28. BASEMENT GEOCHEMISTRY, LEG 92¹

Jörg Erzinger, Mineralogisch-Petrologisches Institut, Justus-Liebig Universität²

ABSTRACT

The chemical composition of the basement in DSDP Holes 597C, 599B and 601B is examined in this chapter. These holes were drilled during Leg 92 west of the East Pacific Rise (EPR) crest along 19°S. Hole 597C reached a depth of 91 m into the basement with a recovery of about 55%, so it is the most successful hole drilled in fast-spreading crust. On the other hand, only drilling breccia and some basaltic cobbles were recovered from Holes 599B and 601B.

In total, 60 samples of the least altered basalts from Hole 597C were analyzed. All these basalts were altered to some extent, as is evident from alteration-sensitive parameters. Oxidative seawater alteration influences the upper portion of basement, with considerable uptake of K, Rb, and H₂O⁺, loss of sulfur, and increased iron oxidation. The lowermost basement was affected by a non-oxidative alteration process, showing only enrichment in H₂O⁺; the other parameters have values typical of fresh basalts. Despite the alteration, the primary basaltic composition and variations can be established. According to their major and trace element data, the magmas appear to have undergone different degrees of high-level crystal fractionation. Several eruption episodes may have caused the observed downhole variations in Hole 597C

Four basalt samples from Hole 599B show the same features as the basalts recovered from Hole 597C. The three basalt samples from Hole 601B, on the other hand, are more evolved and can be defined as Fe-Ti basalts, which are commonly described from young EPR crust.

INTRODUCTION

During Leg 92, basement was reached and basalts were recovered from eight holes drilled at four sites (597, 599, 601, 602). The sites are situated along a transect west of the East Pacific Rise (EPR) crest at 19°S.

This paper deals with the geochemistry of basalt samples from Holes 597C, 599B, and 601B. Whereas a depth of 91 m into the basement was reached at Hole 597C (with 55% recovery), only a few meters of drilling breccia and basalt fragments were recovered at Holes 599B and 601B. For further information about hole locations, presumed ages, downhole operations, and core descriptions, see the site chapters in this volume.

Enough basalt was recovered at re-entry Hole 597C (total length of basalts: 48.5 m) to allow the detailed sampling and chemical analysis of the basement at the site. The limited basaltic material recovered from Holes 599B and 601B permitted the determination of the chemical composition of the uppermost basement only.

Hole 597C

Microscopic thin section analysis indicates that all the basalts recovered from Hole 597C are olivine-poor tholeiites containing plagioclase, clinopyroxene, magnetite, olivine, and glass, features that usually characterize deepsea basalts from mid-ocean ridges. All the samples are more or less altered as the result of different post-magmatic alteration processes.

Massive flows appear to make up the entire sequence. One piece with a glassy rim was recovered from the top of the basalt column. No igneous contacts were found, but several individual flows, defined by finer grained flow boundaries, could have been recognized. For detailed mineralogic and petrographic information see Goldfarb (this volume) and Pearce et al. (this volume).

Hole 599B

About 2 m of basaltic cobbles and drilling gravel were recovered at Hole 599B. The cobbles may all be fragments of pillows, but only two of them have glassy rims. All pieces are altered in their outer zones and look relatively fresh in their interiors. These basalts are nearly nonvesicular olivine-poor tholeiites comparable to those found at Hole 597C.

Hole 601B

At Hole 601B, 3.12 m of igneous basement were drilled, and 1.05 m of basalt were recovered. The pieces are fragments of fresh vesicular ferrobasalts, definitively more evolved than the basalts from Holes 597C and 599B. The outer rims have been altered to some extent and are coated with secondary minerals.

MAJOR AND TRACE ELEMENT COMPOSITION

ANALYTICAL METHODS

The freshest possible (i.e., the macroscopically least altered) basalt samples were selected for chemical analysis. Nearly all selected samples had no visible veins, and weathered rims were cut off. After the samples were washed with distilled water, dried, and crushed, they were powdered in an agate mill to a grain size suitable for analysis. The following techniques were used:

1. The major-element oxides were analyzed by X-ray fluorescence (XRF) on samples prepared as fused glass disks of lithium metaborate (sample-to-flux ratio 1:4). A Philips PW 1400 computerized spectrometer and the Philips "alphas" program were used to calculate concentrations.

¹ Leinen, M., Rea, D. K., et al., Init. Repts. DSDP, 92: Washington (U.S. Govt. Printing Office). ² Address: Mineralogisch-Petrologisches Institut, Justus-Liebig Universität, Senckenberg-

strasse 3, D-6300 Giessen, F.R.G.

^{2.} Ferrous iron was analyzed by manganometric titration.

3. H_2O^+ was determined by coulometric Karl Fischer titration after thermal decomposition of the basalts at 1200°C.

 CO₂ was measured coulometrically following thermal decomposition at 1200°C.

 Sulfur analyses were performed on a LECO sulfur determinator SC 132.

6. Measurements of Co, Cr, Cu, Ga, Ni, Rb, Sr, Y, Zn, and Zr were conducted by XRF on pressed powder pellets. The rhodium Compton peak of the X-ray tube was used for matrix correction.

7. Fluorine was analyzed with a fluoride-sensitive electrode, following a pyrohydrolytic decomposition and enrichment method (Erzinger and Puchelt, 1982).

8. The rare earth elements (REE) were analyzed by optical emission spectroscopy using an inductively coupled argon plasma for excitation (ICP-OES). For this purpose the REE had to be quantitatively separated from rock dissolutions and concentrated by a previously described chromatographic technique (Erzinger et al., 1984).

The precision of the determinations was tested by multiple measurements of selected samples. The accuracy was checked by analyzing different international reference rocks, as well as two interlaboratory reference samples (ILB 1 and ILB 2).

RESULTS

Data obtained on USGS reference basalt BHVO-1 are given in Table 1, along with the statistical error expressed as one standard deviation $(\pm 1s)$ and the recommended values from the literature. The results obtained on the ILB 1 and ILB 2 reference samples, which were distributed among all the laboratories that participated in the chemical analysis of Leg 92 basalts, are given in Table 2 and in an interlaboratory comparison (Erzinger, this volume).

Table 2 summarizes the chemical compositions of the 67 least altered basement rocks sampled during Leg 92. The samples are identified by hole, core, and section number, section interval (in cm), and depth below sea-floor (BSF, in m). Also given are $Fe_2O_3^t$ (total iron calculated as Fe_2O_3), FM value (FeO total $\times 100/(FeO$ to-tal + MgO)), and an oxidation index (expressed as $(Fe_2O_3 \times 100)/Fe_2O_3$ total).

The rare earth element data are presented for 19 samples in Table 3. The samples were selected for analysis according to their major and trace element characteristics.

DISCUSSION OF BASALT CHEMISTRY

Effects of Alteration

The response of the basaltic oceanic crust to postmagmatic alteration processes has been summarized by Scheidegger and Corliss (1981), Erzinger (1981), and Emmermann (1985).

1. Oxidative low temperature seawater alteration usually affects deep-sea basalts exposed to cold, oxygenated ocean water. Iron hydroxides and oxides and celadonite seem to be the characteristic stable secondary minerals. This type of alteration produces enrichments in basalt composition of K_2O , $Fe_2O_3^t$, H_2O^+ , CaO and CO₂ (if calcite occurs), Rb, Tl, REE, and higher degrees of ferric iron (expressed here by an oxidation index equal to $[Fe_2O_3 \times 100]/Fe_2O_3^t$). Coupled with these enrichments are considerable depletions of MgO, sulfur, and Se.

2. Non-oxidative hydrothermal alteration, which occurs at low or higher temperatures, is due to the interaction, under suboxic to anoxic conditions, of the base-

	Recomm	ended	Th	iis study	
	Variation	Mean	Mean	s.d.	N
SiO ₂		49.90	50.1	0.08	22
TiO ₂		2.69	2.71	0.006	22
AlpÕa		13.85	13.9	0.03	22
FeoO2		12.23	12.4	0.03	22
MnO		0.17	0.17	0.002	22
MgO		7.31	7.28	0.04	22
CaO		11.33	11.5	0.02	22
NapO		2.29	2.28	0.02	22
KoÔ		0.54	0.53	0.001	22
P205		0.28	0.28	0.004	22
Co		45	44	2.9	18
Cr		300	278	2.4	18
Cu		140	128	1.5	18
Ga		21	20	0.8	18
Nb		19	18	0.5	33
Ni		117	109	1.0	18
Rb		10	7	0.9	33
Sr		420	395	1.5	33
Y		27	25	0.5	33
Zr		180	175	1.1	33
Zn		105	103	1.4	18
La	16.0-17.5	16.7	15	0.4	5
Ce	33-46	41	38	1.4	5
Pr	5.54-5.57	5.6	6.5	2.4	3
Nd	15-31	24	24	0.5	5
Sm	5.28-6.84	6.1	6.6	0.7	4
Eu	1.59-2.74	2.0	1.8	0.1	4
Gd	4.8-9.2	7.0	6.2	0.3	5
Tb	0.75-1.41	1.0	0.8	0.04	4
Dy	4.6-5.0	4.8	4.9	0.7	5
Ho	0.90-0.97	0.94	0.9	0.1	4
Er	1.80-2.40	2.0	2.6	0.2	3
Tm	0.27-0.34	0.31	0.28	0.04	3
Yb	1.54-2.81	2.1	2.0	0.1	3
Lu	0.29-0.36	0.32	0.28	0.04	3

Notes: s.d. = standard deviation; N = number of measurements.

^a Recommended values for major and trace elements from Abbey (1982) and for REEs from Gladney and Goode (1981).

ment with seawater that had previously reacted with basalts or with seawater at low water/rock ratios. Fe-rich saponites, talc, and pyrite are common alteration products. This type of alteration can result in increases of alkali metals, TiO₂, MgO (Scheidegger and Corliss, 1981), and H₂O⁺, as well as decreases of Fe₂O₃^t. Often observed are values of rather fresh basalts, with no enrichment in K₂O, Rb, or Tl, low oxidation indices, and no depletion of sulfur or Se, but with remarkable increases in H₂O⁺ (Emmermann, 1985).

3. The trace elements Ba, Co, Cu, Ni, and Sr have variable behaviors during these two types of alteration, whereas Cr, V, Y, Zn, and Zr seem to be relatively immobile.

Basalt Chemistry

Sixty samples from Hole 597C, four from Hole 599B, and three from Hole 601B were investigated. Therefore, a detailed discussion of chemical composition is possible only for the Hole 597C basalts. The results of samples from Holes 599B and 601B will be briefly presented at the end of this section.

Hole 597C

About half of the investigated basalts from Hole 597C can be defined as fresh; they have oxidation indices ≤ 31 (equivalent to Fe₂O₃/FeO ≤ 0.5), total volatiles $\leq 0.8\%$, K₂O $\leq 0.1\%$, and appear fresh in thin section. All the other basalts are altered to some extent in respect to these parameters.

As we see from an AFM diagram (Fig. 1), most of the samples fall into a zone between two boundaries given by the mean values of fresh basalt glasses dredged at the young East Pacific Rise and Galapagos Spreading Center (GSC). Thus, the weathering processes that affected the samples were not so strong as to totally change the samples' original chemical characteristics. In Figure 2 the most sensitive alteration indicators, sulfur, H_2O^+ , and K_2O , are plotted against the degree of oxidation. One can see that the samples represented by solid dots have the element variations described above for oxidation index, the higher the K_2O and H_2O^+ and the lower the sulfur contents. The same holds for $Fe_2O_3^t$ and MgO, although to a lesser degree (Table 2).

The samples represented by open triangles, on the other hand, show almost no increase in oxidation index or K_2O and no decrease in sulfur compared with the fresh basalts, although they show a remarkable increase in H_2O^+ . This behavior can be explained by non-oxidative alteration processes.

In Figures 3 and 4, oxidation index, H_2O^+ , K_2O , and sulfur are plotted versus depth below seafloor. A sharp boundary can be recognized at about 120 m BSF. The upper part of the basement in Hole 597C was affected by oxidative alteration (solid dots in Fig. 2), and the lower part was affected by non-oxidative alteration (open triangles in Fig. 2). In addition, some of the changes in the alteration-sensitive parameters may be primary (see below).

The downhole variations observed in the alterationsensitive elements nicely reflect the mineralogically defined alteration zones. Calcite, aragonite, zeolite, iron oxides, and brown smectite are pervasive in the upper part of Hole 597C, whereas these alteration products are rare or only vein related in the deeper section.

Comparable downhole variations in alteration were described by Emmermann (1985) for DSDP Hole 504B. The uppermost 550 m of basement in Hole 504B were affected by cold seawater interaction similar to that in the upper part of Hole 597C. The underlying 300 m of Hole 504B lavas underwent non-oxidative alteration comparable to that in the lower part of Hole 597C.

These two different processes are present at Hole 597C within a basalt section only about 90 m thick, possibly because the massive flows in Hole 597C may be less permeable than the highly permeable pillow lavas that comprise the upper basement in Hole 504B. At Hole 597C, the late-stage oxidative alteration did not penetrate more than 65 m into the basement.

Major Elements

Few mid-ocean ridge basalts (MORB) represent primary melts derived directly from the mantle. Most primary melts undergo fractionation processes before reaching the surface, usually in sub-ridge magma chambers. Low-pressure fractionation is mainly controlled by the precipitation of variable amounts of olivine \pm plagioclase \pm clinopyroxene. The elements that enter the first solid phases, like Al, Ca, Mg, Ni, and Cr (compatible elements), show decreases in residual liquids with consecutive evolution. Others, like Ti, Fe, K, S, Y, Zr, and REE (incompatible elements), show respective enrichments.

According to recent data on ocean-floor basalts from the EPR (Scheidegger and Corliss, 1981; Campsie et al., 1984 and literature cited therein), all the rocks drilled at Hole 597C are normal mid-ocean ridge tholeiites (N-type MORB) with respect to major oxide composition. The basalts are rather uniform in SiO₂ content ($\approx 50\%$) and have variable amounts of the other major elements (Table 2). The AFM diagram (Fig. 1) clearly shows the more or less evolved basalts from Hole 597C plotting between two lines representing the mean values determined for basalt glasses from the EPR and GSC (data are from Puchelt and Emmermann, 1983).

The downhole variations of the concentrations of TiO₂ and of FM value (Fig. 3) show unexpectedly high compositional fluctuations and concentration changes within Hole 597C, clearly suggesting different evolutionary trends. Figure 5 (TiO2 versus FM value) also shows the evolutionary trend. FM value ((FeO^t \times 100)/(FeO^t + MgO)) is a very sensitive indicator of crystal fractionation, but only if the samples are fairly fresh. As described above, seawater alteration can change the original Fe and Mg contents of the basalts, so FM value increases with greater degrees of weathering. In Figure 5 the regression line (TiO2 versus FM value) of the zeroaged EPR basalt glasses is also plotted. This figure shows that the TiO₂ values of the more evolved Hole 597C basalts are systematically lower than expected from young EPR lavas (Puchelt and Emmermann, 1983; Scheidegger and Corliss, 1981).

Zirconium is thought to be relatively stable upon alteration. It was plotted against MgO, FM value, and TiO₂ (Fig. 6), as well as against CaO and Al₂O₃ (Fig. 7). There is a positive correlation between Zr and both TiO₂ and FM value. Therefore, Zr could be a useful indicator of crystal fractionation. The regression coefficient is near 1 for Zr versus TiO₂, showing that TiO₂ was not strongly affected by alteration. A plot of Zr versus FM value, on the other hand, shows the greater scatter that would be expected as a result of alteration.

Plots of Zr against MgO, CaO, and Al_2O_3 all show negative correlations. This leads to the conclusion that on the average all the samples investigated form a uniform compositional group with respect to their major elements, suggesting that the conditions controlling their liquid compositions were similar and that they followed the same evolutionary trends.

	Hole 597C															
Core-Section Interval (cm) Sub-bottom depth (m)	3-1 11-13 55.62	3-1 59-60 56.10	3-1 65-66 56.16	3-1 138–140 56.89	3-2 60-62 57.61	3-3 51-53 59.02	4-1 11-13 64.62	4-1 119-121 65.70	4-2 25-27 66.26	4-3 33-35 67.84	4-3 68-70 68.19	4-3 96-98 68.47	4-4 48-50 69.49	4-5 90-92 71.41	4-5 ^a 120-130 71.75	4-6 24-27 72.26
SiO ₂	50.1	50.1	49.4	47.3	50.3	50.8	50.2	50.5	50.5	50.6	50.4	50.4	50.4	50.1	50.4	49.8
TiO ₂	0.92	1.14	1.07	1.05	1.26	1.34	1.27	1.34	1.34	1.39	1.35	1.33	1.38	1.30	1.33	1.24
Al2Õ3	14.8	15.5	14.7	14.7	15.5	15.4	14.5	15.3	15.2	14.6	15.0	15.2	15.5	14.8	14.8	14.9
Fe2O3	4.38	3.19	6.08	5.49	3.29	4.45	6.02	3.28	3.29	3.19	3.01	3.52	3.20	3.16	3.39	7.20
FeO	5.69	5.68	5.51	5.05	6.59	5.00	6.10	7.31	7.39	7.84	7.55	7.36	7.38	8.05	7.67	5.13
MnO	0.17	0.14	0.16	0.20	0.15	0.16	0.17	0.16	0.16	0.16	0.15	0.15	0.15	0.17	0.17	0.15
MgO	8.17	8.25	7.16	6.97	7.71	7.30	6.77	7.21	7.20	7.20	7.18	7.18	6.98	7.19	7.40	6.52
CaO	12.8	12.5	12.2	13.9	12.2	12.4	11.8	11.9	11.9	11.7	11.6	11.8	11.9	11.9	11.9	11.4
Na ₂ O	2.10	2.35	2.23	2.27	2.46	2.56	2.32	2.49	2.49	2.50	2.51	2.45	2.52	2.37	2.44	2.31
K ₂ Õ	0.18	0.10	0.59	0.32	0.10	0.21	0.52	0.10	0.10	0.11	0.10	0.11	0.11	0.10	0.10	0.59
P205	0.07	0.09	0.10	0.09	0.11	0.11	0.11	0.11	0.12	0.12	0.12	0.11	0.12	0.12	0.11	0.11
H ₂ O ⁺	0.69	0.65	0.77	0.69	0.62	0.56	0.50	0.48	0.50	0.47	0.50	0.46	0.49	0.47	0.42	0.87
cõ ₂	0.07	0.25	0.14	1.84	0.05	0.04	0.05	0.05	0.05	0.06	0.06	0.05	0.04	0.08	0.04	0.06
Total	100.14	99.94	100.11	99.87	100.34	100.33	100.33	100.23	100.24	99.58	99.53	100.12	100.17	99.81	100.18	100.28
S	< 0.01	0.085	-	-	0.023		< 0.01	0.078	0.097	0.110	0,106	0.109	0.076	0.104	0.105	< 0.01
Fe ₂ O ₃ ¹	10.7	9.50	12.2	11.1	10.6	10.0	12.8	11.4	11.5	11.9	11.4	11.7	11.4	12.1	11.9	12.9
FM value	54	51	61	59	55	55	63	59	59	60	59	59	60	60	59	64
Ox. index	41	34	50	50	31	45	47	29	29	27	26	30	28	26	28	56
Co	44	48	39	36	47	86	42	48	47	47	47	41	48	45	44	40
Cr	354	292	308	249	242	211	222	207	206	198	194	199	192	200	200	224
Cu	112	105	69	110	120	144	83	123	125	128	127	123	125	120	124	118
F	153			159	_	255	_	$\sim - 1$	—	199	_	_	777.		182	
Ga	15	17	15	16	17	16	16	17	18	18	17	17	18	17	17	16
Ni	89	110	63	61	82	211	61	67	66	60	66	62	65	65	62	45
Rb	<5	<5	14	7	<5	7	17	<5	< 5	<5	<5	< 5	<5	< 5	<5	16
Sr	76	90	84	92	95	100	94	96	97	95	96	96	98	91	93	92
Y	22	24	25	24	27	28	29	30	30	30	29	30	31	30	30	29
Zn	80	76	78	70	84	92	78	89	84	95	89	86	90	101	91	78
Zr	55	72	69	69	81	86	83	88	88	90	88	86	91	85	87	78

Table 2. Major oxide and trace element composition of least altered Leg 92 basement rocks. Values are in wt. % for major oxides and sulfur and ppm for traces.

Note: — = not measured. ^a Interlaboratory reference sample ILB 1. ^b Interlaboratory reference sample ILB 2.

Table 2 (continued).

								Hole	597C								
5-1 46-48 73.97	5-2 29-31 75.30	6-1 78-80 83.29	6-4 59-60 87.60	6-4 60-61 87.61	6-4 117-119 88.18	6-5 80-82 89.31	7-1 90-91 92.41	7-2 39-41 93.40	7-4 134-136 97.35	7-5 8–10 97.59	7-5 65-66 98.16	8-1 13-15 100.64	8-1 74-76 101.25	8-2 53-55 102.54	8-2 ^b 85-96 102.86	8-3 92-94 104.43	8-4 31-33 105.32
50.4	50.1	49.4	49.5	50.7	50.6	49.1	49.9	50.0	50.2	50.2	50.4	50.6	50.5	50.3	50.5	50.4	50.8
1.35	1.22	1.20	1.15	1.22	1.42	1.10	1.20	1.17	1.18	1.20	1.20	1.41	1.40	1.50	1.49	1.57	1.68
15.1	15.1	15.2	15.0	16.4	14.2	15.5	15.9	15.9	15.6	15.8	15.8	14.2	14.0	13.9	13.8	13.7	14.6
3.42	3.05	5.23	7.47	3.09	3.90	5.68	3.41	3.11	2.92	4.03	3.15	4.27	3.96	4.00	4.15	5.82	4.45
7.36	7.61	6.09	4.89	5.91	7.11	5.60	6.20	6.47	7.18	6.18	6.89	7.14	7.69	8.19	8.31	7.09	7.34
0.16	0.16	0.18	0.15	0.14	0.17	0.17	0.16	0.16	0.17	0.16	0.17	0.19	0.18	0.19	0.20	0.30	0.18
7.21	7.75	6.64	6.24	6.96	7.62	6.35	7.65	7.35	7.42	7.17	7.33	7.79	7.64	7.24	7.31	6.54	6.34
11.9	11.9	12.6	11.9	12.9	11.7	12.7	12.6	12.7	12.5	12.5	12.5	11.4	11.5	11.2	11.2	11.4	11.4
2.47	2.24	2.22	2.18	2.38	2.40	2.19	2.29	2.23	2.27	2.29	2.30	2.46	2.40	2.45	2.49	2.48	2.61
0.10	0.10	0.44	0.93	0.10	0.17	0.61	0.09	0.08	0.07	0.07	0.05	0.15	0.16	0.16	0.13	0.38	0.18
0.11	0.10	0.11	0.10	0.09	0.12	0.09	0.10	0.09	0.10	0.10	0.09	0.11	0.12	0.13	0.13	0.14	0.14
0.47	0.79	0.56	0.80	0.34	0.36	0.68	0.52	0.44	0.52	0.48	0.44	0.57	0.58	0.47	0.52	0.47	0.45
0.07	0.05	0.12	0.07	0.13	0.05	0.31	0.05	0.87	0.07	0.07	0.06	0.06	0.05	0.05	0.03	0.12	0.03
100.12	100.17	99.99	100.38	100.36	99.82	100.08	100.07	100.57	100.20	100.25	100.38	100.35	100.18	99.78	100.19	100.41	100.20
0.088	0.097		< 0.01	0.012	0.137	_	0.041	0.056	0.090	0.089	0.064	0.114	0.113	0.128	0.126	< 0.01	0.166
11.6	11.5	12.0	12.9	9.66	11.8	11.9	10.3	10.3	10.9	10.9	10.8	12.2	12.5	13.1	13.4	13.7	12.6
59	57	62	65	56	58	63	55	56	57	58	57	59	60	62	62	65	64
30	27	44	58	32	33	48	33	30	27	37	29	35	32	31	31	43	35
45	43	37	33	45	56	35	49	42	40	42	43	48	46	50	47	50	61
203	272	291	254	251	211	295	299	287	279	273	283	220	192	140	124	101	102
124	116	105	97	99	133	55	113	101	112	112	105	131	134	135	125	143	143
			123	_						160					197		168
17	16	16	16	17	17	16	16	17	17	16	17	17	17	17	18	18	19
65	73	63	46	102	80	65	94	80	83	83	74	69	67	53	52	49	61
-5	-5	14	26	<5	<5	16	-5	<5	<5	-5	-5	<5	-5	-5	<5	88	<5
93	86	91	86	94	89	89	89	89	87	89	90	87	88	88	88	90	96
29	28	27	26	25	31	25	25	25	26	27	25	31	30	32	32	34	35
96	84	77	78	86	100	76	83	76	76	76	76	89	89	87	101	85	93
87	77	75	74	68	90	71	75	71	75	76	71	84	87	90	93	99	107
	1. S			00								0.1					

Table 2 (continued).

								Hole 597C							
Core-Section Interval (cm) Sub-bottom depth (m)	8-5 67-69 107.18	8-6 52-54 108.53	8-6 101-103 109.02	8-7 33-35 109.84	9-1 14-16 109.65	9-1 99-100 110.50	9-1 134-136 110.85	9-2 23-25 111.24	9-3 61-65 113.13	9-4 82-84 114.83	10-1 77-79 119.28	10-1 122-124 119.73	10-2 12-14 120.13	10-2 94-96 120.95	10-2 125-127 121.26
SiO ₂	50.5	50.5	50.5	50.4	50.5	50.6	50.7	50.9	50.2	50.3	50.1	50.4	50.9	50.3	50.1
TiO ₂	1.54	1.68	1.52	1.54	1.49	1.55	1.51	1.44	1.46	1.55	1.52	1.39	1.41	1.24	1.17
Al2Õ3	14.0	14.1	13.7	14.1	13.6	14.0	13.8	13.8	13.4	13.6	13.5	13.9	14.5	14.4	14.6
Fe ₂ O ₃	4.13	4.57	5.65	4.22	4.92	4.05	4.03	4.56	6.21	6.37	5.27	4.97	4.58	3.15	2.91
FeO	7.98	8.22	7.16	7.81	7.72	7.88	8.16	7.15	7.37	6.51	7.68	6.69	6.32	7.70	7.55
MnO	0.19	0.19	0.22	0.19	0.23	0.19	0.20	0.20	0.19	0.26	0.19	0.18	0.21	0.18	0.18
MgO	7.09	6.67	6.90	7.16	7.10	7.17	7.30	7.36	6.74	6.83	7.11	7.40	6.97	7.98	8.12
CaO	11.5	10.9	11.6	11.4	11.7	11.5	11.4	11.8	11.1	11.4	11.1	11.6	11.7	12.0	12.2
NapO	2.41	2.54	2.38	2.45	2.34	2.43	2.40	2.40	2.44	2.50	2.55	2.39	2.48	2.31	2.20
KaÔ	0.10	0.13	0.29	0.14	0.21	0.15	0.13	0.20	0.40	0.44	0.14	0.14	0.22	0.10	0.11
PaOs	0.13	0.14	0.13	0.13	0.12	0.13	0.13	0.12	0.12	0.13	0.13	0.11	0.12	0.10	0.09
H-0+	0.60	0.62	0.43	0.52	0.43	0.54	0.54	0.42	0.66	0.58	0.51	0.61	0.50	0.76	0.80
CO ₂	0.05	0.04	0.05	0.05	0.13	0.06	0.04	0.04	0.04	0.06	0.05	0.04	0.04	0.04	0.12
Total	100.22	100.30	100.53	100.11	100.49	100.25	100.34	100.39	100.33	100.53	99.85	99.82	99.95	100.26	100.15
S	0.147	0.147		0.128		0.141	0.099	0.085	0.058		0.031	0.144	0.076	0.105	0.115
Fe ₂ O ₃ ^t	13.0	13.7	13.6	12.9	13.5	12.8	13.1	12.5	14.4	13.6	13.8	12.4	11.6	11.7	11.3
FM value	62	65	64	62	63	62	62	61	66	64	64	60	60	57	56
Ox. index	32	33	42	33	36	32	31	37	43	47	38	40	40	27	26
Co	48	53	46	52	46	51	52	60	43	54	45	47	59	44	43
Cr	129	84	112	111	115	114	108	119	107	98	90	142	145	194	224
Cu	138	131	125	133	136	148	137	142	166	70	143	214	180	173	170
F	-			$\sim - 1$	140	_	_	_		_	152	$a \rightarrow b$	-	134	
Ga	18	18	17	18	16	17	17	16	17	18	17	16	17	16	16
Ni	54	48	54	60	53	59	55	85	53	53	53	68	85	75	85
Rb	<5	<5	75	<5	28	<5	<5	<5	8	137	<5	<5	<5	<5	<5
Sr	88	93	89	90	89	88	88	90	87	89	88	87	91	83	83
Y	32	34	33	33	33	31	33	37	34	33	33	30	31	27	26
Zn	97	101	93	95	90	99	93	92	79	82	83	90	87	78	74
Zr	97	107	91	95	93	99	95	88	89	91	90	90	91	75	72

Table 2 (continued).

					Hole 597C	:						Hole	599B			Hole 601B	
10-3 52-54 122.03	10-3 103-105 122.54	10-4 124-126 124.25	10-5 64-66 125.15	10-5 94-96 125.45	10-6 49-51 126.50	10-7 74-76 128.25	11-1 16-18 127.67	11-1 99-101 128.50	11-2 100-102 130.01	11-3 40-42 130.91	3-1 98-100 41.79	3-2 30-32 42.61	3-2 60-62 42.91	4-1 27-30 44.09	1,CC 140-141 21.46	2-1 78-81 24.80	3-1 5-7 25.56
49.8	49.8	49.9	49.2	49.3	49.9	49.4	49.2	49.3	49.1	49.3	50.3	51.4	51.1	51.3	49.8	49.9	48.9
14.8	14.9	15.1	17.0	16.3	15.7	16.4	17.2	0.00	17.0	16.7	14.0	15.4	15.7	15 3	13.0	12.9	12.8
3 22	2 46	2.51	2.10	2.69	2.02	2 57	2.65	2 27	2 22	2.35	14.9	2.80	4 23	3 20	5.19	7.07	8.76
6.19	6.71	5 98	5 47	6.41	6 46	6.32	5.85	6 28	5 87	5.88	6.43	5.83	5.55	5.78	9.82	8.13	7.33
0.17	0.16	0.16	0.14	0.15	0.15	0.15	0.14	0.14	0.14	0.14	0.18	0.17	0.17	0.17	0.25	0.24	0.27
8 54	8.90	9.28	8 79	8 55	8 45	8 41	8 15	8 41	8 39	8 53	7.05	7 34	6.88	7.28	5.69	5.51	5.33
12.9	13.1	13.4	13.4	12.5	12.7	12.7	12.9	12.9	13.3	13.2	12.2	12.8	12.6	12.5	9.91	9.66	9.64
2.05	1 94	1 89	1.87	2.03	2.02	2.01	2.00	1.96	1.96	2.00	2.97	2.96	2.84	2.97	2.89	2.99	2.94
0.08	0.06	0.06	0.05	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.23	0.08	0.26	0.17	0.24	0.35	0.48
0.08	0.07	0.06	0.06	0.08	0.08	0.08	0.07	0.07	0.06	0.07	0.08	0.08	0.08	0.08	0.26	0.25	0.24
0.83	0.90	0.95	1.01	1.04	0.82	0.93	0.90	0.88	0.76	0.78	0.45	0.26	0.35	0.31	0.71	0.62	0.89
0.06	0.10	0.07	0.19	0.06	0.06	0.06	0.09	0.05	0.16	0.09	0.11	0.11	0.05	0.11	0.07	0.07	0.08
99.71	100.03	100.16	100.06	100.11	100.30	100.02	100.08	100.10	99.93	99.94	100.13	100.44	100.47	100.37	100.45	100.27	100.24
0.097	0.095	0.076	0.063	0.084	0.079	0.074	0.065	0.067	0.063	0.062	0.03	< 0.01	< 0.01	< 0.01	0.122	0.039	0.014
10.1	9.91	9.15	8.27	9.81	10.1	9.59	9.15	9.35	8.84	8.88	11.2	9.28	10.4	9.62	16.1	16.1	16.9
52	50	47	46	51	52	51	50	50	49	48	59	53	58	54	72	72	74
32	25	27	27	27	29	27	29	25	26	27	36	30	41	33	32	44	52
37	38	39	34	38	45	38	39	43	39	34	42	35	33	32	51	-	51
344	364	349	312	286	343	339	326	388	404	440	258	241	236	243	70		70
138	145	142	115	124	124	105	94	100	96	95	80	69	76	60	61		59
		80	_		154		_		102	-	-	-	134		-	283	283
15	15	13	15	15	16	15	16	15	15	16	16	17	16	17	20		19
90	105	103	117	103	102	96	96	100	103	100	55	47	47	51	33		34
<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	6	<5	6	<5	<5		7
81	79	76	82	82	86	87	87	83	84	82	93	92	92	91	116	-	116
22	20	17	15	21	22	21	19	19	18	19	29	31	29	30	61		59
66	61	65	55	63	67	62	59	60	58	56	84	91	80	89	131		120
66	55	48	43	57	61	55	55	54	51	54	78	72	74	77	190		191

Table 3. Rare earth element abundances of selected Leg 92 basalts. Values are in ppm.

		Hole 597C															Hole 601B		
Core-Section Interval (cm)	4-3 96-98	4-5 120-130	5-2 29-31	6-4 59-60	6-5 80-82	7-2 39-41	8-2 85-96	8-3 92-94	8-4 31-33	9-1 14-16	9-2 23-25	10-1 77-79	10-2 12-14	10-2 125-127	10-3 52-54	10-3 103-105	10-4 124-126	10-6 49-51	2-1 78-81
La	2.94	3.21	2.40	2.36	2.28	3.74	3.53	2.98	3.68	3.16	3.30	4.02	3.70	2.42	3.16	2.24	1.54	2.06	5.20
Ce	9.16	9.22	7.08	7.12	6.68	9.92	10.2	9.62	10.76	9.24	9.74	11.9	11.4	7.34	8.82	6.48	4.50	6.34	18.0
Pr	2.00	2.03	1.36	1.48	1.48	2.10	2.19	2.18	2.22	2.10	2.10	2.16	2.16	1.58	1.78	1.30	0.96	1.12	3.60
Nd	7.58	7.40	6.32	6.18	6.10	7.60	8.56	8.42	9.14	8.60	8.70	9.84	9.92	6.30	7.08	5.66	4.02	5.30	18.4
Sm	2.82	2.75	2.30	2.40	2.26	2.04	3.74	3.24	2.28	3.00	3.06	4.12	4.28	2.30	2.76	2.30	1.54	2.00	7.34
Eu	0.94	1.06	0.82	0.84	0.80	0.82	1.23	1.04	1.18	1.06	1.06	1.24	1.24	0.30	0.90	1.04	0.62	0.70	2.18
Gd	3.44	5.03	2.58	2.52	3.52	3.08	-	4.32	4.00	4.36	4.38	4.48	4.20	3.14	3.16	3.00	2.16	2.66	8.82
Tb	0.74	0.58	0.42	0.42	0.56	0.58	0.73	0.70	0.70	0.72	0.70	0.80	0.86	0.56	0.52	0.56	0.38	0.46	1.52
Dy	4.56	4.97	3.92	4.00	3.86	3.98	5.82	4.74	5.02	5.02	5.38	6.06	6.16	3.90	4.32	3.92	2.64	3.30	10.7
Ho	0.72	0.87	0.68	0.66	0.66	0.64	0.94	0.74	0.82	0.82	0.90	1.06	1.10	0.64	0.74	0.66	0.44	0.58	1.78
Er	2.76	3.21	2.58	2.50	2.50	2.48	3.57	2.78	2.92	3.00	3.52	3.68	3.82	2.28	2.58	1.04	1.54	2.02	6.64
Tm	0.32	0.43	0.36	0.36	0.30	0.26	0.44	0.36	0.32	0.36	0.24	0.48	0.44	0.22	0.32	0.32	0.10	0.28	0.98
Yb	2.38	3.07	2.44	2.52	2.42	2.46	3.25	2.46	2.74	2.46	3.38	3.38	3.60	1.88	2.34	2.18	1.06	2.00	6.30
Lu	0.32	0.45	0.36	0.38	0.36	0.36	0.48	0.36	0.40	0.34	0.52	0.48	0.52	0.26	0.32	0.32	0.14	0.30	0.96

Note: - = not measured.



Figure 1. AFM diagram of Leg 92 basalts. Dashed lines represent mean values of basalt glasses dredged at East Pacific Rise (EPR) and Galapagos Spreading Center (GSC). The data are from Puchelt and Emmermann (1983).

Minor and Trace Elements

The REE of 18 selected samples were determined, because the REE are useful for distinguishing different tectonic settings, fractionation mechanisms, and magma source compositions (Saunders, 1984).

Samples from Hole 597C (Fig. 8) show a broad band of chondrite-normalized REE ratios in which light REE are depleted relative to heavy REE, but La/Yb ratios show little difference and REE concentrations increase upsection. Such patterns are usual for N-type to T-type MORBs (Saunders, 1984). A plot of Σ REE versus Zr shows positive correlation (Fig. 9), suggesting that the REE enrichments are due to greater degrees of magma evolution.

Some authors show that magmas from different sources (e.g., different mantle or partial melt composition) have distinct Ce/Y, Ce/Yb, or La/Tb ratios (Wood et al., 1979; Campsie et al., 1984; Emmermann, 1985). These ratios are rather uniform when calculated with our data, suggesting that all the lavas that built up the



Figure 2. Plots of sulfur, H₂O⁺, and K₂O versus oxidation index (Hole 597C). Solid dots represent samples with oxidative seawater alteration. Triangles represent samples affected by nonoxidative alteration processes.

basement at Hole 597C had the same source. The major element data suggested a similar conclusion.

The other trace elements analyzed show the behavior described above. For example, Cr (Fig. 4) and Ni (Table



Figure 3. Downhole variation of TiO₂, FM value, oxidation index, and H_2O^+ in Hole 597C. Zones of normal and reversed polarity are indicated.



Figure 4. Downhole variations of Zr, Cr, K₂O, sulfur, and Cu/Zr ratio in Hole 597C.



Figure 5. Plot of TiO_2 versus FM value for Leg 92 basalts. The regression line for zero-age basalt glasses dredged from the EPR is included.

2) clearly correlate negatively with Zr, whereas Co, Cu, Sr, Y, and Zn (Table 2) vary positively with Zr.

The average copper content is 130 ppm, almost twice the Cu concentration reported from MORBs. Cu data normalized to different degrees of evolution (Cu/Zr ratio) are rather uniform downhole but show an enrichment at about 125 m BSF (Fig. 4). The enrichment at that depth may be due to the circulation of copper-rich hydrothermal solutions, which pervasively penetrated the basement at Hole 597C, resulting in generally high Cu concentrations and sometimes distinct enrichments. Precipitation from hydrothermal solution may also explain the occurrence of native copper in some veins.

Interestingly enough, despite the variable degree of alteration, sulfur is positively correlated with Zr (Fig. 9). However, the S values from Hole 597C are on the average lower than expected from basalt glass composition at the same degree of fractionation. This may be because sulfide has been oxidized to sulfate during alteration and then dissolved and advected into the ocean.

Another interesting feature of the Hole 597C basalts is the enormously high level of Rb (up to 140 ppm). Our practical XRF detection limit for Rb is about 5 ppm, but all Rb values higher than 5 ppm correlate positively with K₂O (>0.2%), which can be explained by low temperature seawater alteration (Cann and Heath, 1976). The Rb/K₂O ratio is about 0.002 to 0.003 at Rb < 20 ppm, but rises to 0.03 at higher Rb and K₂O values. This pronounced Rb enrichment occurs only in the zone from 100 to 120 m BSF.

Hole 599B

The basalts analyzed from Hole 599B have elemental compositions comparable to those of the Hole 597C basement rocks. The basalts are less evolved (TiO₂ =

1.2%), but when cross-plotted all the data show the same trends as the data for Hole 597C.

Hole 601B

The samples analyzed from Hole 601B are clearly more evolved than the basalts from Holes 597C or 599B, as is apparent from the AFM diagram (Fig. 1) and the correlation plot of TiO₂ versus FM value (Fig. 5). The samples from Hole 601B have higher values of TiO₂ (2.6%) and Fe₂O₃^t (16.5%) and lower values of MgO (5.5%).

TiO₂ from Hole 601B plots exactly on the regression line for EPR basalt glasses. The Σ REE are about three times as high, and the REE pattern shows a distinct negative Eu anomaly (Fig. 8), which can be attributed to a higher degree of plagioclase crystallization (Saunders, 1984). Therefore, the samples from Hole 601B can be described as Fe-Ti basalts; in overall composition they fit published EPR data better than do samples from Holes 597C and 599B (Scheidegger and Corliss, 1981). The limited number of samples from Hole 601B does not allow further speculation on mantle heterogeneity or the change in magma composition with time.

CONCLUSIONS

Chemical analyses were performed on 67 basaltic rocks recovered from DSDP Holes 597C, 599B, and 601B. The results of the analyses support the following conclusions:

1. Massive basalt flows appear to make up the entire sequence in Hole 597C, which reaches 91 m into the basement and represents the most successful hole drilled into fast-spreading oceanic crust. Several individual flows are defined by finer grained flow boundaries. The lavas consist predominantly of fine- to medium-grained phyric basalts containing plagioclase-olivine \pm clinopyrox-



Figure 6. Plots of MgO, FM value, and TiO₂ versus zirconium (Hole 597C).

ene \pm magnetite. All rocks recovered from Hole 597C are mineralogically and chemically altered to some extent.

2. From major and trace element analysis, the basalts from Hole 597C can be described as more or less evolved normal mid-ocean ridge basalts (N-type MORBs). The TiO₂ values are, on the average, lower than described for EPR basalts. All lavas form a uniform compositional group, suggesting that the conditions controlling original liquid compositions were similar and that the lavas followed similar evolutionary trends.

3. Remarkable chemical downhole variation is the most striking feature of Hole 597C, where the basement can be divided into at least four distinct zones, each of rather uniform chemical composition (Fig. 3). An uppermost zone I extends from top of the basement down to 57 m BSF, with mean values of $\text{TiO}_2 = 1.05\%$, $\text{Fe}_2\text{O}_3^{\text{t}} = 10.9\%$, MgO = 7.6%, and Zr = 66 ppm. A second zone II from 57 to 100 m BSF has mean values of $\text{TiO}_2 = 1.27\%$, $\text{Fe}_2\text{O}_3^{\text{t}} = 11.4\%$, MgO = 7.1%, and



Figure 7. Plots of CaO and Al₂O₃ versus zirconium (Hole 597C).



Figure 8. Chondrite-normalized REE distribution patterns for Hole 597C and 601B basalts. Shaded area represents the bandwidth of Hole 597C lavas.



Figure 9. Plots of ΣREE and sulfur versus zirconium. Dashed line in S versus Zr plot is the regression line of zero-aged basalt glasses from EPR. Data for S are from Erzinger (1981) and for Zr from Puchelt and Emmermann (1983).

Zr = 84 ppm. It is followed by a third, more evolved zone III from 100 to 121 m BSF, which has mean values of TiO₂ = 1.51%, Fe₂O₃^t = 13.1%, MgO = 7.0%, and Zr = 93 ppm. A lowermost less evolved zone IV has mean values of TiO₂ = 0.93%, Fe₂O₃ = 9.7%, MgO = 8.5%, and Zr = 57 ppm. Within zone IV two subzones may be defined, which formed as the lavas forming zone IV became more and more evolved with time and then began a new sequence of evolution.

The observed chemical variation of the basalts within all units may be due to the mixture of variable amounts of more evolved magmas with parental magma.

Interestingly enough, on board the *Glomar Challeng*er we never observed an igneous contact; several flow boundaries could be defined, but only by the presence of finer grained basalts. Possible explanations are that (1) the basement at Hole 597C was built up relatively quickly or (2) any igneous contacts were lost in the coring voids.

4. All basalts were altered, as is evident from analyses of alteration-sensitive elements. The uppermost basement down to 120 m BSF is characterized by a pronounced uptake of K, Rb, and H_2O^+ , loss of sulfur, and increasing iron oxidation, demonstrating oxidative low temperature seawater interaction. The lower portion of Hole 597C does not show those elemental variations, but a considerable H_2O^+ uptake is evident from the data. This alteration behavior can be caused by non-oxidative processes. A remarkable increase of Rb/K₂O ratio is established in samples with Rb values >20 ppm, commonly found in Unit III.

A significant enrichment of Cu can be observed at 120 to 127 m BSF. Also, the Cu content is about twice that normally found in MORB (\approx 130 ppm), explaining the native copper found in some veins.

5. The basalts analyzed from Hole 599B are comparable in composition to those drilled at Hole 597C. On the other hand, the rocks from Hole 601B can be defined as Fe-Ti basalts, with $TiO_2 = 2.6\%$, $Fe_2O_3 = 16.5\%$, MgO = 5.5%, and Zr = 190 ppm, like basalts normally found at the young EPR.

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REFERENCES

- Abbey, S., 1982. An evaluation of USGS III. Geostandards Newsl., 6: 47-76.
- Campsie, J., Johnson, G. L., Rasmussen, M. H., and Lawsen, J., 1984. Dredged basalts from the western Nazca Plate and the evolution of the East Pacific Rise. *Earth Planet. Sci. Lett.*, 68:271-285.
- Cann, J. R., and Heath, R., 1976. Some trace elements in basalts from Leg 34. In Yeats, R. S., Hart, S. R., et al., Init. Repts. DSDP, 34: Washington (U.S. Govt. Printing Office), 289-292.
- Emmermann, R., 1985. Basement geochemistry, Hole 504B. In Anderson, R. N., Honnorez, J., Becker, K., et al., Init. Repts. DSDP, 83: Washington (U.S. Govt. Printing Office), 183-199.
- Erzinger, J., 1981. Zur Geochemie von Selen und Thallium in magmatischen Gesteinen-mit einem Beitrag zur Analytik von Selen in geochemischen Matrizes [Ph.D. dissert.]. University of Karlsruhe, F.R.G.
- Erzinger, J., Heinschild, H. J., and Stroh, A., 1984. Bestimmung der seltenen Erden in Gesteinen mit der ICP-AES. In Welz, B. (Ed.), Fortschritte in der atomspectrometrischen Spurenanalytik (Vol. 1): Weinheim (Verlag Chemie), 251-260.
- Erzinger, J., and Puchelt, H., 1982. Methods for the determination of trace elements in geological materials. *Erzmetall*, 35:173-179.
- Gladney, E. S., and Goode, W. E., 1981. Elemental concentrations in eight new USGS rock standards: a review. *Geostandards Newsl.*, 5: 31-64.
- Puchelt, H., and Emmermann, R., 1983. Petrogenetic implications of tholeiitic basalt glasses from East Pacific Rise and the Galapagos Spreading Center. Chem. Geol., 38:39-56.
- Saunders, A. D., 1984. The rare earth element characteristics of igneous rocks from the ocean basins. In Henderson, P. (Ed.), Rare Earth Element Geochemistry: New York (Elsevier).
- Scheidegger, K. F., and Corliss, J. B., 1981. Petrogenesis and secondary alteration of upper layer 2 basalts of the Nazca Plate. Geol. Soc. Am., 154:77-107.
- Wood, D. A., Varet, J., Bougault, H., Corre, O., Joron, J. L., Treuil, M., Bizouard, H., Norry, M. J., Hawkesworth, C. J., and Roddick, J. C., 1978. The petrology, geochemistry, and mineralogy of North Atlantic basalts: a discussion based on IPOD Leg 49. *In* Luyendyk, B. P., Cann, J. R., et al., *Init. Repts. DSDP*, 49: Washington (U.S. Govt. Printing Office), 597-655.

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