fresh-appearing glassy samples from Units I through IV suggests that these water contents may be primary.

Sample 41,CC, from the highly fractionated, plagioclase-rich portion of Unit IV, has a higher $(La/Yb)_N$ ratio (0.83), and higher REE and TiO_2 contents than other samples from Units I through IV. Although this sample is petrographically similar to samples from Unit V, its low Ti/Zr ratio suggests that it is related to the high-Mg bronzite andesites which occur above and below it in the section. Relative REE abundances in 41,CC are consistent with its derivation from a liquid similar in relative REE content to the high-Mg bronzite andesites by fractionation of orthopyroxene and clinopyroxene, which would remove HREE relative to LREE. In order to produce the high absolute REE abundances in Sample 41,CC from a liquid similar in REE content to Sample 43-2, 34-37 cm or 28-1, 136-139 cm, removal of 70-80 percent crystalline material would be required. Alternatively, Sample 41,CC could be derived from a liquid similar in composition to Unit V lavas by fractionation of a smaller amount of clinopy-

roxene and minor plagioclase, if an Fe-Ti oxide had also been removed. If the Core 41 (Unit IV) and Unit V lavas are related, and if the Site 458 volcanics are in their original stratigraphic sequence, this indicates that "boninite" and arc tholeiite type lavas were alternately erupted within a single area of the arc.

Unit V, Site 458 and Units II and IV, Hole 459B can be distinguished from Units I through IV, Site 458 by the occurrence of plagioclase as the primary phenocryst in glassy samples. Chemically, these samples are distinguished by TiO_2 contents (0.76–1.16%) and REE abundances (4 to 20 \times chondrites) two to four times greater than high-Mg bonzite andesites from the upper part of Site 458, and by Ti/Zr ratios of 89–133. These characteristics, along with their low Ni and Cr abundances (Wood et al., this volume) are typical of lavas of the island-arc tholeiite series (Jakeš and Gill, 1970; Pearce and Cann, 1973).

REE distributions in three arc tholeiite samples (Sample 46-1, 100–109 cm, Unit V, Site 458; Samples 71-2, 21–24 cm and 73-1, 80–82 cm, Unit IV, Hole 459B) are subparallel, with $(\text{La}/\text{Yb})_N = 0.49\text{--}0.57$, and LREE abundances of 4 to 8 \times chondrites and HREE 9 to 14 \times chondrites. Sample 49-1, 143–147 cm (Unit V, Site 458) has higher LREE abundances and higher $(\text{La}/\text{Yb})_N$ (0.70). Because this sample has similar MgO, Ni, and Cr contents to Sample 46-1, 100–109 cm and other samples from Unit V, Site 458, it is unlikely that the relative LREE enrichment results from the fractionation of mafic minerals from a common parent. On the basis of its altered appearance, unusually high $(\text{Ce}/\text{Nd})_N$ ratio (~ 1.0), and evidence from Sample 39-1, 81–84 cm that mobilization of LREE has occurred in severely altered areas of the section, it may be that the REE distribution in this sample has been modified during alteration.

Sample 65-1, 34–38 cm (Unit II, Hole 459B) has similar absolute and relative LREE and middle REE abundances to Samples 71-2, 21–24 cm and 73-1, 80–82 cm (Unit IV, Site 459B) (Fig. 5), but has significantly higher HREE abundances (20 \times chondrites) and lower $(\text{La}/\text{Yb})_N$ (0.35). On the basis of REE abundance data, Units II and IV are not related by fractionation or accumulation of the common phenocrysts (plagioclase, clinopyroxene, Fe-Ti oxides) in these samples. More detailed chemical study of Hole 459B is required before relationships between the lithologic units can be established.

Several generalizations can be drawn from the data. The high-Mg bonzite andesites from Units I through IV, Site 458 have much lower absolute REE abundances than the arc tholeiite samples from Unit V, Site 458 and Hole 459B. In addition, the high-Mg bonzite andesites, with the exception of Sample 39-1, 81–84 cm, show less relative depletion of the LREE than the arc tholeiite samples, with the exception of Sample 49-1, 143–147 cm. The higher $(\text{La}/\text{Yb})_N$, and $\text{MgO}/(\text{MgO} + \Sigma\text{FeO})$ (Figs. 6 and 7) in the high-Mg bonzite andesites indicate that they have been derived from a source which is relatively less LREE-depleted than the source for the arc tholeiites. This conclusion is likely even if the "boninite series" lavas have undergone extensive crystal

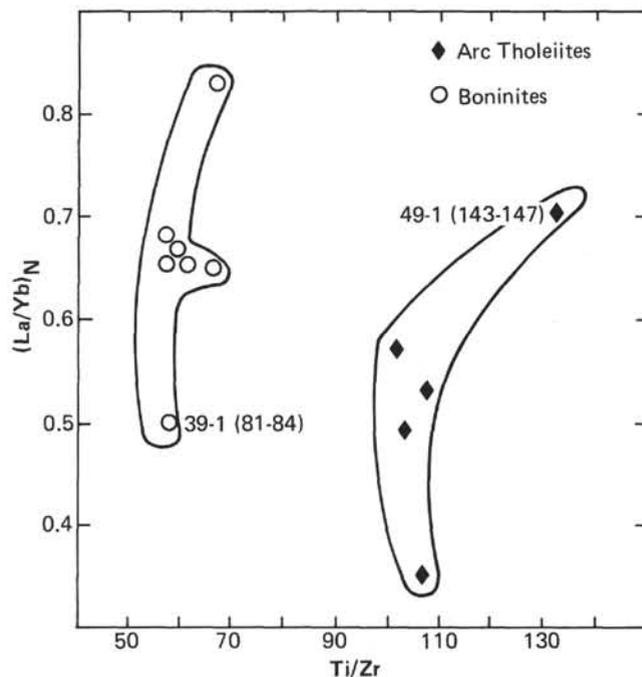


Figure 6. Plot of $(\text{La}/\text{Yb})_N$ versus Ti/Zr ratio for island-arc tholeiites and high-Mg bonzite andesites from Site 458 and Hole 459B. The two volcanic groups have distinctly different Ti/Zr ratios. Differences in relative REE distribution are less clearly defined; however, the majority of high-Mg bonzite andesites have higher $(\text{La}/\text{Yb})_N$ than arc tholeiites.

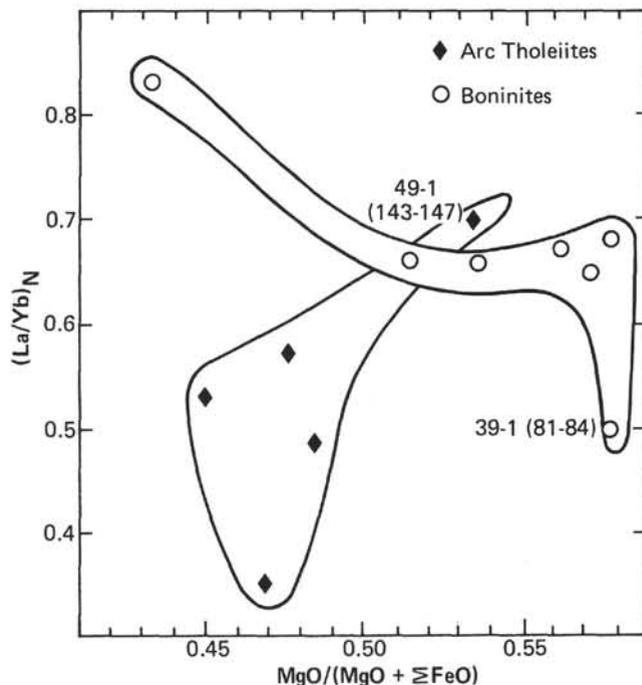


Figure 7. Plot of $(\text{La}/\text{Yb})_N$ versus $\text{MgO}/(\text{MgO} + \Sigma\text{FeO})$ for arc tholeiites and high-Mg bonzite andesites from Site 458 and Hole 459B. Although high-Mg bonzite andesites appear less fractionated [higher $\text{MgO}/(\text{MgO} + \Sigma\text{FeO})$], they have higher $(\text{La}/\text{Yb})_N$. This suggests that the differences in REE distribution for the two volcanic groups reflect differences in their source characteristics.

fractionation. Moreover, if the REE patterns for Samples 39-1, 81-84 cm and 49-1, 143-147 cm are primary, they indicate variation of relative REE abundances within the sources of arc tholeiites and "boninite series" rocks in this area of the Mariana arc.

High-Mg bronzite andesites overlie arc tholeiites at Site 458, and are located to the west of the tholeiitic basalts of Hole 459B. Therefore, a shift is required, in terms of the history of this section of the fore-arc, from a volcanic source material which is more depleted to one which is less depleted in LREE relative to HREE. The change in Ti/Zr ratio from values averaging 100 for the arc tholeiites to values ~60-70 for the bronzite andesites also reflects this shift. Since "boninite"-type liquids are commonly believed to be the product of near-water-saturated partial melting of peridotite (Green, 1973; 1976; Kuroda and Shiraki, 1975), it can be speculated that the change in source character may be related to an influx of water into the sub-arc mantle. With the present data set, several models are possible, for example:

1) The arc tholeiites are derived by H₂O-undersaturated partial melting of subarc mantle peridotite plus a component derived from the subducted oceanic slab. The high-Mg bronzite andesites are derived by H₂O-saturated partial melting of a shallower level, highly depleted peridotite, residual from MORB generation, which has been secondarily enriched in incompatible elements by slab-derived, hydrous fluid, which also initiates melting. A shallow depth of origin (~30-40 km) for "boninite series" lavas is consistent with experiment petrology (Green, 1973, 1976), and is required for these H₂O-rich melts to reach the surface in an unfractionated condition. In this model, differences in trace element character between "boninite" and arc tholeiite result from differences in peridotite composition in addition to variation in the composition of the slab component due to changes in slab mineralogy with depth.

2) An alternative model can be inferred from the stratigraphic sequence at Site 458. Generation of the older arc tholeiites creates a highly depleted, residual peridotite. Remelting of the residual mantle to produce the high-Mg bronzite andesites is initiated by addition of a slab-derived, H₂O-rich fluid, containing incompatible elements. Differences in trace element character between the two volcanic types in this case result from differences in source peridotite composition and the amount of slab component incorporated during partial melting.

A critical problem in either of these models is that melting or remelting of a refractory peridotite to produce the high-Mg bronzite andesites requires anomalously high temperatures (1100-1200°C, for H₂O-saturated conditions, Green, 1973, 1976) in a fore-arc regime.

RELATIONSHIP TO OTHER "BONINITES"

In general, "boninites" or high-Mg andesites can be described as magnesium-rich (>9% MgO), intermediate-silica (55-60% SiO₂) volcanic rocks, containing

abundant magnesian orthopyroxene, little or no plagioclase, and having high compatible-trace-element abundances, but exceptionally low TiO₂ and other incompatible-element abundances relative to most basalts (Fig. 8). This description applies to high-Mg andesites which have been found in the Bonin Islands (Kuroda and Shiraki, 1975) and Cape Vogel, Papua-New Guinea (Dallwitz, 1968), and dredged from the Mariana Trench (Dietrich et al., 1978). The Site 458 high-Mg bronzite andesites, which have an average 7 percent MgO (Wood et al., this volume), thus represent fractionated "boninite" material, similar to the bronzite andesite described by Kuroda and Shiraki (1975) from the Bonin Islands. In addition, a key trace element characteristic of "boninites" is a low Ti/Zr ratio of 23 to 67 (Fig. 6, this chapter; Sun and Nesbitt, 1978; Hickey et al., in preparation), as compared to values near 100 for island-arc tholeiites, MORB, and oceanic island basalts (Sun et al., 1979). These characteristics are very consistent in high-Mg andesites from different geographic areas, and suggest a similar source and mode of origin for these rocks. However, REE abundances in high-Mg andesites are variable. Figure 8 shows representative REE patterns for "boninite series" volcanics, plus the field for high-Mg bronzite andesites from Site 458. A hypothesis for the relative LREE enrichment of these samples, as well as their low absolute abundance of REE and Ti, is that they are derived from an extremely incompatible-element-depleted-source peridotite which has been modified by the addition of an LREE-enriched, but Ti-

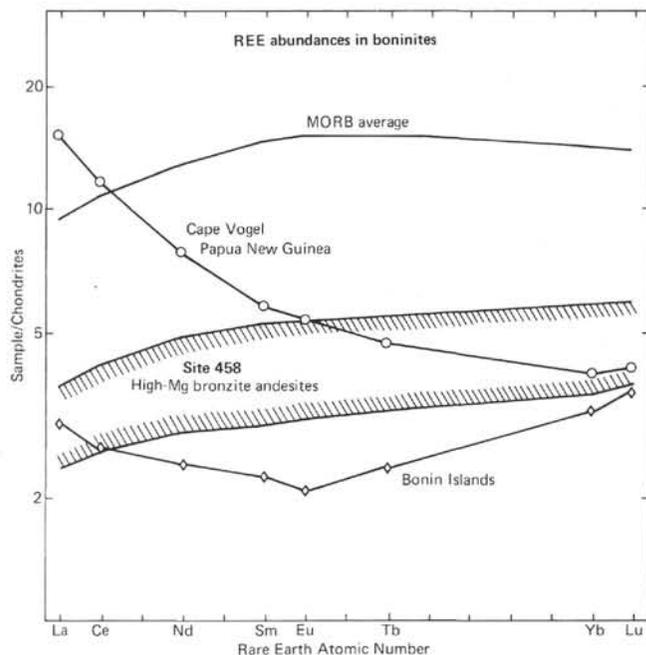


Figure 8. Chondrite-normalized REE abundances in "boninites" from Cape Vogel, Papua New Guinea, and Bonin Islands, compared with the range for high-Mg bronzite andesites from Site 458. A sample (not plotted), dredged from the Mariana Trench, has REE abundances similar to those for the Bonin Island sample. Plot illustrates the variability of LREE abundances in this volcanic group. Data from Hickey et al., in preparation.

poor material (Sun and Nesbitt, 1978; Hickey and Frey, 1979). Such material might be derived from the subducted plate as a hydrous fluid released during dehydration (Green, 1976; Mysen, 1979), or as a low-degree partial melt in equilibrium with a Ti-bearing residual mineral (Hickey et al., in preparation). Apparently, the Site 458 high-Mg bronzite andesites were derived from LREE-depleted source materials; therefore, they represent an unmodified or only slightly modified "end member" in the proposed secondary enrichment scheme.

CONCLUSIONS

Volcanic rocks recovered from Site 458 and Hole 459B in the Mariana fore-arc basement have REE abundances in the range from 2 to 20 × chondrites; in all cases, they are relatively depleted in LREE [(La/Yb)_N < 1]. REE distributions for the samples can be divided into two groups which correspond to the major petrologic and chemical types found within the sections. "Boninite series" lavas (high-Mg bronzite andesites) occur in the upper four lithologic units of Site 458, and have lower absolute REE abundances but higher (La/Yb)_N than arc tholeiites, which occur in the lower unit of Site 458 and at Hole 459B. These differences probably reflect differences in source composition. Since high-Mg bronzite andesites overlie arc tholeiites at Site 458, a shift from a volcanic source which is less depleted in LREE relative to HREE is required at the initiation of the "boninite" volcanism. The Site 458 high-Mg bronzite andesites are the only examples of this lava type which are relatively LREE-depleted; they may represent a little modified end member in the two-stage depletion-enrichment process which has been proposed to account for the variable LREE content of these rocks (Sun and Nesbitt, 1978; Hickey and Frey, 1979). In addition, the exceptionally low REE abundances found in many of the samples (2–6 × chondrites) confirm the tendency for island-arc volcanics to have lower REE abundances than typical MORB.

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