

14. TRACE ELEMENT GEOCHEMISTRY OF BASALTIC ROCKS RECOVERED AT SITE 516, RIO GRANDE RISE, DEEP SEA DRILLING PROJECT LEG 72¹

B. L. Weaver, N. G. Marsh, and J. Tarney, Department of Geology, University of Leicester, Leicester LE1 7RH, United Kingdom

ABSTRACT

The geochemistry of basalts recovered during Leg 72 is described with emphasis on trace elements. Only Hole 516F penetrated basement; the basalts recovered are plagioclase-phyric and olivine-phyric and pervasively altered. Chemically, the basalts from Hole 516F are rather uniform in composition. However, four distinct geochemical units can be recognized, although the chemistry of two of the units appears to be controlled by chemical mobility associated with alteration. The two less-altered units cannot be related by fractional crystallization processes. Hole 516F basalts have a trace element chemistry characteristic of T-type mid-ocean ridge basalt; rare-earth element patterns (as indicated by Ce/Y ratios) are mildly fractionated (light rare-earth element enriched), and a number of incompatible element ratios are close to chondritic.

INTRODUCTION

Site 516 lies on the Rio Grande Rise at 30° 16.6' S, 35° 17.1' W, where the water depth is only 1328 m. Basaltic basement was encountered at a depth of 1252.6 m sub-bottom and cored for 18 m. Calcareous biogenic and calcareous volcanogenic sediments immediately overlie the basement. The volcanogenic sediments include sandy mudstones with dispersed glauconitic grains, breccias, and ashes with dark gray altered volcanic glass, and fining-upward sequences of sandstones that are coarse grained to fine grained and are rich in feldspar, glauconite, and biotite.

The basement itself was continuously cored with about 70% recovery. The basalts are vesicular and rather altered and veined, particularly in the upper part of the section, with the vesicles infilled by calcite and clay minerals. They are not therefore ideal for geochemical study. Hence, emphasis has been placed on their trace element chemistry, especially the more immobile trace elements, in trying to characterize them geochemically. Because of the severe alteration, implying significant transport and redistribution of major elements, major element analyses are unreliable. Nonetheless major element analyses have been determined, but on powder pellets only, rather than fusion discs, in order to give a broad indication of the chemical characteristics.

PETROGRAPHY

The basalts are dominantly plagioclase-phyric and olivine-phyric, but there are a few clinopyroxene phenocrysts in some samples. Olivine phenocrysts range from 0.2–1.0 mm in size, plagioclase up to 4 mm, and it is common for them to form glomeroporphyritic groups. Some fresh olivines are preserved in the deeper part of the hole, but most are replaced by fine-grained clay min-

erals and calcite. Plagioclase (labradorite) phenocrysts commonly show oscillatory zoning and some show partial resorption. They are better preserved than the olivines, but in the more severely altered samples, near the top of the hole, the feldspars are saussuritized and even partly replaced by calcite.

The groundmass shows quench textures and is composed of small plagioclase laths (<0.5 mm), granular clinopyroxenes, titanomagnetite, and altered glassy material. A high proportion of fine-grained smectite and granular calcite occurs in the more badly altered samples. The titanomagnetite shows partial replacement by granular brownish translucent material.

Vesicles are fairly common, and strings of vesicles are generally associated with more severe alteration. The vesicles are veined by calcite and clay minerals, sometimes in concentric fashion. Calcite veins cross-cut several samples.

ANALYTIC TECHNIQUES

Major and trace element analyses were performed using a Philips PW1400 automatic X-ray fluorescence spectrometer at the University of Leicester. The analytic procedure followed that described by Tarney and others (1979) and Marsh and others (1983). Both major and trace element concentrations were determined on pressed powder briquettes. For the major elements (particularly SiO₂, Al₂O₃, Fe₂O₃, and MgO), the powder briquette technique is inferior to the fusion bead technique, and little emphasis will be placed on the reported major element data. In contrast to the methods of Tarney and others (1979) and Marsh and others (1983), Zr concentrations were determined on the Rh tube using long count times on the Zr K β peak, in order to avoid the problem of the Sr K β overlap on the Zr K α peak. Ba was determined on the W tube using the Ba L α line corrected for interference from TiK α . Additionally, V was determined on the W tube using the VK α line corrected for interference from TiK β , allowing the CrK α line to be corrected for VK β overlap. It should be noted that two of the samples analyzed in this study were crushed in a tungsten carbide ball mill (Samples 516F-128-2, 15-21 and 101-106 cm; Table 1); the remaining samples were crushed in agate. These two samples have high Nb contents compared to the other analyzed basalts, and this would appear to be due to contamination from the ball mill. Consequently, these two samples are not included in any discussion of the geochemistry that uses Nb abundances or element ratios involving Nb.

¹ Barker, P. F., Carlson, R. L., Johnson, D. A., et al., *Init. Repts. DSDP, 72*: Washington (U.S. Govt. Printing Office).

Table 1. Major and trace element analyses of basalts from Hole 516F.

Element	Unit 1		Unit 2					
	126-1 (2n, 100-103)	126-1 (3a, 123-126)	126-2 (1a, 9-13)	126-2 (1e, 55-59)	126-3 (3b, 66-72)	126-3 (5a, 116-123)	127-1 (2c, 131-134)	127-2 (2c, 57-63)
SiO ₂ (%)	53.3	49.7	51.9	50.7	48.7	53.9	49.1	51.1
TiO ₂	2.59	3.10	3.15	2.90	3.02	3.15	2.84	3.06
Al ₂ O ₃	11.4	13.5	13.6	13.9	13.9	14.3	12.6	13.4
Fe ₂ O ₃	14.3	10.7	9.8	10.8	11.8	9.1	13.3	11.8
MnO	0.13	0.16	0.13	0.12	0.13	0.09	0.16	0.13
MgO	3.1	2.6	2.5	2.8	2.9	2.7	3.9	3.2
CaO	7.8	12.6	10.5	11.3	12.1	9.2	10.8	10.1
Na ₂ O	2.00	2.80	2.84	2.80	2.81	2.73	2.36	2.55
K ₂ O	2.13	0.37	0.33	0.24	0.24	0.29	1.26	0.56
P ₂ O ₅	0.36	0.39	0.34	0.31	0.33	0.32	0.29	0.32
Total	97.11	95.92	95.07	95.87	95.93	95.78	96.61	96.22
Ni (ppm)	35	35	35	31	43	35	39	41
Cr	46	47	59	56	59	56	40	55
V	431	473	505	480	507	495	423	466
Zn	113	95	77	112	109	88	93	98
Ga	21	24	25	25	25	25	23	24
Rb	52	4	4	4	4	5	20	9
Sr	260	351	351	332	348	330	310	323
Ba	105	309	207	124	115	250	646	212
Zr	192	191	196	189	204	181	177	181
Nb	10	14	12	12	12	13	11	12
La	19	22	20	16	14	16	16	19
Ce	50	47	46	41	40	41	41	42
Nd	29	30	29	25	26	26	25	26
Y	53	52	44	37	35	34	41	39
Pb	2	3	2	3	<2	<2	<2	2
Th	2	3	<2	5	2	2	3	3
mg ^a	33	35	36	37	36	40	40	38
Zr/Nb	19.8	14.1	17.0	15.5	17.0	14.4	16.2	15.6
Ti/Zr	81	97	96	92	89	104	96	101
Ce _N /Y _N	2.2	2.1	2.4	2.6	2.7	2.8	2.3	2.5

Note: Sample numbers indicate core-section (piece number, location of piece in the section in cm).

^a mg = Mg/Mg + Fe²⁺.

GEOCHEMISTRY

Analyses obtained for 18 basalts from Hole 516F are presented in Table 1. All of the analyzed basalts are rather uniform in chemistry (for example: Zr/Nb ratio, Fig. 1A; Ni and Cr abundances, Table 1). The basalts are quite evolved, having high abundances of Zr, Ti, and V as well as moderately high Ce_N/Y_N ratios, but low abundances of Ni and Cr and low (although perhaps unreliable due to alteration and analytic uncertainty) mg numbers (Mg/Mg + Fe²⁺).

Trace element variations within Hole 516F basalts are illustrated using Zr as an index of fractionation in Figure 1. Four geochemical units are apparent. Unit 1 consists of the two analyzed samples from Section 516F-126-1 (Table 1), and are characterized by high contents of, for example, Ce, Y, and P₂O₅ relative to the other basalts from the hole (Fig. 1B-D). Unit 2 is a major geochemical unit consisting of the seven samples from the remainder of Core 516F-126 and the samples from Sections 516F-127-1 and 516F-127-2 and the top of Section 516F-127-3 (Table 1). These samples plot as a coherent group on many of the binary trace element diagrams and define constant trace element ratios (i.e., Figs. 1E-F, 2-3). Geochemical Unit 3 consists of the remaining three samples from Sections 516F-127-3 and 516F-127-4. Al-

though the abundances of many trace elements in Unit 3 are comparable to those in Unit 2 (i.e., Figs. 1C-D), the Unit 3 samples do not plot coherently with this group, nor do they define consistent trace element ratios (Figs. 1F, 2B, 3). Unit 4 consists of the six analyzed samples from Core 516F-128. These samples plot as a coherent group displaying consistent incompatible trace element ratios (Figs. 1D-F, 2-3), but have generally lower abundances of the incompatible trace elements than the other basalts in Hole 516F. In particular, this unit has lower P/Zr, Ti/Zr, Sr/Zr, and Ti/Y ratios (Figs. 1D-F, 2A) than the basalts of Unit 2, but similar P/Ti and P/Sr ratios (Figs. 2B, 3). The chemical boundary between units 2 and 3 (situated between Samples 516F-127-3, 9-13 cm and 516F-127-3, 43-46 cm) corresponds to a lithologic break recognized at this level.

ALTERATION

The rather pervasive alteration of basalts from Hole 516F may be an important factor controlling the geochemical dispersion apparent in some of the trace element data. Many studies have been made of the chemical effects associated with low-temperature basalt-seawater interaction (i.e., Pearce and Cann, 1973; Thompson and Humphris, 1977; Floyd and Tarney, 1979). Amongst the minor and trace elements, TiO₂, P₂O₅, Zr,

Table 1. (Continued).

Unit 2		Unit 3			Unit 4				
127-3 (1a, 9-13)	127-3 (1e, 43-46)	127-3 (1h, 80-84)	127-4 (1a, 5-11)	128-1 (1, 5-8)	128-1 (6b, 52-57)	128-2 (2a, 15-21)	128-2 (2c, 45-48)	128-2 (4a, 101-106)	128-3 (2, 16-21)
50.7	48.0	48.5	47.9	47.0	49.1	45.6	47.7	47.9	48.0
2.93	2.87	2.72	2.57	2.41	2.48	2.51	2.37	2.34	2.38
13.3	13.5	13.0	12.5	12.4	12.8	12.7	12.4	12.9	12.7
12.2	13.5	13.7	13.4	12.7	11.9	15.6	13.5	12.9	13.0
0.13	0.12	0.12	0.15	0.16	0.16	0.21	0.18	0.16	0.16
3.6	4.0	4.7	4.4	3.5	3.6	4.9	3.8	3.7	3.6
10.0	9.9	9.4	9.5	9.2	9.3	8.7	9.2	9.1	9.2
2.56	2.84	2.77	2.63	2.74	2.78	2.66	2.66	2.77	2.79
0.35	0.47	0.24	0.41	0.39	0.30	0.25	0.33	0.39	0.38
0.30	0.30	0.30	0.30	0.24	0.26	0.30	0.24	0.24	0.23
96.07	95.50	95.45	93.76	90.74	92.68	93.43	92.38	92.42	92.44
45	46	54	47	40	40	52	43	44	40
58	51	47	47	44	41	45	45	73	40
495	476	437	421	374	388	412	372	362	368
57	100	100	80	116	82	86	96	97	98
23	24	22	22	21	22	21	22	21	22
4	4	4	8	10	8	5	8	11	11
315	406	334	364	254	266	367	253	252	253
126	311	139	133	170	170	2280	207	170	184
189	196	183	182	181	178	175	171	175	174
11	11	11	10	10	11	16	10	18	11
17	14	14	12	15	13	13	14	14	15
40	40	39	35	39	39	33	36	38	38
25	24	25	20	20	23	20	21	22	22
33	33	32	30	38	36	32	36	39	37
2	<2	2	5	3	2	2	2	<2	<2
2	2	4	3	2	4	<2	<2	3	2
40	40	43	42	38	41	41	39	39	38
16.6	17.2	17.1	18.4	17.4	16.2	10.9	17.4	9.7	16.6
93	88	89	85	80	82	86	83	80	82
2.8	2.8	2.9	2.7	2.4	2.5	2.4	2.3	2.3	2.4

Nb, Y, Cr, and Ni are generally considered to be immobile, whereas the light rare-earth elements (LREE), K₂O, Rb, Ba, Sr, La, and Ce, often show increased abundances with alteration. Plots of Zr against K₂O, Rb, and Ba (Fig. 4) display marked scatter, particularly so for Ba, indicative of mobility of K, Rb, and Ba due to alteration. For Units 2 and 4 (except for Sample 516F-128-2, 15-21 cm, in Unit 4), however, Sr displays a good correlation with Zr (Fig. 1F), suggesting a lack of mobility, whereas there is little correlation between Sr and Zr abundance in Units 1 and 3 (Fig. 1F). The rather divergent geochemistry of Units 1 and 3 may be controlled by extensive chemical mobility, but Units 2 and 4 have a more coherent chemistry due to more limited mobility.

Amongst the 'immobile' elements there is good evidence that P, particularly, may be mobilized during alteration. In Unit 4, Sample 516F-128-2, 15-21 cm (the uppermost sample from that section) has very high Ba and Sr contents (Table 1). The P₂O₅ content of this sample is also high (Figs. 1D, 2B, 3), whereas the Y content is low, as is the Ce content (Figs. 1B-C, 2A, 5). Additionally, the P/Ti and P/Sr ratios, which are consistent in both Units 2 and 4, are variable in Units 1 and 3 and in the altered basalt from Unit 4 (Figs. 2B, 3). It would appear that extensive alteration may lead to the mobilization of P, as noted by Marsh and others (1980).

DISCUSSION

A large part of the geochemical dispersion apparent in Hole 516F basalts may be due to alteration and associated chemical mobility. However, the trace element chemistry of Units 2 and 4 may be closely representative of the original igneous chemistry. Unit 2 basalts are somewhat more fractionated than Unit 4 basalts, having higher abundances of such incompatible elements as Ti and Zr. It is not possible, though, to relate the two units by fractional crystallization: the 'fractionated' basalts of Unit 2 have higher concentrations of Cr than Unit 4 basalts (Table 1), and substantially higher Sr/Zr ratios (Fig. 1F). This pattern is not predicted by low-pressure fractional crystallization models involving plagioclase, olivine, and pyroxene.

Mid-ocean ridge basalts (MORB) can be classified on the basis of trace element chemistry (Sun et al., 1979; Wood, 1979). Normal (or N-type) MORB have LREE-depleted rare-earth element (REE) patterns and high (greater than chondritic or primordial mantle) ratios of Zr/Nb, Ti/P and P/Sr, reflecting depletion of more-incompatible relative to less-incompatible trace elements (i.e., Sun et al., 1979). On the other hand, enriched (or E-type) MORB have LREE-enriched REE patterns and low (less than chondritic or primordial mantle) ratios of

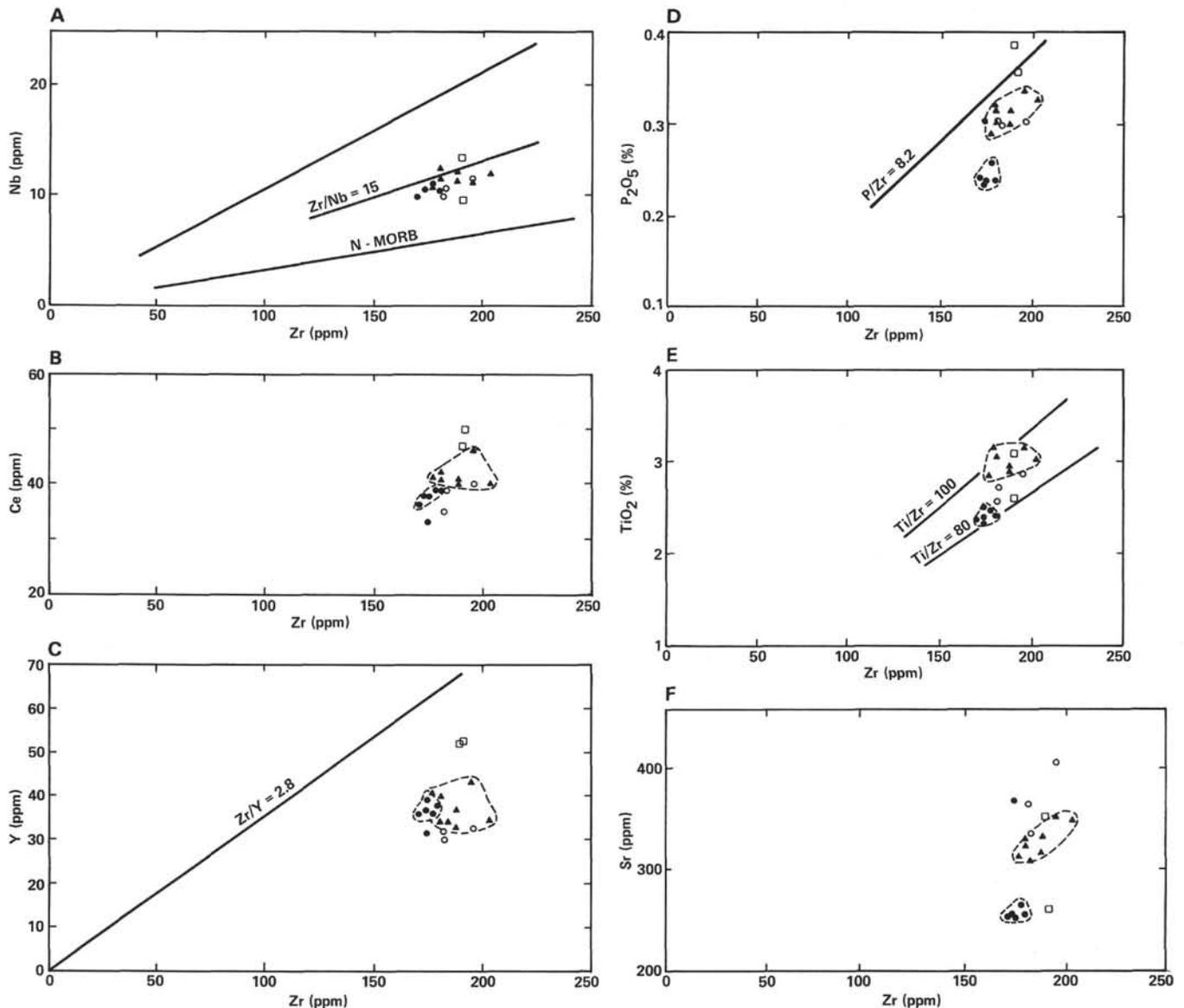


Figure 1. Trace element variations for Hole 516F basalts with Zr as an index of fractionation. Open squares = Unit 1; triangles = Unit 2; open circles = Unit 3; closed circles = Unit 4. Ratios are from Sun, 1980. A, Zr versus Nb; N-type (normal) ratio = 30; E-type (enriched) ratio = 9.4. B, Zr versus Ce. C, Zr versus Y; chondritic ratio = 2.8. D, Zr versus P_2O_5 ; primordial mantle ratio = 8.2. E, Zr versus TiO_2 ; Ratios = 100 and 80. F, Zr versus Sr.

Zr/Nb, Ti/P, P/Sr, reflecting *enrichment* of more-incompatible relative to less-incompatible elements. In terms of this classification, Hole 516F basalts are transitional, or T-type. This is apparent from Figures 1A and 2B, where Hole 516F basalts define element ratios that are intermediate between those of N-type and E-type MORB and that are close to chondritic (or primordial mantle) values. However, Sr/Zr and P/Zr ratios are lower, and Ti/Y, Zr/Y, and Ce_N/Y_N ratios higher than in primordial mantle (Sun, 1980), indicating some elemental fractionation either in the source or during the partial melting event that produced the basalts.

In terms of the abundance levels and abundance ratios of many trace elements, Hole 516F basalts are very similar to basalts recovered from Hole 407 (chemical Unit 3) by Leg 49 at 63°N in the North Atlantic (Tarney et al., 1979). Exceptional in this respect is the Zr/Nb ra-

tio, which is considerably lower in Hole 407 basalts (Zr/Nb ~ 9) because of enhanced Nb levels. This characteristic contrasts with the truly transitional nature of the basalts recovered from the Rio Grande Rise.

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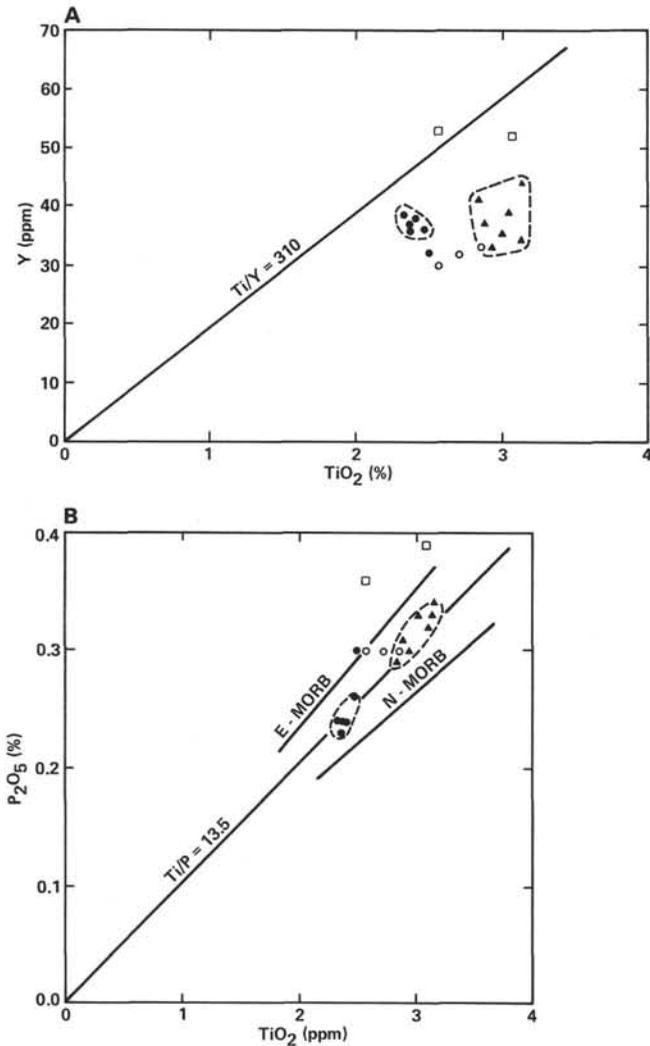


Figure 2. TiO₂ plots for Hole 516F basalts. Symbols as in Figure 1. A, TiO₂ versus Y; chondritic ratio = 310. B, TiO₂ versus P₂O₅; N-type (normal) ratio = 15.5; E-type (enriched) ratio = 11.7; primordial mantle ratio = 13.5.

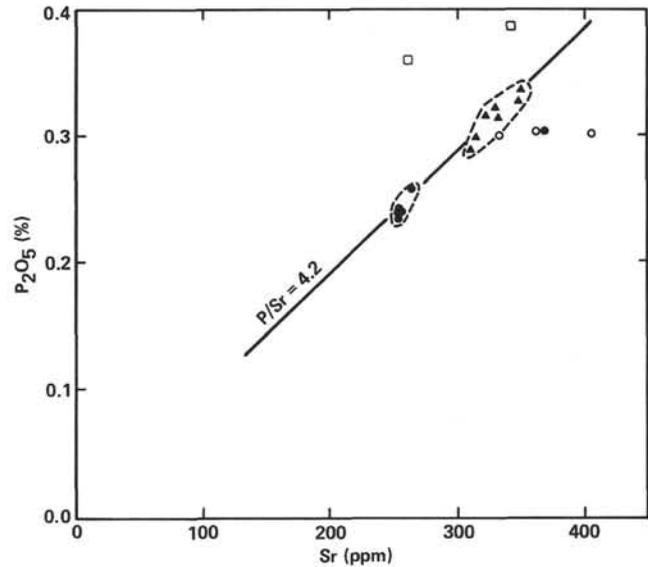


Figure 3. Sr versus P₂O₅ for Hole 516F basalts. Symbols as in Figure 1. Primordial mantle ratio = 4.2.

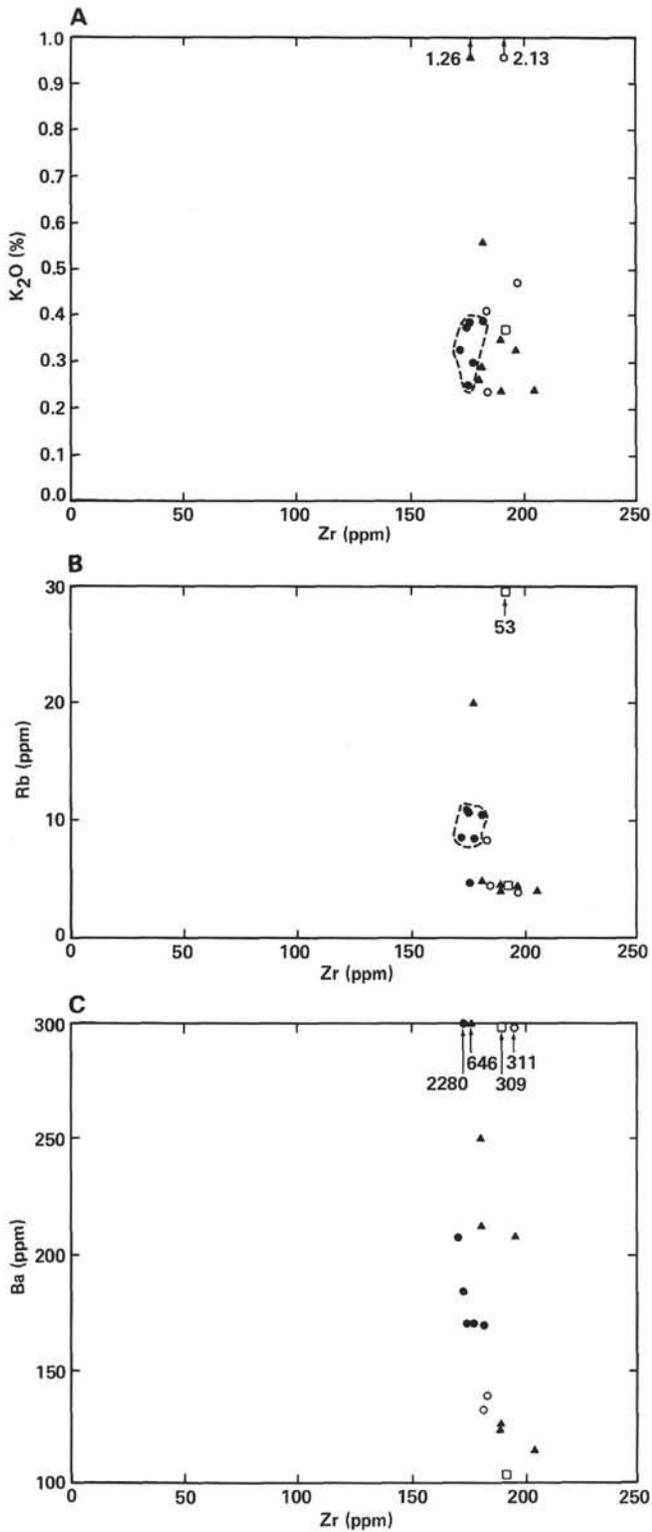


Figure 4. Zr versus K₂O (A), Rb (B), and Ba (C) for Hole 516F basalts. Symbols as in Figure 1.

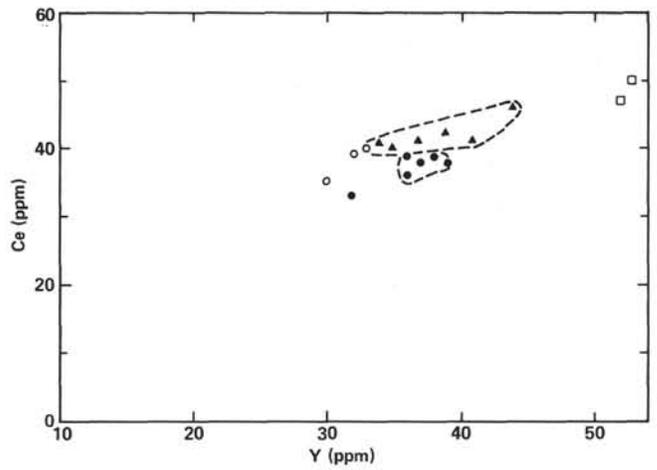


Figure 5. Y versus Ce for Hole 516F basalts. Symbols as in Figure 1.