9. GEOCHEMISTRY OF HYDROTHERMALLY ALTERED BASALTS: DEEP SEA DRILLING PROJECT HOLE 504B, LEG 83¹

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ABSTRACT

This chapter documents the chemical changes produced by hydrothermal alteration of basalts drilled on Leg 83, in Hole 504B. It interprets these chemical changes in terms of mineralogical changes and alteration processes and discusses implications for geochemical cycling.

Alteration of Leg 83 basalts is characterized by nonequilibrium and is heterogeneous on a scale of centimeters to tens or hundreds of meters. The basalts exhibit trends toward losses of SiO₂, CaO, TiO₂; decreases in density; gains of MnO, Na₂O, CO₂, H₂O⁺, S; slight gains of MgO; increased oxidation of Fe; and variable changes in Al₂O₃. Some mobility of rare earth elements (REE) also occurred, especially the light REE and Eu. The basalts have lost Ca in excess of Mg + Na gains. Variations in chemical trends are due to differing water/rock ratios, substrate control of secondary mineralogy, and superimposition of greenschist and zeolite facies mineralogies. Zeolitization resulted in uptake of Ca and H₂O and losses of Si, Al, and Na. These effects are different from the Na uptake observed in other altered basalts from the seafloor attributed to the zeolite facies and are probably due to higher temperatures of alteration of Leg 83 basalts.

Basalts from the transition zone are enriched in Mn, S, and CO_2 relative to the pillow and dike sections and contain a metal-sulfide-rich stockwork zone, suggesting that they once were located within or near a hydrothermal upflow zone. Samples from the bottom of the dike section are extensively fractured and recrystallized indicating that alteration was significantly affected by local variations in permeability.

INTRODUCTION

Site 504

Alteration of the oceanic crust in submarine hydrothermal systems has been suggested to play a significant role in geochemical cycling of elements in the oceans (e.g., Humphris and Thompson, 1978; Edmond et al., 1979). Leg 83 of the Deep Sea Drilling Project has deepened Hole 504B, drilled previously on Legs 69 and 70, to over 1 km into basement. The hole penetrated into a sheeted dike complex, and the first *in situ* basalts containing greenschist facies mineral parageneses were recovered from the oceanic crust. These cores thus provide a unique set of samples from which to study the chemical effects of hydrothermal alteration of the crust.

A detailed description of alteration mineralogy and interpreted conditions of alteration are given elsewhere (Alt et al., this volume). The purpose of this chapter is to document the chemical changes produced by hydrothermal alteration of Leg 83 basalts, to interpret these chemical changes in terms of mineralogical changes and alteration processes, and to discuss implications for geochemical cycling.

DSDP Site 504 is located in 5.9-m.y.-old crust south of the Costa Rica Rift in the eastern Pacific. The hole reaches 1.35 km into the oceanic crust, penetrating 274.5 m of sediment; 571.5 m of pillow and massive basalts and breccias; a 209-m transition zone composed of pillows, massive flows, and dikes; and 295 m of dikes and massive units that are interpreted to be part of a sheeted dike complex. The Leg 69 and 70 sections penetrated through the sediment and 561.5 m into basement. The Leg 83 section discussed in this chapter begins at 836 m below seafloor and consists of the lowermost 10 m of pillow basalts, plus the transition zone and dike sections. Details of the lithostratigraphy are given in Cann, Langseth, Honnorez, Von Herzen, White, et al. (1983) and Adamson (this volume). Measured heat flow at the site falls close to the theoretical conductive cooling curve for ocean crust, and temperatures in the hole fall on a conductive gradient ranging from 60°C at the basement/sediment interface to 160°C at the bottom of the hole (Becker et al., this volume).

The chemistry of Leg 69 and 70 pillow sections is given in Cann, Langseth, Honnorez, Von Herzen, White, et al. (1983). Basalts from 274.5 to 584.5 m are characterized by the presence of red iron hydroxide-rich oxidation halos and by hydration, oxidation of iron, gain of K, loss of S, and variable CO_2 contents because of the reaction of the basalts with oxygenated seawater. From 584.5 to 836 m the basalts are characterized by generally

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little chemical change. The basalts are hydrated, with possible slight Ca and Al losses and Mg gains that are due either to reaction with seawater at low water/rock ratios or with seawater that had previously reacted with basalt.

Alteration of Leg 83 Basalts

Alteration of Leg 83 basalts is described in detail by Alt et al. (this volume) and is only very briefly summarized in this chapter. The rocks are generally characterized by incomplete replacement of primary phases, although they may be locally totally recrystallized. From 836 to 898 m the basalts are uniformly dark gray in color and contain smectite-chlorite mixtures as the major alteration phase. From 898 m to the bottom of the hole greenschist-and zeolite-facies mineralogies are present in varying amounts. Olivine is replaced by chlorite, chlorite-smectite mixtures, and pyrite; plagioclase is partly replaced by albite, heulandite, laumontite, and minor scolecite; clinopyroxene is partly replaced by actinolite and magnetite; and titanomagnetite is partly to totally replaced by sphene. The rocks below 898 m are generally dark gray with centimeter-sized, light gray or greenish, more extensively altered wall rock zones around veins and vugs.

Alteration of the Leg 83 basalts is interpreted to have taken place in a generally evolving and cooling hydrothermal system (Alt et al., this volume; Honnorez et al., this volume). Three basic stages of alteration have been determined: (1) formation of chlorite, actinolite, albite, sphene, pyrite, and minor quartz in veins and host rocks by reaction of basalts with partially reacted seawater (Mg-bearing, locally metal- and Si-enriched) at temperatures of at least 200–250°C; followed by (2) formation of quartz, epidote, and sulfides in veins from relatively evolved (Mg-depleted, metal- and Si-enriched, and possibly ¹⁸O-enriched) seawater-derived solutions at temperatures of up to 380°C; and finally by (3) zeolite and calcite formation from evolved fluids (Mg-depleted, Caand ¹⁸O-enriched) at temperatures of up to 250°C.

SAMPLING AND METHODS

Samples were selected from throughout the Leg 83 section and include light gray wall rock alteration zones and adjacent dark gray host rocks for comparison (Table 1). Samples were generally selected to be free of veins containing secondary minerals, but two dike margin breccias with abundant clay mineral veins (Table 1, Analyses 24, 25) and one clay-rich brecciated massive basalt (Table 1, Analysis 3) were also sampled. Altered glass from a pillow rim was sampled to compare with the alteration of the adjacent crystalline basalt (Table 1, Analysis 10).

Major and trace elements were determined by X-ray fluorescence carried out on glass beads fused with lithium metaborate (rock/flux ratio of 1:4) using a Philips PW 1400 spectrometer, H_2O^+ was measured by Karl Fischer titration after thermal decomposition of the rock, and Fe²⁺ was determined by manganometric titration. A coulometric titration apparatus was used for the determination of CO₂ and S. Sulfur concentrations above 0.2% were calculated as FeS₂ and are listed among the major components. Sulfur concentrations less than 0.2% are given as S (wt.%) separately. Rare earth elements (REE) were analyzed by inductively coupled plasma emission spectroscopy (Emmermann, this volume). Densities were determined by weighing the samples in air after drying at 110°C for 48 hr. followed by weighing in distilled water to determine volumes. Analyses of basalt standards and Leg 83 interlaboratory standards are given in Table 2. Analytical uncertainty for density measurements determined by repeated measurements of standards is $\pm 1\%$.

CHEMICAL CHANGES

In considering chemical changes during metamorphism, chemical analyses are often normalized to constant Ti, Zr, Y, or occasionally Al, which are considered to be immobile elements, in order to take into account dilution effects or changes in density. At present, we do not have data for Zr and Y, and Ti and Al were not always conserved during alteration of Leg 83 basalts. Bulk rock compositions were recalculated as moles per cubic centimeter, but this did not significantly affect the observed chemical trends. Thus, most of the following discussion is based on oxide weight percentages.

One of the difficulties in determining chemical changes for altered rocks is in finding a reliable unaltered rock composition for comparison. All of the basalts recovered from Hole 504B are mineralogically and chemically altered to some extent (Honnorez et al., 1983; Hubberten et al., 1983; Alt et al., this volume); however, unaltered basaltic glass is common in the Leg 69 and 70 pillow section of the hole. Although the primary composition of the Hole 504B section is relatively uniform (with the exception of a few "anomalous" high P and Ti units; Hubberten et al., 1983; Emmermann, this volume), 13 different glass compositional types have been identified from the pillow section (Natland et al., 1983) indicating that significant compositional variations do occur. The means and standard deviations of 51 glass analyses and of 58 least-altered basalts from Leg 69 and 70 sections of the hole (both excluding the "anomalous" high P and Ti units) are presented in Table 3. The two means are very similar and are statistically indistinguishable at the 99.5% confidence level. Based on the close similarity of the mean fresh glass and least-altered basalt compositions in Table 3 and the relative uniformity of bulk rock compositions among the Leg 69, 70, and 83 sections in the hole, the average glass composition in Table 3 is used in this chapter as the unaltered basalt composition for Hole 504B, thus providing a basis for determining chemical changes arising from hydrothermal alteration. This average does not include the few "anomalous" high P and Ti units, since these units were not sampled for the present study. It should be pointed out, however, that the glass composition in Table 3 is an average, and that the primary composition of individual bulk rock samples could deviate from these values, leading to errors in the chemical changes determined to be due to hydrothermal alteration. The bulk rock composition of a crystalline pillow interior could also differ significantly from that of the glass at the corresponding rim of the same pillow because of phenocryst accumulation (e.g., Staudigel et al., 1979). However, since we are using the mean glass composition (which is nearly identical to the average least-altered basalt composition) individual glass-whole rock variations should not affect the discussion.

Bulk rock compositions are plotted versus depth in Figure 1, along with the average unaltered glass composition from Table 3 for comparison. Relative to the glass

Tabl	e 1	. Bu	lk	rock	ana	lvses	of	altered	basa	lts.	Hole	504B.
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Core-Section (interval in cm)	Rock type	Analysis	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	к ₂ 0	P205	н ₂ о+	co ₂	FeS ₂	Total	Fe ₂ O ₃ ^T	H ₂ O ⁻	Ni	Zn	S	Cr	Co	Cu	Ga	Density (g/cm ³)	Depth (m)
72-2, 126-129	d	1	49.00	0.85	16.00	2.91	5 46	0.16	8.75	13.00	1.89	0.02	0.06	1.88	0.49	0.00	100.47	8.98	1.52			0.03					2.81	846.3
76-1 65-68	d	2	48 50	0.02	16.40	3 79	5 28	0.17	7 88	12 70	2 04	0.02	0.06	2 36	0.26	0.00	100 37	9.65	1.26			0.10					2.84	880.2
78-1 102-106	b	3	40.50	0.92	14 40	1 70	5.00	0.10	0.68	10.40	2.04	0.02	0.00	2.30	0.17	1 50	100.16	9.42	0.51			1 70					2 74	898 5
70-7, 102-100	1	4	40.00	0.92	15.80	2.57	5.26	0.15	0.00	12 10	2.16	0.03	0.06	2.41	0.10	0.00	100.10	9.53	0.76			0.00					2 78	906.6
79-2, 02-00	1	5	47.40	0.91	15.00	1.62	5.10	0.15	7.95	11.00	2.10	0.02	0.06	2.00	0.12	2 72	00.61	0.90	0.42			3.07					2.80	909.0
90 1 22 27	1	5	47.40	0.91	16.00	1.05	5 49	0.22	7.03	11.50	2.47	0.02	0.00	2.10	0.13	2.21	00.06	9.00	0.42			2.26					2.63	910.3
80-1, 33-37	1	0	47.30	0.00	17.10	1.40	5.40	0.33	1.93	11.00	2.43	0.02	0.05	3.14	0.12	4.00	100.20	0.90	0.32	150	0.0	4.30	207	42	02	15	2.05	012.2
80-2, 03-07	1	/	47.40	0.90	17.10	1.03	5.12	0.33	0.42	10.00	3.05	0.02	0.06	3.97	0.20	4.00	100.20	9.90	0.82	150	90	4.27	391	42	93	15	2.40	014.2
80-3, 124-133	1	8	48.10	0.84	17.10	1.99	5.21	0.27	7.08	13.00	2.42	0.02	0.05	2.20	0.19	1.35	99.88	8.08	0.67			1.44					2.00	914.2
81-1, 83-86	1	9	50.20	0.92	14.30	2.06	5.88	0.31	8.08	10.90	3.14	0.03	0.05	2.90	0.29	1.14	100.20	9.34	0.67			1.22					2.08	920.4
81-1, 83-86	g	10	35.70	1.01	18.00	4.03	10.61	0.43	15.70	3.22	1.58	0.03	0.07	9.52	0.36	0.00	100.26	15.80	1.63			0.03					2.51	920.4
82-1, 68-73	1	11	48.90	0.89	15.40	1.77	6.47	0.23	8.49	12.40	1.82	0.02	0.07	1.87	0.24	0.97	99.54	9.60	0.29			1.04					2.92	929.2
82-1, 68-73	d	12	49.30	0.92	15.40	2.29	6.86	0.25	8.66	12.40	1.67	0.02	0.06	2.01	0.22	0.00	100.06	9.91	0.38			0.09					2.92	929.2
82-1, 90-96	1	13	49.30	0.99	14.50	1.52	4.63	0.37	6.55	8.73	3.92	0.04	0.06	3.21	0.48	5.74	100.04	10.40	0.98			6.13					2.66	929.4
84-2, 48-50	1	14	51.10	0.98	13.50	1.82	5.77	0.27	8.32	8.24	2.72	0.02	0.07	5.30	0.25	1.96	100.32	9.53	1.05			2.10					2.56	948.5
87-1, 116-123	1	15	48.90	0.98	14.70	2.00	7.51	0.30	8.38	12.60	2.23	0.02	0.07	2.38	0.20	0.00	100.27	10.30	0.30			0.04					2.86	968.2
91-1, 66-70	1	16	52.40	0.88	13.10	2.39	5.76	0.29	7.91	8.32	3.81	0.02	0.06	3.93	0.26	0.49	99.62	9.11	1.30			0.52					2.51	1004.2
91-1, 66-70	d	17	50.00	0.74	15.30	2.17	6.86	0.20	9.12	12.90	1.64	0.02	0.06	1.24	0.22	0.00	100.47	9.79	0.38			0.10					2.99	1004.2
94-1, 132-135	d	18	49.20	0.96	15.40	2.09	6.75	0.21	8.48	12.00	2.15	0.02	0.07	2.32	0.19	0.67	100.51	10.00	0.51			0.72					2.92	1031.8
95-1, 140-143	1	19	50.70	0.99	14.30	1.91	7.41	0.20	7.86	12.10	2.02	0.02	0.07	2.01	0.23	0.00	99.82	10.10	0.22			0.04					2.91	1040.9
97-1, 82-84	d	20	49.40	0.93	14.70	2.51	7.10	0.21	8.57	12.50	2.29	0.02	0.07	1.80	0.09	0.00	100.19	10.40	0.40			0.11					2.95	1058.3
97-1, 88-90	1	21	46.70	0.88	12.50	2.16	6.15	0.21	9.01	13.30	0.57	0.03	0.06	6.70	0.43	1.53	100.23	10.00	1.16			1.64					2.61	1058.4
99-1, 70-74	1	22	48.40	0.90	13.40	2.36	8.53	0.23	8.41	10.10	2.74	0.02	0.06	4.89	0.12	0.00	100.16	11.80	0.41			0.03					2.69	1072.2
99-2, 42-50	1	23	47.00	0.98	14.50	2.85	10.06	0.25	8.36	7.47	3.46	0.03	0.06	5.07	0.15	0.00	100.24	14.00	0.83			0.01					2.70	1073.5
100-1 83-87	b	24	50 20	0.89	13.20	2 45	8 98	0.22	7 78	7 61	2.95	0.03	0.07	5 73	0.09	0.00	100.20	12.40	1.05			0.06					2.60	1081.4
101-1 134-138	h	25	50.00	0.91	13 90	2 58	7 22	0.21	8 01	10.60	3 30	0.03	0.06	3.09	0.09	0.00	100.09	10 60	0.64			0.05					2.82	1090.9
104-2 57-61	1	26	50.00	0.57	17 10	1 78	5 38	0.14	7 73	12 40	2 57	0.03	0.04	2 27	0.09	0.00	100.10	7 76	0.37	85	54	0.01	304	33	10	14	2.88 ^a	1118.5
104-2, 57-61	d	20	49 10	0.94	16 60	2.96	6 10	0.17	7.75	12.40	2.01	0.03	0.07	1.58	0.10	0.00	100.10	9.84	0.38	96	68	0.07	338	43	64	16	2 93a	1118.6
104-2, 67-72	d	28	49.10	0.94	16.00	2.90	6 30	0.17	9 19	12.70	2.01	0.02	0.06	2 21	0.10	0.00	100.30	0.18	0.38	104	66	0.07	342	37	50	16	2 88a	1118 7
104-2, 07-72	d	20	49.10	0.84	16.30	2.10	6.30	0.10	0.10	12.70	1.00	0.02	0.00	2.21	0.09	0.00	100.17	9.10	0.40	154	66	0.03	414	45	64	15	2.80 2.88a	1118.8
107 1 00 02	u I	29	40.10	0.09	14.90	2.09	6.37	0.17	0.40	12.00	1.00	0.03	0.07	1.42	0.09	0.00	100.30	9.97	0.67	104	72	0.09	202	20	80	15	2.00	1144.4
107-1, 90-92	1	30	30.10	0.88	14.60	2.04	0.43	0.17	0.00	13.10	2.00	0.02	0.07	1.42	0.09	0.00	100.39	9.81	0.55	275	75	0.08	£93 520	57	101	15	2.71	1161.0
111-1, 41-45	a	31	44.70	0.93	17.50	3.43	0.23	0.15	8.80	12.10	1.95	0.03	0.07	3.48	0.13	0.00	99.30	10.30	0.91	107	75	0.03	344	37	76	13	2.70	1171.5
113-1, 47-50	1	32	49.30	0.69	15.70	2.03	0.48	0.16	9.24	12.90	1.85	0.02	0.05	1.75	0.10	0.00	100.27	9.23	0.47	127	12	0.03	344	39	/0	14	2.93	1100.0
117-1, 109-113	1	33	46.10	0.60	15.30	2.87	9.76	0.20	9.25	1.41	2.68	0.03	0.04	5.90	0.14	0.00	100.34	13.70	0.85		00	0.03	242	41	62	10	2.12	1109.0
121-1, 65-69	1	34	49.50	0.76	15.00	1.91	7.41	0.17	8.32	10.90	2.93	0.02	0.06	2.68	0.09	0.00	99.75	10.10	0.39	84	90	0.03	242	41	53	15	2.82	1208.2
123-2, 58-62	d	35	48.40	1.00	14.30	2.75	7.40	0.19	8.46	12.50	2.12	0.02	0.07	2.78	0.15	0.00	100.14	10.90	0.62	86	93	0.05	235	43	55	16	2.84	1224.6
127-1, 109-112	d	36	49.10	0.76	16.10	2.08	6.29	0.15	9.28	13.00	1.69	0.02	0.06	1.49	0.13	0.00	100.15	9.07	0.45	153	67	0.08	384	46	85	15	2.95	1254.6
132-1, 118-122	1	37	49.10	0.73	15.60	1.72	6.87	0.17	9.01	12.30	2.22	0.02	0.05	2.43	0.10	0.00	100.32	9.35	0.35			0.03					2.90	1296.2
133-2, 34-43	1	38	51.00	0.70	14.00	2.31	7.02	0.19	8.39	11.00	2.38	0.02	0.05	3.19	0.09	0.00	100.44	10.10	0.65	40	74	0.04	327	89	21	14	2.75ª	1305.9
133-2, 34-43	d	39	49.90	0.98	14.30	2.13	7.23	0.21	8.48	13.00	2.17	0.02	0.07	1.62	0.10	0.00	100.21	10.10	0.29	43	73	0.01	301	86	103	14	2.93ª	1305.9
134-1, 147-150	1	40	45.80	0.41	14.50	5.09	9.30	0.19	9.96	5.26	2.35	0.03	0.03	7.18	0.14	0.00	100.24	15.40	1.52	77	123	0.01	255	91	8	15	2.70 ^a	1313.2
134-1, 147-150	d	41	50.00	0.93	14.30	2.63	7.44	0.21	8.06	12.50	1.92	0.02	0.07	1.80	0.19	0.00	100.17	10.90	0.29	79	79	0.07	171	79	106	16	2.93 ^a	1313.2
141-1, 67-71	1	42	40.10	1.07	16.00	5.09	14.30	0.16	9.93	3.42	2.78	0.02	0.08	7.43	0.11	0.00	100.49	21.00	1.08			0.06					2.59	1346.2

Note: Major element oxides and S reported as wt.%, trace elements in ppm. Rock types: d = dark gray, l = light gray, b = breccia, g = altered glass. Blanks indicate elements not analyzed. Analysis (Column 2) indicates our laboratory number. ^a Density was not measured on this sample but it was assigned a density value of a sample exhibiting similar alteration and H_2O^+ content.

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Major		BIR-	1		BM		Interlab	. comparison	samples
elements (wt.%)	This study	28	Gladney (1983)	This study	2s	Abbey (1980)	77-1, 44–53 cm	97-2, 74-89 cm	130-2, 44-58 cm
						()			
SiO ₂	47.89	0.30	47.94 ± 1.39	49.69	0.34	49.60	48.96	50.12	49.14
TiO_2	0.95	0.012	0.93 ± 0.05	1.11	0.02	1.14	0.92	0.955	0.7.5
Al ₂ O ₃	15.76	0.10	14.76 ± 0.79	16.22	0.10	16.20	16.35	14.73	16.39
Fe ₂ O ₃ ¹	11.51	0.10	11.06 ± 0.56	9.66	0.10	9.68	9.84	10.56	9.01
MnO	0.18	0.004	0.17 ± 0.03	0.146	0.004	0.145	0.179	0.177	0.151
MgO	9.68	0.10	9.70 ± 0.99	7.49	0.08	7.46	8.27	8.39	9.12
CaO	13.32	0.10	13.02 ± 0.48	6.37	0.08	6.46	12.41	12.73	13.19
Na ₂ O	1.84	0.06	1.62 ± 0.09	4.87	0.10	4.64	2.45	2.00	1.73
K2Õ (XRF)	0.033	0.022	0.017.0.040	0.183	0.004	0 202	0.032	0.017	0.015
K ₂ O (AAS)	0.037	0.002	0.01/-0.040	0.183	0.004	0.203	0.024	0.009	0.008
P205	0.026	0.005	0.030-0.100	0.12	0.006	0.105	0.06	0.07	0.05
Trace	BE-N			BHVO-1		Interlab	comparison	samples	
elements	This		Govindaraju	This		Abbey	77-1	97-2	130-2
(ppm)	study	2s	(1980)	study	2s	(1982)	44–53 cm	74-89 cm	44-58 cm
							83	66	63
r Cr	373	7 1	360			_	301	259	373
Co	64	6.4	61	_		_	43	42	40
Ni	264	3.6	267				126	88	145
Cu	82	3.6	72	_			89	93	84
Zn	123	2.0	120	_		_	65	67	58
Ga	17	1.6	17	_		_	15	16	15
Rh		1.0		9	0.8	10	< 5	<5	< 5
Sr				300	1.6	400	77	67	66
v				. 27	1.0	27	25	27	21
7r				176	1.6	180	61	63	51
Nb	_	_	_	18	0.8	19	<5	< 5	<5

Table 2. Major and trace element data for reference samples and Leg 83 interlaboratory comparison samples.

Note: Analytical errors are given as ±2 standard deviations (2s; i.e., on a 95% confidence level). Dashes indicate elements not analyzed.

Table 3. Mean and standard deviation of least-altered basalt and unaltered glass analyses from Hole 504B.

	Basa	lt ^a	Glass	sb
	Mean	1σ	Mean	1σ
SiO ₂	50.06	0.45	50.66	0.66
TiO ₂	0.94	0.09	0.97	0.07
Al2O3	15.43	0.59	14.96	0.64
Fe2O3	2.98	0.59	1.65 ^c	0.07
FeÕ	6.65	0.67	8.42 ^c	0.36
MnO	0.17	0.02	0.17 ^d	0.02
MgO	8.44	0.38	8.20	0.34
CaO	12.94	0.43	12.78	0.24
Na ₂ O	2.19	0.30	2.00	0.15
K2Õ	0.02	0.01	0.03	0.01
P205	0.07	0.01	0.08	0.01
CÕ2	0.10	.03	0.10 ^d	0.30
Total	99.99		100.02	
Fe ₂ O ₃ ^T	10.37	0.66	11.00	0.47

- ^a Mean and standard deviation of 58 "leastaltered" basalt analyses from the Leg 70 section of Hole 504B (Hubberten et al., 1983). Least-altered analyses were selected based on K₂O contents less than 0.10 wt.% and recalculated water-free. Average does not include "anomalous" high P and Ti units (see text).
- ^b Mean and standard deviation of 51 unaltered glass analyses from Hole 504B, excluding "anomalous" high P and Ti units (see text; Natland et al., 1983). Assuming $Fe^{3+}/Fe^{T} = 0.15$.

Assigned value of average least-altered basalt from (a).

composition, Leg 83 basalts exhibit trends toward losses of SiO₂, CaO, TiO₂; decreases in density (relative to the average least-altered Leg 83 basalt); gains of MnO, Na₂O, CO₂, H₂O⁺, S; slight gains of MgO; increased oxidation of Fe; and variable changes in Al₂O₃.

Rare Earth Elements

Minor differences occur in the rare earth element (REE) patterns of altered samples compared to less-altered samples. The La/Sm enrichment factor generally increases slightly at high H₂O⁺ contents, and the small negative Eu anomaly that is sometimes present disappears with increasing H_2O^+ (Fig. 2A). Similar Eu enrichments of hydrothermally altered submarine basalts have been interpreted to be due to reducing conditions and the presence of secondary albite (Humphris et al., 1978).

The altered glass of Sample 504B-81-1, 83-86 cm, compared to the adjacent crystalline basalt, illustrates the light REE enrichments of the more altered samples (Fig. 2B). Similar light REE enrichment and mobility have been observed in seafloor basalts affected by submarine "weathering" (Ludden and Thompson, 1979) and in "zeolite facies" metabasalts from Iceland and in ophiolites (Humphris et al., 1978; Menzies et al., 1977). In the case of the submarine metabasalt, it was suggested that secondary chlorite may be the source of the La enrichment (Humphris et al., 1978).



Figure 1. Bulk rock chemical analyses of altered basalts versus depth. Oxide data from Table 1 are plotted as wt. %. + = dark gray rock, circles = light gray or green wall-rock alteration zone, triangle = altered glassy pillow rim, x = breccia. Horizontal lines connect adjacent alteration zones from the same hand specimen. Average unaltered glass composition from the pillow section of Hole 504B (Table 3; Natland et al., 1983) is also plotted for comparison (square, and vertical line).

In contrast, either the light gray wall rock alteration zone of Sample 504B-104-2, 57-61 cm has been slightly depleted in total REE compared to the adjacent dark gray host rock or the latter has been enriched (Fig. 2B). This contrast remains a problem since there is apparently no significant difference in alteration mineralogy between these samples and others from Leg 83.

CORRELATION OF CHEMICAL AND MINERALOGICAL CHANGES

The basalts recovered during Leg 83 frequently exhibit multistage alteration histories: Formation of greenschist-facies mineral parageneses was followed by zeolite-facies mineralogies. The chemistry of the bulk rocks



Figure 1. (Continued).

often reflects this complex alteration history. Individual plots of wt. % oxide versus H_2O^+ content frequently exhibit various different trends (Fig. 3), reflecting alteration at differing water/rock ratios, primary substrate control of secondary mineralogy, and superimposed alteration effects. Specific examples are discussed, followed by discussion of the general chemical trends in the hole.

Albitization

Sample 504B-91-1, 66-70 cm is a fine-grained pillow fragment consisting of a dark gray host rock (Table 1,

Analysis 17) and a 1.5-cm-wide light gray alteration zone (Table 1, Analysis 16) adjacent to a quartz vein with a 3mm silicified wall-rock zone. In the light gray zone albite totally replaces plagioclase phenocrysts and extensively replaces microlites, olivine is replaced by chloritesmectite, titanomagnetite is totally replaced by sphene, clinopyroxene phenocrysts are unaltered, groundmass pyroxene is slightly cloudy, and disseminated secondary pyrite is common. In the adjacent dark gray zone plagioclase, clinopyroxene, and titanomagnetite are essentially unaltered, and olivine is replaced by a mixture of chlorite-smectite and talc.



Figure 2. Chondrite-normalized rare earth element (REE) patterns for Leg 83; Hole 504B basalts. A. Variations in REE patterns with wt. % H₂O⁺. B. Altered zones and adjacent less-altered basalts. 1 = light gray wall-rock alteration zone, d = dark gray basalt, g = altered glassy pillow rim.



Figure 3. Bulk-rock chemical analyses of altered basalts plotted as oxide wt. % versus wt. % H₂O⁺. Symbols as in Figure 1. Individual samples discussed in text are labeled with analysis numbers from Table 1.

It can be seen from Figure 3 that the light gray zone is enriched in Si and Na and depleted in Al and Ca relative to the dark gray host rock, reflecting the replacement of plagioclase by albite in the light gray zone. The large range in Al₂O₃ values at H₂O contents below 2.5 wt.% in Figure 2 falls mostly within the range of least-altered basalts from the pillow section of the hole (Hubberten et al., 1983) and probably reflects primary compositional variation to a large degree. Recalculation of Al₂O₃ contents as moles per cubic centimeter decreases the variability and, by eliminating the effects of density variations caused by alteration, supports this suggestion. The trends between adjacent samples connected by lines in Figure 3 are not primary, however: normalization does not remove these differences. The dark gray zone is slightly enriched in Mg and Fe relative to the light gray zone, probably because talc and pyrite are present in the dark gray zone.

Chloritization

Sample 504B-81-1, 83–86 cm consists of a light gray fine-grained pillow rim (Table 1, Analysis 9) and adjacent former glassy pillow crust (Table 1, Analysis 10). The glass is totally replaced by chlorite, and plagioclase phenocrysts in both samples are extensively replaced by albite and minor amounts of Ca-zeolites. In the crystalline rock clinopyroxene phenocrysts have reaction rims of actinolite, and titanomagnetite is replaced by sphene. The former glassy rim is highly enriched in Al, Fe, Mg, and H₂O and depleted in Si and Ca relative to the adjacent crystalline rock (Fig. 3), reflecting the total breakdown of the glass and replacement by chlorite. The bulk glass composition reflects the presence of albite and relict clinopyroxene and plagioclase phenocrysts in addition to the chlorite. The higher Na content of the crystalline pillow rim reflects the albitization of plagioclase microphenocrysts and microlites, which are not present in the altered glassy portion.

Formation of secondary minerals in Leg 83 basalts is strongly controlled by precursor mineralogy, with glass being replaced by clay minerals (Alt et al., this volume). Glass also reacts more readily than crystalline basalt (Seyfried and Bischoff, 1979, 1981). These observations suggest that a crystalline basalt undergoing alteration under the same conditions as the glassy pillow rim would not exhibit the same alteration products or bulk composition. A similar substrate control of secondary mineralogy was described in submarine basalts from the Carlsberg Ridge where glassy pillow rims were replaced by chlorite, and crystalline pillow interiors were replaced by actinolite, chlorite, albite, and sphene (termed hyalospilite and orthospilite, respectively; Cann, 1969). This variation was interpreted to result from differing nucleation effects of the various substrates (Cann, 1969). From experimental data, this same sort of variation was interpreted to result from varying water/rock ratios by Seyfried et al. (1978); the glassy pillow rim was interpreted to have been altered at a higher water/rock ratio than the crystalline pillow interior. However, the latter interpretation does not take into account the kinetic effects: glass alters more readily than crystalline basalt at these temperatures (70–300°C; Seyfried and Bischoff, 1979, 1981). Thus, although a high water/rock ratio is required to account for the large MgO increase in the altered glass, the complete alteration of the glass to chlorite probably reflects the effects of both water/rock ratio and substrate control of secondary mineralogy.

In the case of identical substrates (i.e., crystalline basalt), variations in the water/rock ratio should lead to differences in mineral assemblages and bulk chemistry. Both theoretical and experimental evidence indicate that chlorite and quartz should be more abundant at higher water/rock ratios, whereas albite should be more common at lower ratios (Mottl, 1983; Reed, 1983). Such effects ae often present adjacent to veins in Leg 83 basalts where narrow (hundreds of microns) wall-rock zones are totally recrystallized to chlorite and quartz, whereas farther from the vein the rock is less extensively altered and contains albite and chlorite, lacking quartz. Similar effects can be observed on a slightly larger scale, where the centimeter-sized light gray alteration zones around clay mineral veins are more extensively recrystallized than adjacent dark gray host rocks. Variations in the water/rock ratio probably caused these differences in extent of recrystallization, as well as in mineral assemblages, contributing to the scatter of trends in Figure 3.

Zeolitization

Sample 504B-97-1, 88-90 cm (Table 1, Analysis 21) consists of a light gray friable dike rock and is characterized by total replacement of plagioclase by laumontite. Olivine is replaced by chlorite with minor expandable layers, titanomagnetite is replaced by sphene, clinopyroxene is slightly cloudy, and disseminated secondary pyrite is common. The adjacent dark gray host rock (Table 1, Analysis 20) is much less extensively altered. Plagioclase is only partly replaced by albite, chlorite, and minor prehnite and laumontite. Olivine is replaced by chlorite with minor expandable layers, titanomagnetite is partly replaced by sphene, clinopyroxene is slightly cloudy, and secondary pyrite is much less abundant than in the adjacent light gray zone.

The zeolite-rich light gray zone is enriched in Ca and H_2O and depleted in Si, Al, and Na relative to the adjacent dark gray host rock (Fig. 3), reflecting the total replacement of plagioclase by laumontite in the light gray rock. The slight variation in Fe and Mg contents may reflect differences in clay mineral abundances between the two zones.

The chemical changes associated with zeolite formation in Leg 83 basalts are different from those of dredged "zeolite facies" metabasalts from the seafloor, which exhibit increased Na₂O and H₂O contents (Miyashiro et al., 1971; Shido et al., 1974). The Na-enriched basalts contain zeolite assemblages characterized by Na-zeolites (mostly analcite; Miyashiro et al., 1971), which are restricted to the lower zeolite facies (Coombs, 1971) and have been observed in drilled submarine basalts altered at relatively low temperatures (i.e., less than 100°C; Alt, 1982). Thus, the Ca and H₂O⁺ enrichments and Si, Al, and Na depletions characteristic of Ca-zeolite formation in Leg 83 basalts probably represent higher-temperature effects than the Na-enrichments observed in other seafloor basalts interpreted to have been metamorphosed under "zeolite-facies" conditions.

The formation of zeolites postdates that of greenschist-facies mineralogies in Leg 83 basalts, and both parageneses occur in the same samples. This suggests that many altered basalts from Leg 83 must have undergone, first, albitization of plagioclase and loss of Ca and gain of Na, followed by zeolitization of the remaining plagioclase with concomitant gain of Ca and loss of Na. The resultant bulk rocks thus may often reflect the combined effects of both alteration stages.

Variation in Composition with Depth

Variation in composition of basalts with depth (Fig. 1) can be correlated with mineralogical changes. Bulkrock H₂O⁺ contents increase from an average of about 1 wt. % in the overlying pillow section (Emmermann, this volume) to greater than 2 wt. % below 836 m. where clay minerals become more chloritic and sphene appears. Greenschist-facies mineral parageneses first appear at 898 m and are present to the bottom of the hole (Alt et al., this volume). Below about 900 m the breakdown of plagioclase results in the lower CaO contents and some of the variability in Al₂O₃. The greater H₂O contents below about 900 m reflect the greater extent of alteration of basalts containing greenschistfacies parageneses. The decrease in dry bulk density of all altered samples relative to the average least-altered basalt (2.9 g/cm³; Fig. 1; Hole 504B summary chapter) indicates a net loss of material from the bulk rocks during alteration.

MnO and S are enriched in the transition zone below about 900 m and reach a maximum around 910–930 m (Fig. 1). Bulk CO_2 contents exhibit similar enrichment, although no clear maximum occurs and high CO_2 contents also occur at shallower depths. Bulk-rock sulfur distribution reflects the abundance of secondary sulfides, mainly pyrite, which is more common in the transition zone than in the underlying dikes and reaches maximum abundance in the sulfide-rich stockwork zone at 910–928 m (Alt et al., this volume; Honnorez et al., this volume).

The high MnO contents of the transition zone rocks are due in part to the presence of Mn-rich clay minerals in the rocks. Clay mineral MnO contents versus depth follow the bulk rock MnO contents exactly (Fig. 1; Alt et al., this volume). Calcites enriched in Mn have been identified from 910 to 946 m, and there is a general trend toward increasing MnO with CO_2 in bulk rocks (Fig. 4A), indicating that Mn-rich calcite may also contribute to the higher bulk-rock MnO contents in the transition zone.

Bulk-rock CO_2 contents reflect the distribution of calcite in the hole: calcite is abundant in the stockwork zone (910–928 m), relatively common in the transition zone, but extremely rare in the dike section (Alt et al., this volume).

The bulk rock Mn and S enrichments in the transition zone and the presence of Fe, Cu, Zn, and Pb sulfides in stockwork-like veins near the top of the transition zone (Honnorez et al., this volume) suggest that the transition zone section penetrated by Hole 504B was once within or near a hydrothermal upflow zone. Such metal enrichments and sulfide deposits would be expected to occur where hot metal- and sulfur-rich hydrothermal fluids passed through the crust. The Mn and S enrichments in the transition zone basalts indicate that these rocks were not the source rocks for the mineralizing fluids depositing the sulfides in the stockwork-like zone. Cu and Zn contents of the basalts from the underlying dike section are similar to unaltered basalts (Table 1; Cann, 1981), indicating that these rocks were also probably not the source of the mineralizing fluids. Variations in the Cu and Zn contents of the dike rocks suggest that some mobilization of these elements did occur, however.

Several samples are enriched in total iron relative to the fresh glass composition, whereas most samples exhibit lower total iron concentrations (Fig. 4B). The samples enriched in total iron are also clay-rich, and all except one (Table 1, Analysis 33) are from intervals in the



Figure 4. Bulk rock analyses of altered basalts. Symbols as in Figure 1. A and B plotted as oxide wt. %, C plotted as fluxes in moles oxide/100 cm³ basalt (from Table 4, see text).

hole where clay minerals are enriched in iron (965–1070 m and 1300 m; Alt et al., this volume), suggesting that the presence of Fe-rich clay minerals are responsible for the observed iron enrichments. No correlation exists between total iron and sulfur contents, indicating that the presence of pyrite is not responsible for iron enrichment of the rocks. However, sulfur-rich rocks do tend to have lower ferric iron contents than sulfur-poor rocks. The range of total iron content of the remainder of the samples falls within that of "least altered" pillow basalts from the hole (Hubberten et al., 1983).

The general trend toward higher Fe_2O_3 content with higher total iron (Fig 4B), especially in clay-rich samples, suggests that ferric iron in clay minerals is responsible. However, Sample 504B-76-1, 65-68 cm (Table 1, Analysis 2) contains secondary hematite overgrowths on primary titanomagnetite that may account for the high Fe_2O_3 content of this sample.

Several samples of light gray and green alteration halos from below 1118 m have lost large amounts of TiO_2 relative to adjacent host rocks (Table I, Analyses 26, 32, 33, 37, 38 and 40; Fig. 1). Titanomagnetite is only slightly altered to sphene in the dark gray host rock, but is almost totally replaced by sphene in the light gray zones. Thus breakdown of titanomagnetite has led to loss of Ti, but it is uncertain where the Ti was deposited, perhaps as sphene in nearby veins or in the adjacent host rock.

The sample from the bottom of the drilled dike section (Table 1, Analysis 42) is enriched in total iron and H_2O^+ , and depleted in Si and Ca relative to most of the dike samples (Fig. 1 and 3). This sample is from a zone at the bottom of the dike section (1340–1350 m) where the basalts are highly fractured and extensively recrystallized, in contrast to the generally small extent of fracturing and recrystallization observed in the central part of the dike section. The lowermost 10 m of the dike section may have been a zone of higher primary permeability allowing circulation of greater amounts of fluid and facilitating more extensive reaction of the basalts.

WATER/ROCK RATIOS AND CHEMICAL FLUXES

Chemical fluxes were calculated as g oxide/100 cm³ basalt relative to the average unaltered glass composition from the pillow section of the hole and assuming constant volume alteration. This assumption appears justified since the basalts are generally only partly recrystallized and have recognizable igneous texture. Dry bulk densities calculated from shipboard wet-bulk density and porosity measurements made on least-altered Leg 83 samples average 2.9 g/cm³, with a standard deviation of 3% and a maximum range of 5% (Hole 504B summary chapter). This average value is identical to that for the pillow section of the core (excluding two lowdensity breccia samples; Karato, 1983). The value of 2.9 g/cm³ was chosen for the average unaltered basalt density, and altered rock densities were taken from Table 1 for the flux calculations. Calculated gains and losses are given along with errors in Table 4.

Comparison with Dredged Rocks

Humphris and Thompson (1978) normalized bulkrock data to constant A1 to calculate chemical changes. Since Al was mobile during the alteration of Leg 83 basalts, normalization to Al was not reasonable for the data in Table 1. To make a more direct comparison, the data from Humphris and Thompson (1978) were recalculated in the same way as the Leg 83 data in Table 4. The recalculated fluxes are generally similar to those based on Al normalization, but exhibit greater Si losses. With the exception of the altered glass sample (Tables 1 and 4, Analysis 10) MgO gains for Leg 83 basalts are generally much less than those reported for the dredged basalts (Fig. 5). The MgO fluxes for Leg 83 basalts center around zero, with about one third of the values being negative. More than half of the analyses have MgO gains within $\pm 2 \text{ g}/100 \text{ cm}^3$ of zero, which can be attributed to primary compositional variability if one assumes that the range in composition of the least-altered basalts from the pillow section of the hole (Hubberten et al., 1983; Honnorez et al., 1983) reflects primary compositional variation. Losses of CaO are generally smaller and Na₂O more consistently gained in Leg 83 basalts than in the dredged rocks, whereas SiO₂ losses are generally similar in the two groups. The net negative changes in Table 4 are due to the decrease in density and net loss of material from altered samples.

Part of the differences in chemical changes between the dredged and drilled rocks may arise because of the multiple alteration effects observed in Leg 83 basalts. Superimposition of zeolitization of plagioclase on rocks in which plagioclase had been previously partly albitized could have resulted in addition of Ca and loss of Na from rocks that had previously lost Ca and gained Na. Another difference results from the alteration of the Hole 504B transition zone basalts in a hydrothermal upflow zone: Mn and S are consistently enriched in these basalts, but not in the dredged rocks.

The dredged basalts that were studied by Humphris and Thompson (1978) also were extensively recrystallized (mostly greater than 90%) and contain abundant chlorite, whereas the Leg 83 samples are only locally more than about 50% recrystallized (e.g., in narrow wall-rock alteration zones along veins and at the bottom of the dike section). Dredged samples of hydrothermally altered submarine basalts are obtained from tectonically exposed areas such as fracture zones and faults. Such fractures, if they existed at the time of alteration of the rocks, could have served as conduits for fluid circulation causing alteration at high water/rock ratios and resulting in the extensive recrystallization often observed in dredged samples.

Pillow basalts apparently composed all the samples studied by Humphris and Thompson (1978), whereas the Leg 83 samples consist of both pillows and dikes. Of the 462 m of basalts containing greenschist-facies parageneses penetrated by Hole 504B, only about 100 m consist of pillow basalts, and these are restricted to the transition zone. This suggests that if the Hole 504B sec-

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	Table 4. Chemic	al fluxes	in	grams	per	100	cm ³	basalt,	Hole	504B
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Core-Section (interval in cm)	Rock type	Analysis	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	н ₂ 0+	CO2	Fe ₂ O ₃ ^T	sa
72-2, 126-129	d	1	-9.22	-0.42	1.58	3.39	-9.08	-0.04	0.32	-0.53	-0.49	-0.03	-0.06	5.28	1.09	-6.67	-0.06
76-1, 65-68	d	2	-9.17	-0.20	3.19	5.95	-9.42	-0.01	-1.41	-0.99	-0.01	-0.03	-0.06	6.70	0.45	-4.49	0.14
78-1, 102-106	b	3	-11.01	-0.29	- 3.93	-0.13	-8.01	0.03	5.19	-8.57	2.45	-0.00	-0.04	6.60	0.18	- 6.09	4.51
79-2, 62-66	1	4	- 10.69	-0.28	0.54	2.36	-9.52	-0.08	1.53	- 3.42	0.20	-0.03	-0.07	7.39	0.24	-8.19	0.11
79-3, 147-149	1	5	- 14.19	-0.27	1.14	-0.22	-10.08	0.12	-0.68	-3.74	1.12	-0.03	-0.06	6.10	0.35	-4.46	10.98
80-1, 33-37	1	6	- 21.99	-0.58	1.06	-1.10	-10.01	0.37	-2.33	-6.55	0.59	-0.03	-0.10	8.26	0.03	-8.34	6.06
80-2, 63-67	1	7	- 30.31	-0.60	-1.32	-0.78	-11.82	0.32	-6.28	-12.46	1.70	-0.04	-0.08	9.77	0.20	-7.35	10.37
80-3, 124-133	1	8	-18.01	-0.56	2.44	0.55	-10.46	0.23	-4.12	-2.22	0.69	-0.03	-0.10	6.06	0.22	- 8.64	3.71
81-1, 83-86	1	9	-12.38	-0.35	- 5.06	0.74	- 8.66	0.34	0.49	-7.85	2.62	-0.01	-0.10	7.77	0.49	-6.87	3.12
81-1, 83-86	g.	10	- 57.31	-0.28	1.80	5.33	2.21	0.59	13.79	- 28.98	-1.83	-0.01	-0.06	23.90	0.61	7.76	-0.07
82-1, 68-73	1	11	-4.13	-0.21	1.58	0.38	- 5.53	0.18	0.53	-0.85	-0.49	-0.03	-0.03	5.46	0.41	- 3.87	2.88
82-1, 68-73	d	12	- 2.96	-0.13	1.58	1.90	-4.39	0.24	0.58	-0.85	-0.92	-0.03	-0.06	5.87	0.35	-2.96	0.12
82-1, 90-96	1	13	- 15.78	-0.18	-4.81	-0.74	-12.10	0.49	-1.73	-13.84	4.63	0.02	- 0.07	8.54	0.99	-4.24	16.16
84-2, 48-50	1.	14	- 16.10	-0.30	-8.82	-0.13	-9.65	0.20	-1.32	-15.97	1.16	-0.04	-0.05	13.57	0.35	-7.50	• 5.22
87-1, 116-123	1	15	-7.06	-0.01	-1.34	0.94	- 2.94	0.37	0.76	-1.03	0.58	-0.03	- 0.03	6.81	0.28	-2.44	-0.03
91-1, 66-70	1	16	-15.39	-0.60	-10.50	1.21	- 9.96	0.23	-0.16	-16.18	3.76	-0.04	-0.08	9.86	0.36	-9.03	1.16
91-1, 66-70	. d	17	2.59	-0.60	2.36	1.70	- 3.91	0.10	2.59	1.51	-0.90	-0.03	-0.05	3.71	0.37	-2.63	0.15
94-1, 132-135	d	18	- 3.25	-0.01	1.58	1.32	-4.71	0.12	1.46	-2.02	0.48	-0.03	-0.03	6.77	0.26	-2.70	1.95
95-1, 140-143	1	19	0.62	0.07	-1.77	0.77	-2.85	0.09	-0.83	-1.85	0.08	-0.03	-0.03	5.85	0.38	-2.51	-0.03
97-1, 82-84	d	20	-1.18	-0.07	-0.02	2.62	- 3.47	0.13	2.46	-0.19	0.96	-0.03	-0.03	5.31	-0.02	-1.22	0.18
97-1, 88-90	1	21	- 25.03	-0.52	- 10.76	0.85	-8.37	0.06	-4.58	-2.35	-4.31	-0.01	-0.08	17.49	0.83	- 5.80	4.12
99-1, 70-74	1	22	- 16.72	-0.39	-7.34	1.56	-1.47	0.13	0.41	-9.89	1.57	-0.03	-0.07	13.15	0.03	-0.16	-0.06
99-2, 42-50	1	23	-20.01	-0.17	-4.23	2.91	2.74	0.18	2.33	- 16.89	3.54	-0.01	-0.07	13.69	0.11	5.90	-0.12
100-1, 83-87	b	24	- 16.39	-0.50	-9.06	1.58	-1.07	0.08	-1.68	-17.28	1.87	-0.01	-0.05	14.90	-0.06	0.34	0.01
101-1, 134–138	b	25	- 5.91	-0.25	-4.19	2.49	-4.06	0.10	2.57	-7.17	3.76	-0.00	-0.06	8.71	-0.04	-2.01	-0.00
104-2, 57-61	1	26	- 2.91	-1.17	5.86	0.34	- 8.92	-0.09	0.08	-1.35	1.60	0.00	-0.12	6.54	-0.03	-9.55	-0.12
104-2, 61-65	d	27	- 3.05	-0.06	5.25	3.89	-6.28	0.01	-1.07	0.74	0.09	-0.03	-0.03	4.63	0.00	-3.07	0.06
104-2, 67-72	d	28	- 5.51	-0.39	3.56	1.49	-6.27	-0.03	-0.18	-0.49	0.05	-0.03	-0.06	6.36	-0.03	- 5.46	-0.06
104-2, 79-82	d	29	- 8.39	-0.25	3.85	3.54	- 6.07	-0.00	0.26	-0.20	-0.39	0.00	-0.03	6.36	-0.03	- 3.19	0.11
107-1, 90-92	1	30	-1.12	-0.25	-0.32	2.90	- 5.65	0.00	1.41	1.06	0.02	-0.03	-0.03	4.13	-0.03	- 3.35	0.09
111-1, 41-45	a	31	- 26.22	-0.30	3.87	4.48	-7.60	-0.09	-0.56	-4.39	-0.54	-0.01	-0.04	9.40	0.06	- 4.09	-0.06
113-1, 47-50	1	32	- 2.47	-0.79	2.62	1.16	- 5.43	-0.02	2.91	0.74	-0.38	-0.03	-0.09	5.13	0.00	-4.80	0.00
117-1, 109-113	1	33	- 21.52	-1.18	-1.//	3.02	2.13	0.05	-2.8/	- 16.74	1.49	-0.01	-0.12	10.05	0.09	3.30	-0.00
121-1, 05-09	1	34	- 7.32	-0.6/	-1.08	0.60	- 3.52	-0.01	2.14	- 6.32	2.40	-0.03	-0.00	7.00	-0.04	- 3.42	-0.00
123-2, 58-62	D I	35	- 9.40	0.03	-2.77	3.02	- 3.40	0.05	0.4/	-1.50	0.22	-0.03	-0.03	1.90	0.14	-0.94	-0.00
127-1, 109-112	1	30	- 2.07	-0.57	4.11	1.35	- 5.80	-0.05	2.78	1.29	-0.81	-0.03	-0.03	4.40	0.09	- 3.14	0.09
132-1, 110-122	1	3/	-4.52	-0.70	1.80	0.20	- 4.49	0.00	2.99	- 1.39	0.04	-0.03	-0.09	0.05	0.00	-4.78	-0.00
133-2, 34-43	d	30	- 0.00	-0.89	-4.88	1.3/	- 5.11	0.03	0.04	-0.81	0.74	-0.03	- 0.09	0.77	-0.04	- 4.12	-0.12
133-2, 34-43	u I	39	-0.71	1 71	- 1.49	1.40	- 3.23	0.12	1.02	1.03	0.50	- 0.03	-0.03	4.75	0.00	0.69	-0.12
134-1, 147-150	d	40	- 23.25	-1./1	-4.23	8.90	0.69	0.02	3.00	· - 22.80	0.54	-0.01	-0.13	5 27	0.09	0.04	0.04
141 1 67 71	1	41	-0.41	-0.09	- 1.49	2.92	- 2.02	0.12	-0.34	-0.44	-0.17	-0.03	-0.03	10.24	0.27	22.40	0.00
141-1, 0/-/1	1	42	- 43.00	-0.04	- 1.94	8.40	12.02	-0.08	3.34	- 28.20	1.40	-0.04	-0.02	19.24	-0.01	22.47	0.01

Note: See text for methods of calculation and discussion. Errors calculated from data in Tables 1-3 are given as ± g/100 cm³ basalt at the 95% confidence level: SiO₂: 10.96, TiO₂: 0.53, Al₂O₃: 5.76, Fe₂O₃: 0.42, Fe₀: 0.89, MnO: 0.41, MgO: 3.06, CaO: 3.17, Na₂O: 1.12, K₂O: 0.03, P₂O₅: 0.16, Fe₂O₃T: 4.18. Not determined for H₂O⁺, CO₂, or S. ^a S fluxes calculated assuming 500 ppm S in unaltered basalt.





tion is representative of the upper oceanic crust, then the volume of pillow basalts altered under greenschist facies conditions is very small.

The crust of Site 504 was buried by sediment relatively rapidly (Anderson et al., 1982). However, this rapid burial did not necessarily influence the hydrothermal alteration of Leg 83 basalts, since the high alteration temperatures indicate that the metamorphism occurred relatively close to the spreading axis (see discussions in Alt et al., this volume; Honnorez et al., this volume). Greenschist-facies parageneses may have formed near the surface of the crust close to the axis of spreading with no sediments present, followed by burial by basalt pillows and flows and eventually sediments as the crust moved away from the axis.

On the other hand, the metamorphism may have occurred slightly further off-axis (but not more than a few km) under the existing 571 m of pillows and flows and some sediment cover. In this case it is possible that the basalt and sediment cover may have restricted fluid circulation in the deeper parts of the hole and resulted in alteration at lower water/rock ratios. However, the recovery of highly fractured and extensively recrystallized basalts from the bottom of the dike section suggests that water/rock ratios and extent of alteration were controlled more by local permeability variations in the crust than by sediment burial.

A plot of Δ CaO versus Δ MgO (Fig. 4C) shows that Leg 83 basalts generally have not exchanged Mg for Ca on a 1:1 molar basis as seen in dredged rocks and in experimental basalt-seawater reactions at high water/rock ratios (Humphris and Thompson, 1978; summary in Mottl, 1983). Most Leg 83 basalts have gained Na (Fig. 1 and 3, Table 4), suggesting that Na uptake may account for much of the Ca loss in excess of the Mg uptake shown in Figure 4C. However, on a plot of ΔCaO versus $\Delta MgO + Na_2O$ (moles/100 cm³ basalt; not shown) it is seen that although samples that have lost large amounts of CaO lie further to the right than in Figure 4C, they still fall well below the 1:1 exchange line. This is most likely due to the decreased densities and net loss of material from many samples.

Water/Rock Ratios

In basalt-seawater reactions the water/rock ratio is simply defined as the mass of water relative to the mass of basalt initially present. Experiments indicate that Na is taken up by the basalt at water/rock mass ratios less than about 10, whereas it is leached from the rocks at higher ratios (summary in Mottl, 1983). Based on this observation, the general Na-enrichments of Leg 83 basalts would suggest alteration at water/rock mass ratios (as defined previously) less than about 10. However, water/rock mass ratios calculated on the assumption that all Mg was extracted from unaltered seawater (1280 ppm Mg) that reacted with rocks of density 2.90 g/cm³ to produce the Mg fluxes and densities in Tables 4 and 1, respectively, range up to a maximum value of 22 for the altered glassy pillow rim (Analysis 10). All other values are less than 9, and most fall in the range from -3 to +5, averaging +1.38. Actual water/rock ratios were certainly greater than were calculated using Mg uptake, since the hydrated nature of the rocks prohibits negative values, and alteration is interpreted to have occurred by reaction of basalts with at least partly Mg-depleted solutions (Alt et al., this volume). These examples point out some of the difficulties associated with calculating water/rock ratios for natural systems.

Crustal Fluxes

It is not the purpose of this discussion to quantitatively characterize bulk crustal chemical changes arising from hydrothermal alteration, but, rather, to comment on the significance of Leg 83 samples. Humphris and Thompson (1978) calculated seawater-crustal fluxes arising from hydrothermal alteration of the crust using as variables Mg uptake of basalt and volume of rock altered. From an assumed average uptake rate of 5 g MgO/100 cm³ basalt and a depth of hydrothermal penetration of 2-5 km, it was calculated that 50-20% of the available crust must be altered to account for the excess river Mg input to the oceans. If it is assumed that Hole 504B samples are representative of the upper oceanic crust (i.e., only a small volume of pillow basalts contain greenschist-facies parageneses), then sample sets consisting only of altered pillow basalts are biased. Also, rocks dredged from fault scarps may have been altered at high water/rock ratios localized along fractures in the crust. The MgO gains for Leg 83 basalts average +0.8g/100 cm³. If we use an uptake value of 1 g MgO/100 cm³ basalt and otherwise make the same assumptions as in the previous calculation, we arrive at an unrealistic estimate of the amount of crust that must be altered to account for the excess river Mg flux (250-100% of the available crust). Based on submarine hot spring chemistry and heat flow data, Mottl (1983) suggested that Mg

uptake by the oceanic crust in high temperature submarine hydrothermal systems may not be an adequate sink for solving the Mg mass balance in the oceans.

The gains and losses in Table 4 do not take into account the redistribution of material lost from the basalts and the uptake of seawater components into vein minerals, which can have a significant effect on net crustal fluxes (Staudigel and Hart, 1983; Alt, 1982). The abundant Ca-rich zeolites occurring in veins indicate that much of the Ca lost by the basalts is retained in the crust as vein minerals. By the same token, much of the silica released by the basalts must be retained in the crust in the frequent quartz veins observed in the transition zone, and Mg uptake should also be increased by taking into account the abundant Mg-rich clay minerals in veins and breccias.

Since recovery of basalts on Leg 83 averaged only about 15%, it is possible that the rocks recovered from the hole are not representative of the crust and that more extensively altered portions were not recovered. Also, the distribution of alteration minerals and extent of alteration in the Leg 83 basalts is heterogeneous on a scale ranging from centimeters to tens or hundreds of meters. Localized zones of highly fractured and extensively altered basalt such as those recovered from the bottom of the drilled dike section also have been observed in ophiolites (e.g., Elthon, 1981; Rosencrantz, 1983). This sort of heterogeneity, if it is typical of altered oceanic crust, should have a significant effect on calculation of crustal chemical fluxes from whole-rock data.

CONCLUSIONS

Alteration of Leg 83 basalts is characterized by nonequilibrium and is heterogeneous on a scale of centimeters to tens or hundreds of meters. The basalts exhibit trends towards losses of SiO2, CaO, TiO2; decreases in density; gains of MnO, Na₂O, CO₂, H₂O⁺, S; slight gains of MgO; increased oxidation of Fe; and variable changes in Al₂O₃. Some mobility of rare earth elements (REE) also occurred, especially the light REE and Eu. The basalts have lost Ca in excess of Mg + Na gains. Variations in chemical trends are due to differing water/rock ratios, substrate control of secondary mineralogy, and superimposition of greenschist- and zeolitefacies mineralogies. Zeolitization resulted in uptake of Ca and H₂O and losses of Si, Al, and Na. These effects are different from the Na uptake observed in other altered basalts from the seafloor attributed to the zeolite facies and are probably due to higher temperatures of alteration of Leg 83 basalts.

Basalts from the transition zone are enriched in Mn, S, and CO_2 relative to the pillow and dike sections, and contain a metal-sulfide-rich stockwork zone, suggesting that they were at one time located within or near a hydrothermal upflow zone. Samples from the bottom of the dike section are extensively fractured and recrystal-lized indicating that alteration was significantly affected by local variations in permeability.

Calculation of crustal fluxes from bulk-rock chemical data is complicated by the heterogeneity of alteration effects. Individual bulk-rock MgO fluxes are smaller than those from dredged basalts. If we take into account vein minerals, we may significantly increase the estimates of Mg uptake by the crust and retain much of the Ca and Si lost by the basalts.

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