65. MINERALOGY AND CHEMISTRY OF SECONDARY PHASES IN SOME BASALTIC ROCKS FROM DSDP LEG 37

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INTRODUCTION

Secondary minerals in basalts and basaltic breccias from Holes 332A, 332B, 333A, and Site 335 from DSDP Leg 37 provide information about the alteration of the volcanic layer of the oceanic crust. Previous work has stressed changes in bulk rock composition resulting from seawater-rock alteration (e.g., Hart et al., 1974); however, with a few exceptions (e.g., Bass et al., 1973; Bass, 1976), detailed studies of the mineralogical evidence for these changes have not been undertaken. A clear understanding of the alteration processes, and by implication the nature of the geochemical balance between seawater and the oceanic crust (e.g., Hart, 1970; Muehlenbachs and Clayton, 1976) depends on the mineralogical evidence.

METHODS

Standard petrographic and X-ray diffraction methods were used for identification purposes. Quantitative chemical analyses were obtained using an ARL EMX microprobe fitted with an Ortec energy-dispersive spectrometer. Methods used for background shaping and scaling, overlap corrections, and adjustment for instrumental drift have been described by Smith (1975), Smith et al. (1975), and Smith and Gold (1976). Normal operating conditions were 15-kV operating voltage, 30-nA probe current, and 400-sec counting times. The limit of detection using the above methods is ~500 ppm, and accuracies for major and minor elements are comparable to wavelength dispersive analysis. Strontium, which is masked by the Si K peak in the energy-dispersive spectrum, was checked by wavelength dispersive methods.

Because of sodium mobility, special methods were used for the analysis of zeolites. A beam current of 20 nA, counting times of 100 sec, and a moving sample technique were used to avoid sample damage. In addition, to ensure homogeneous areas for analysis, X-ray scanning photographs were taken of each zeolite analyzed for the three major charge-balancing cations, Na, K, and Ca.

RESULTS

Table 1 summarizes the results of petrographic, X-ray, and microprobe analyses. Samples (10-50 g) were selected for their high degree of alteration. They are basalts and basaltic breccias which have undergone varying degrees of alteration estimated to be between 10%-75%. Secondary phases include carbonates, zeolites, clays, palagonite, and hydrated Fe-oxides.

Glass and Palagonite

Fresh glass fragments with palagonite rims occur in all holes (Table 1 and Plate 1, Figure 1). In some cases the glass has been completely altered, the palagonite exhibiting concentric bands of birefringent, cryptocrystalline material. X-ray powder diffraction patterns of this material, however, are poorly resolved and give no clear identification of the mineralogy.

Representative analyses of glass and palagonite are given in Table 2. Fresh glass is tholeiitic in composition and similar to average Atlantic Ridge tholeiite (Melson and Thompson, 1971). Alteration of fresh glass to palagonite involves the addition of H_2O, K_2O, and total Fe, and the loss of SiO_2, Al_2O_3, CaO, MgO, and Na_2O. Since there is no textural evidence of expansion or contraction during palagonitization, these gains and losses are calculated on the assumption that alteration takes place at constant volume (see also Hay and Iijima, 1968; Muehlenbachs and Clayton, 1972).

Carbonates

The carbonate is usually calcite and occurs in veins, cavities, or vesicles. Calcites contain ~5 mol% $MgCO_3$ and only traces of $FeCO_3$ and $MnCO_3$. One sample (332B-28-1, 67-70 cm) contains both calcite and siderite. The latter is present as a vesicle lining in the form of encrustations exhibiting radial structure in two generations (Plate 1, Figure 2). The $CaCO_3$ content of the siderite (~15 mol%) is surprisingly high, suggesting formation at temperatures in excess of 400°C (Rosenberg, 1967) during cooling of the lava pile.

Zeolites

Zeolites occur in some samples as infilling between breccia fragments, while in others they are confined to small veins, cavities, or vesicles. The habit ranges from granular or blocky to prismatic. Where prismatic crystals are abundant, they commonly form radiating clusters with individual crystals up to 0.5 mm in length (Plate 1, Figures 3 and 4).

Based upon X-ray identification, with confirmation by microprobe analysis, phillipsite is present in all four holes (Table 1). Representative microprobe analyses are given in Table 3. Based on 72 oxygens, ideally Si + Al should be close to 36 and the sum of 2Ca + Na + K should equal Al (see also discussion by Steele et al., 1975). Since these phillipsites are somewhat deficient in Al and Ca and are enriched in Si and alkalis, departures from the ideal composition are attributed to replacements of the type CaAl $\rightleftharpoons$ (Na,K)Si. These deviations from ideality are not surprising, since a wide range of Si:Al ratios and concentrations of Ca, Na, and

TABLE 1
Summary of Secondary Minerals Identified in DSDP Leg 37 Basalts

Sample (Interval in cm)	Lab. No.	Sample Type	Palagonite	Fresh Glass	Hydrated Fe-Oxides	Clays	Zeolites	Carbonates
Hole 332A								
12-2,20-22 (12)	190	B	x			x		x
26-2,10-12 (2)	191	GFCM	x	x			x	x
30-1,22-24	192	VPB	x				x	x
31-3,20-22 (1C)	193	VBB				x	x	x
40-3,106-109 (8B)	194	PB					x	x
Hole 332B								
3-1~108 (8A)	195	PB				x		
21-1,55-59 (3)	196	PB				x	x	x
21-1,55-59 (3)	197	BB	x	x	x			
28-1,8-10	198	VB				x	x	x
28-1,67-70 (7)	199	VB				x		x
36-5,5-7 (1)	200	GFCM	x	x			x	x
36-5,5-7 (1)	201	PB			x		x	
44-5,16-18 (2A)	202	PB					x	
44-6,40-42	203	VB						
45-1,132-134 (13)	204	BB	x	x			x	
Hole 333A								
3-1~69 (7B)	205	PB				x		x
5-2~17 (3)	206	BB	x	x		x		x
5-2~17 (3)	207	BB	x	x				
6-1~94 (12)	208	BB			x			
6-1,140-143 (18)	209	BB			x			x
7-1~100 (14)	210	BB				x		
8-1~123 (15)	211	B	x	x		x	x	x
8-4~106 (11)	212	VBB			x	x	x	
8-7~74 (7)	213	BB					x	x
9-1~90 (11A)	214	BB	x	x	x		x	x
10-1~13 (2)	215	B				x		
Site 335								
6-6,22-24 (2)	220	GFCM	x	x			x	x

Note: B = Basalt; BB = Basaltic breccia; GF = Glass fragments; P = Abundant phenocrysts; V = Abundant vesicles; CM = Calcareous matrix (sedimentary).

TABLE 2
Representative Microprobe Analyses of Glass and Palagonite

	a	b	c	d	e	f	g	h
Hole	332A	332B	333A	335	332A	332B	333A	335
Lab No.	191	197	207	220	191E4	197A	207A4	220A2
SiO_2	49.0	48.9	50.0	49.3	44.4	35.9	45.3	42.6
TiO_2	1.4	0.8	1.5	1.2	2.9	1.4	2.0	2.2
Al_2O_3	13.8	15.9	14.2	15.5	9.4	12.5	11.7	12.1
FeO^*	10.1	8.8	11.2	9.4	19.0	16.5	17.0	17.0
MnO	0.2	0.2	0.1	0.1	–	–	–	–
MgO	7.3	9.1	5.9	10.1	4.1	3.0	3.8	4.9
CaO	11.6	12.4	11.5	11.7	1.1	1.1	2.6	1.1
Na_2O	1.9	1.8	2.5	2.5	0.2	0.5	0.5	1.9
K_2O	0.2	–	0.2	0.2	3.3	1.9	2.7	3.0
Total	95.5	97.9	97.1	100.0	84.4	72.8	85.6	84.8

Note: Refer to Table 1 for DSDP Sample No ; a-d: fresh glass (averages); e-h: palagonite; FeO* total iron calculated as FeO.

TABLE 3
Representative Microprobe Analyses of Phillipsites

Hole	332A	332B	333A
Lab No.	194E	198A	213A
SiO_2	53.0	50.8	51.0
Al_2O_3	17.0	18.4	18.3
Fe_2O_3*	0.3	0.2	0.2
MgO	0.1	-	-
CaO	0.5	0.3	0.5
Na_2O	5.7	4.1	5.5
K_2O	4.0	6.3	5.4
Total	80.6	80.1	80.9
Cations per 72 oxygens			
Si	26.3	25.6	25.5
Al	9.9	10.9	10.8
Fe^{3+}	0.1	0.1	0.1
Mg	0.1	-	-
Ca	0.3	0.2	0.3
Na	5.5	4.0	5.3
K	2.5	4.1	3.4

Note: Refer to Table 1 for DSDP Sample No; Fe_2O_3* total iron calculated as Fe_2O_3.

TABLE 4
Representative Microprobe Analyses of Clay Minerals

Hole	332B	332B
Lab No.	195H	199D
SiO_2	47.2	47.3
Al_2O_3	7.0	3.3
Fe_2O_3*	8.7	32.8
MgO	22.7	2.4
CaO	1.2	0.8
Na_2O	0.1	0.2
K_2O	0.6	4.9
Total	87.5	91.7
Cations per 22 oxygens		
Si	6.8	7.2
Al	1.2	0.6
Fe^{3+}	0.9	3.7
Mg	4.9	0.5
Ca	0.2	0.1
Na	-	0.1
K	0.1	0.9

Note: Refer to Table 1 for DSDP Sample No; Fe_2O_3* total iron calculated as Fe_2O_3.

K have been found in phillipsites in both sedimentary and nonsedimentary environments (Hay, 1966; Iijima and Harada, 1969).

Clays

Clays occur in small veins, clots, or as vesicle linings (Plate 1, Figures 5 and 6). Frequently the clays are brown or green in color. X-ray powder patterns of unglycolated samples were poorly resolved and separation into two categories was made solely on differences in chemical analyses (Table 4). The brown Mg-rich type is saponite, while the green Fe-K-rich type is difficult to identify further.

DISCUSSION

Phillipsite is a common zeolite in sea-floor sediments (Cronan, 1974) and in basalts of the oceanic crust (Bass, 1975). Phillipsite forms at temperatures well below 150°-200°C (Miyashiro and Shido, 1970). Oxygen isotope analyses of calcite in Leg 37 basalts (Muehlenbachs, this volume) and calcite and smectites in Leg 34 basalts (Seyfried et al., 1976; Muehlenbachs, 1976) indicate sea-floor alteration takes place at temperatures as low as 4°C. The oxygen isotope work further shows that low temperature alteration of Leg 37 basalts caused by circulating seawater penetrates to the bottom of Hole 332B, a depth of 583 meters below the sediment-basalt interface. Thus, over the 13 m.y. period sampled in Leg 37, substantial volumes of cold seawater passed through the basalts of oceanic layer 2.

If the basalts of Leg 37 are typical of the oceanic crust, the high K-content of zeolites, palagonite, and some clays suggests that significant amounts of K are removed from seawater by these secondary minerals.

SUMMARY

Basalts of DSDP Leg 37 have been altered by cold (4°C) seawater to a depth of nearly 600 meters below the sediment-basalt interface. Secondary minerals formed during alteration include phillipsite, calcite, saponite, an Fe-K-rich clay, and hydrated Fe-oxides. Siderite found in one sample may have formed at temperatures above 400°C during cooling of the lava pile. Since palagonite, phillipsite, and some clays show considerable enrichment in K relative to the host basalt, it is suggested that significant amounts of K are removed from seawater annually by these minerals.

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PLATE 1

Photomicrographs of secondary minerals and glass

Figure 1	Fresh glass with palagonite rim (332B-21-1, 55-59 cm). Plane polarized light.
Figure 2	Siderite lining vesicle (332B-28-1, 67-70 cm). Plane polarized light.
Figure 3	Colorless prismatic phillipsite infilling between basalt fragments (333A-8-7, ~74 cm). Plane polarized light.
Figure 4	Colorless prismatic phillipsite filling vesicle (332B-44-5, 16-18 cm). Plane polarized light.
Figure 5	Saponite filling vesicle (332B-3-1, ~108 cm). Plane polarized light.
Figure 6	Fe-K-rich clay lining vesicle (333A-3-1, ~69 cm). Plane polarized light.

PLATE 1