63. THE PETROLOGY OF ALTERATION IN THREE DISCRETE FLOW UNITS OF SITES 332 AND 335

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INTRODUCTION

The objective of the present work is to determine the changes in chemical composition of oceanic lavas brought about by their reaction with seawater. The results should have important implications in the interpretation of analyses of submarine lavas in the geological column.

The majority of the samples obtained for this study are in three sequential sets in Hole 332B and Site 335 (Figure 1). Each set comprises closely spaced samples that span at least one flow unit; a pillow in the case of Site 335 and probably thin flows for the sets of Hole 332B. A set of two samples from Hole 332A (not shown in Figure 1) represents the rim (7-1, 125 cm) and interior (7-1, 130 cm) of the same pillow. The remaining samples (Figure 1, and two samples from Hole 332A) are mostly pillow rims from a variety of depths.

Chemical analyses are presented in Chapters 2 and 5 (this volume). Microprobe analyses (Table 1) are limited to representative samples of the upper set of Hole 332B and the set of Site 335.

METHODS

The surface of a number of the samples showed a metallic sheen and accordingly all samples were thoroughly cleaned before analysis.

Chemical analyses were made in the Geological Survey of Canada laboratories under the direction of J.L. Bouvier by a variety of techniques collectively termed the "neoclassical" method (Abbey et al., 1974). It is the standard precise method presently in use by the Geological Survey.[1] Among the minor elements Li, Rb, and Cs were done by atomic absorption and the remainder by spectrograph under the supervision of K.A. Church.[2] Minor elements searched for but not detected are: Ce, Nd, Nb, La, Be, and W. Microprobe analyses were done using an energy-dispersive spectrometer that enabled simultaneous determinations to be made of all elements (Plant and Lachance, 1973).

PETROGRAPHY

Hole 332B, Upper Set

Two flow units may be represented by the eight samples of this set; the upper four, very uniform samples belong to one and the lower four samples to the other. A vesicular zone logged at a depth of 497.20 meters may represent the boundary. The upper unit is a fine-grained basalt (0.1-0.2 mm) comprising sparse (1%-2%) plagioclase microphenocrysts with oscillatory zoning set in a groundmass of mutually intergrown skeletal plagioclase and pyroxene. A largely indeterminate, brownish mesostasis heavily charged with iron oxide crystallites fills the interstices and composes about 10% of the rocks. Olivine is a rare minor constituent. The lower unit differs from the upper unit mainly in containing olivine as both phenocryst and groundmass phases and in its slightly coarser (0.2-0.5 mm) and more maturely crystallized groundmass.

Vesicles and amygdules are sparse (<1%) and small (0.25-0.75 mm) and essentially limited to the upper unit. The filling is variously yellow to reddish brown smectite, pale gray fibrous montmorillonite, and carbonate. These substances fill or rim the vesicle singly or
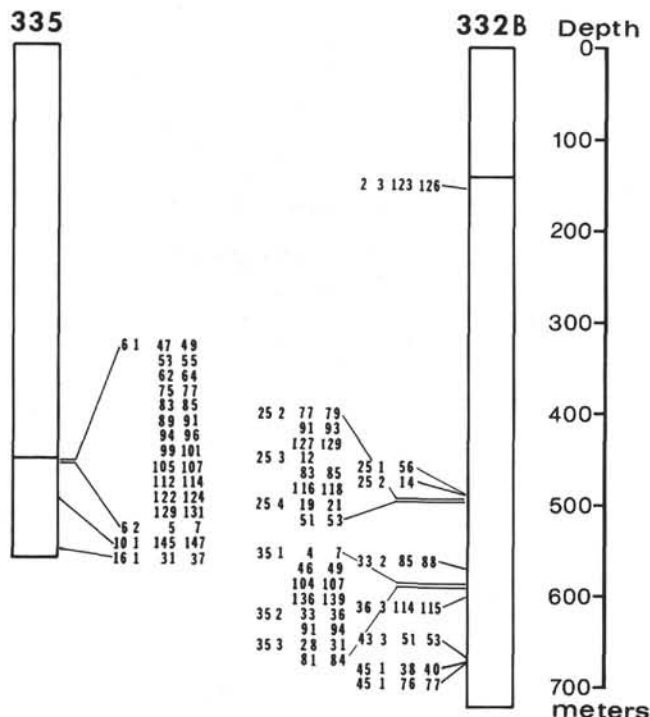

Figure 1. *Index diagram showing the positions in the holes of samples received in the present study. Not shown are four samples from Hole 332A.*

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[1]Precision estimated to be (Bouvier, personal communication, 1975): SiO_2 - ±0.3%; Al_2O_3 - ±0.2%; Fe_2O_3, CaO, and MgO - ±0.1%; Na_2O, K_2O, and FeO ±0.05; TiO_2 and MnO - ±0.02%; S and F - ±0.01%; C - ±0.03%; Li - ±3 ppm; Rb - ±2 ppm; Cs - ±0.9 ppm.

[2]Spectrographic laboratory estimates precision for refractory elements - ±15%, and for volatile elements - ±30% of quantity reported.

TABLE 1
Mineral Analyses Electron Microprobe

Sample (Interval in cm)		SiO_2	TiO_2	Al_2O_3	Cr_2O_3	Total Fe as Fe_2O_3	Total Fe as FeO	MnO	MgO	CaO	Na_2O	K_2O	CO_2 calc.	Total	
Hole 332B															
25-2, 91-93 cm, 13	BAR	40.50	0.00	0.01	0.01		14.32	0.09	45.05	0.23	0.03	0.00		100.24 Olivine	5 anal
25-3, 116-118 cm, 17	BAR	40.29	0.03	0.00	0.04		14.42	0.14	44.68	0.27	0.02	0.00		99.89 Olivine	6 anal
25-2, 77-79 cm, 10	BAR	40.13	0.04	0.01	0.05		15.24	0.11	44.16	0.25	0.03	0.00		100.02 Olivine	4 anal
25-1, (ca. 56) 8	AU	39.78	0.04	0.11	0.06		15.23	0.16	43.67	0.25	0.02	0.00		99.32 Olivine	13 anal
25-3, 83-85 cm, 11	BAR	39.54	0.03	0.00	0.06		18.96	0.18	41.22	0.29	0.01	0.00		100.29 Olivine	6 anal
25-3, 83-85 cm, 11	BAR	39.53	0.04	0.01	0.05		19.30	0.17	41.09	0.30	0.01	0.00		100.50 Olivine	
25-3, 83-85 cm, 11	BAR	38.55	0.03	0.00	0.05		26.14	0.25	35.12	0.32	0.01	0.00		100.47 Olivine	
25-2, 91-93 cm, 13	BAR						0.02	0.00	3.48	51.79			44.44	99.73 Mg-Calcite	3 anal
25-2, 127-129 cm, 15C	BAR						0.00	0.00	3.19	52.27			44.49	99.95 Mg-Calcite	5 anal
25-3, 83-85 cm, 11	BAR						0.00	0.00	3.00	52.03			44.09	99.12 Mg-Calcite	3 anal
25-3, 116-118 cm, 17	BAR						0.00	0.00	2.55	52.83			44.23	99.61 Mg-Calcite	5 anal
25-2, 91-93 cm, 13	BAR						0.08	0.46	4.41	50.74			44.96	100.65 Mn, Mg-Calcite	
25-3, 83-85 cm, 11	BAR						0.00	0.94	3.33	50.41			43.76	98.44 Mn, Mg-Calcite	
25-3, 116-118 cm, 17	BAR						0.02	3.23	3.26	48.59			43.69	98.79 Mn, Mg-Calcite	3 anal
25-2, 127-129 cm, 15C	BAR						0.00	0.00	0.16	55.29			43.55	99.00 Aragonite	3 anal
25-2, 77-79 cm, 10	BAR	50.92	0.05	2.33	0.00		10.03	0.00	21.66	0.41	1.95	0.77		88.12 Mg-Smectite	
25-2, 77-79 cm, 10	BAR	47.66	0.02	2.74	0.01		13.72	0.02	20.94	0.51	1.17	0.75		87.54 Mg-Smectite	
25-3, (ca. 12 cm), 2	BAR	46.00	0.04	3.29	0.00		9.48	0.05	20.71	0.61	1.36	0.69		82.23 Mg-Smectite	
25-2, 77-79 cm, 10	BAR	47.48	0.05	2.41	0.02		17.97	0.07	19.88	0.42	1.23	0.76		90.29 Mg-Smectite	
25-2, 77-79 cm, 10	BAR	43.86	0.06	2.09	0.04		20.58	0.06	16.64	0.62	1.19	0.85		85.99 Mg-Smectite	
25-2, 91-93 cm, 13	BAR	39.23	0.06	4.48	0.05		23.32	0.09	14.97	0.50	1.47	0.90		85.07 Mg-Smectite	
25-3, 83-85 cm, 11	BAR	45.08	0.09	1.09	0.04		30.35	0.02	7.27	0.38	0.92	2.28		87.52 K, Fe-Smectite	2 anal
25-3, 83-85 cm, 11	BAR	45.05	0.02	1.32	0.01		29.35	0.01	6.10	0.25	1.95	2.98		87.04 K, Fe-Smectite	2 anal
25-3, (ca. 12 cm), 2	BAR	20.21	0.16	0.86	0.10	62.67		1.86	1.98	1.07	0.36	0.18		89.45 Hyd. Fe-Oxide	
25-3, (ca. 12 cm), 2	BAR	19.96	0.08	0.72	0.03	57.95		3.64	1.99	1.34	0.95	0.08		86.74 Hyd. Fe-Oxide	
25-3, (ca. 12 cm), 2	BAR	25.45	0.17	0.83	0.01	57.08		0.42	1.85	1.59	0.25	0.14		87.79 Hyd. Fe-Oxide	
25-3, 116-118 cm, 17	BAR	56.54		19.12			0.14			0.10	3.80	5.92		85.62 Zeolite	5 anal
Site 335															
6-1, 62-64 cm, 2C	BAR	49.00	1.09	5.02	0.27		8.22	0.13	15.96	19.12	0.71	0.04		99.56 Pyroxene	
6-1, 105-107 cm, 3C	BAR	48.92	0.98	4.27	0.18		6.67	0.02	14.27	22.49	0.67	0.03		98.50 Pyroxene	
6-1, 62-64 cm, 2C	BAR	49.34	1.08	3.46	0.20		13.47	0.29	14.16	17.73	0.90	0.08		100.71 Pyroxene	
6-1, 105-107 cm, 3C	BAR	47.96	1.70	5.45	0.92		6.64	0.12	13.38	22.76	1.14	0.04		100.11 Pyroxene	
6-1, 105-107 cm, 3C	BAR	45.71	2.15	6.54	0.27		9.42	0.08	11.99	22.15	0.87	0.08		99.26 Pyroxene	
6-1, 105-107 cm, 3C	BAR	44.31	2.41	7.99	0.17		9.36	0.05	11.44	22.62	0.95	0.03		99.33 Pyroxene	
6-1, 105-107 cm, 3C	BAR	49.48	1.72	6.89	0.22		8.98	0.13	11.43	19.02	1.40	0.15		99.42 Pyroxene	
6-1, 62-64 cm, 2C	BAR	45.59	1.74	5.56	0.18		14.11	0.19	10.39	19.57	0.73	0.48		98.54 Pyroxene	
6-1, 105-107 cm, 3C	BAR	49.93	2.80	8.72	0.09		10.83	0.07	10.14	22.73	1.24	0.04		100.59 Pyroxene	
6-1, 105-107 cm, 3C	BAR	45.20	2.73	7.07	0.10		11.64	0.13	9.99	22.11	1.08	0.01		100.06 Pyroxene	
10-1, 145-147 cm, 12C	AU	41.06	0.01	0.07	0.04		10.25	0.15	48.40	0.24	0.00	0.00		100.22 Olivine	
6-1, 129-131 cm, 3E	BAR	40.75	0.00	0.16	0.05		10.19	0.09	47.88	0.24	0.00	0.00		99.36 Olivine	
6-1, 105-107 cm, 3C	BAR	40.81	0.00	0.00	0.04		11.20	0.15	47.51	0.23	0.00	0.00		99.94 Olivine	
10-1, 145-147 cm, 12C	AU	40.66	0.02	0.03	0.03		11.76	0.11	46.90	0.24	0.00	0.00		99.75 Olivine	
6-1, 53-55 cm, 2B	BAR	40.96	0.00	0.07	0.00		12.53	0.12	46.72	0.22	0.07	0.00		100.69 Olivine	
10-1, 145-147 cm, 12C	AU	40.26	0.03	0.21	0.03		13.75	0.12	45.62	0.21	0.00	0.00		100.23 Olivine	
6-1, 62-64 cm, 2C	BAR	40.41	0.04	0.19	0.06		13.70	0.18	45.36	0.28	0.00	0.00		100.22 Olivine	
10-1, 145-147 cm, 12C	AU	40.20	0.06	0.07	0.03		13.49	0.20	45.32	0.32	0.00	0.00		99.69 Olivine	
6-1, 129-131 cm, 3E	BAR	40.05	0.03	0.09	0.05		13.92	0.15	45.11	0.25	0.00	0.00		99.65 Olivine	

		A	B	C	D	E	F	G	H	I	J	K	L	Total	Mineral	Analyses
6-1, 53-55 cm, 2B	BAR	40.19	0.02	0.03	0.03		13.94	0.17	44.99	0.19	0.00	0.00		99.56	Olivine	
6-1, 62-64 cm, 2C	BAR	40.15	0.01	0.09	0.05		14.45	0.22	44.66	0.22	0.00	0.00		99.85	Olivine	
6-1, 53-55 cm, 2B	BAR	40.18	0.00	0.06	0.00		14.37	0.14	44.61	0.19	0.00	0.00		99.55	Olivine	
6-1, 105-107 cm, 3C	BAR	39.66	0.00	0.13	0.04		15.48	0.20	43.82	0.22	0.00	0.00		99.55	Olivine	
10-1, 145-147 cm, 12C	AU						0.00	0.00	2.54	52.99			44.35	99.88	Mg-Calcite	10 anal
6-1, 53-55 cm, 2B	BAR						0.00	0.00	2.52	52.57			44.00	99.09	Mg-Calcite	10 anal
6-1, 129-131 cm, 3E	BAR						0.02	0.00	2.40	52.12			43.52	98.06	Mg-Calcite	9 anal
6-1, 62-64 cm, 2C	BAR						0.00	0.00	2.16	52.39			43.47	98.02	Mg-Calcite	2 anal
6-1, 105-107 cm, 3C	BAR						0.01	0.00	2.06	53.50			44.23	99.80	Mg-Calcite	4 anal
6-1, 47-49 cm, 2A	AU						0.00	0.00	2.05	53.37			44.11	99.53	Mg-Calcite	5 anal
6-1, 62-64 cm, 2C	BAR						0.01	0.44	2.83	51.33			43.64	98.25	Mn, Mg-Calcite	3 anal
6-1, 105-107 cm, 3C	BAR						0.46	4.44	2.62	46.89			42.68	97.09	Mn, Mg-Calcite	
6-1, 62-64 cm, 2C	BAR						0.22	4.08	2.57	48.35			43.41	98.63	Mn, Mg-Calcite	2 anal
6-1, 105-107 cm, 3C	BAR						0.00	0.00	0.28	54.55			43.11	97.94	Aragonite	9 anal
6-1, 53-55 cm, 2B	BAR	50.30	0.06	3.65	0.01		4.75	0.03	24.41	0.40	1.11	0.39		85.11	Mg-Smectite	10 anal
6-1, 62-64 cm, 2C	BAR	51.53	0.05	3.39	0.01		6.59	0.01	23.51	0.44	1.23	0.59		87.35	Mg-Smectite	3 anal
6-1, 105-107 cm, 3C	BAR	49.93	0.05	2.60	0.03		10.03	0.05	22.08	0.49	0.74	0.77		86.77	Mg-Smectite	4 anal
6-1, 129-131 cm, 3E	BAR	47.00	0.02	3.72	0.01		7.13	0.02	22.07	0.47	0.76	0.66		81.86	Mg-Smectite	9 anal
6-1, 129-131 cm, 3E	BAR	47.82	0.04	3.83	0.04		7.35	0.02	21.90	0.64	0.72	0.64		83.00	Smectite after Olivine	5 anal
6-1, 105-107 cm, 3C	BAR	47.45	0.00	2.19	0.02		20.15	0.02	16.50	0.46	0.65	1.46		88.90	K, Fe-Smectite	
6-1, 105-107 cm, 3C	BAR	45.31	0.01	1.97	0.00		24.50	0.09	15.16	0.27	1.18	1.98		90.47	K, Fe-Smectite	
6-1, 105-107 cm, 3C	BAR	38.67	0.03	0.58	0.08		30.62	0.11	8.11	0.44	7.23	2.09		87.96	K, Fe-Smectite	
6-1, 62-64 cm, 2C	BAR	47.00	0.00	1.90	0.03		25.48	0.00	6.42	0.28	0.55	6.46		88.12	K, Fe-Smectite	
6-1, 129-131 cm, 3E	BAR	47.26	0.05	5.03	0.04		27.32	0.00	5.51	0.79	1.24	4.50		91.74	K, Fe-Smectite	
6-1, 62-64 cm, 2C	BAR	45.54	0.04	1.26	0.00		31.87	0.00	4.08	0.16	0.00	7.15		90.10	K, Fe-Smectite	
6-1, 62-64 cm, 2C	BAR	10.67	0.08	1.33	0.09	71.90		0.34	3.61	0.24	0.11	0.01		88.38	Goethite	5 anal
6-1, 105-107 cm, 3C	BAR	14.43	0.08	1.08	0.63	66.22		0.30	4.29	0.57	0.00	0.09		87.69	Goethite	2 anal
6-1, 47-49 cm, 2A	AU	56.36		19.23			0.06			0.26	5.26	7.19		88.36	Zeolite	10 anal
6-1, 47-49 cm, 2A	AU	46.44		26.28			0.20			0.52	4.00	5.54		82.98	Zeolite	3 anal
6-1, 129-131 cm, 3E	BAR	57.70		18.65			0.13			0.16	6.36	5.40		88.40	Zeolite	4 anal
6-1, 47-49 cm, 2A	AU	38.44	3.10	9.98	0.14		20.86	0.00	2.28	1.42	2.47	2.59		81.28	Palagonite	
6-1, 47-49 cm, 2A	AU	42.36	1.64	12.62	0.08		17.90	0.00	3.87	0.55	0.51	3.64		83.17	Palagonite	
6-1, 47-49 cm, 2A	AU	41.34	1.72	12.38	0.07		17.54	0.06	4.43	0.65	0.35	3.90		82.44	Palagonite	
6-1, 47-49 cm, 2A	AU	42.28	1.58	12.07	0.08		17.32	0.00	4.71	0.51	0.62	3.97		83.14	Palagonite	

in combination. In the latter case they appear successively from the rim to the center in the order listed above.

With the exception of one sample (332B-25-3, 116-118 cm), which is profusely carbonated, secondary mineral development in the two units is at a generally uniform level estimated to be between 20% and 30% of the rock. The chief alteration minerals are smectites ranging in color from yellow-greens to yellowish and reddish-browns and to lesser extent, deep reddish-brown hydrous iron oxides. Of the major minerals olivine is the only one that is extensively replaced. Most of the alteration is present in the mesostasis where it presumably has developed in the magmatic residue.

Hole 332B, Lower Set

The samples of this set span a single picrite flow about 4 meters thick and include upper and lower marginal zones. In its interior the unit typically comprises about 25% olivine (0.5-5 mm) and rare plagioclase phenocrysts (±1 mm) in a moderately coarse-grained groundmass (0.2-1.0 mm). Two generations of olivine phenocrysts are suggested by what appears to be two distinct size ranges of 0.5-1.5 and 2 to 5 mm. Some of the coarser crystals contain rounded inclusions of devitrified glass and brown chromite. The groundmass consists of a framework of plagioclase laths and olivine pellets with fronds of fibrous, radiating clinopyroxene and, less commonly, iron oxide-charged magma residue filling the interstices. Chromite is a minor framework crystal. The marginal zones of the flow are finer grained and less rich in olivine phenocrysts than the interior.

Amygdules are 0.1 to 0.8 mm diameter and range from 5% to 10% of the rock at the flow margins to 2%-3% in its interior. They are invariably filled; generally with exterior zones of fibrous yellow to brown smectites and centers of carbonate. The lower marginal zone shows, in addition, amygdules filled with magma residue.

Alteration is generally minor and confined mainly to olivine and the interstitial magma residue. The alteration minerals have not yet been studied but appear to be mainly yellow to brown and green smectites, hydrous iron oxides, and carbonate. In the specimen from the lower margin olivine is totally replaced by carbonate and interstitial pyroxene by brownish smectite.

Site 335

The set of 13 closely spaced specimens from this site (Figure 1) span a thickness of 1.1 meters. The uppermost of them (335-6-1, 47-49 cm) is a glassy pillow rind and both the detailed log of the hole and the petrography of the specimens suggest that the succeeding 11 specimens are parts of the same pillow. Only the lowermost specimen (335-6-2, 5-7 cm), which is separated from the others by a missing section of core and represents an inversion in the trend to finer grain size shown by the specimens immediately above, appears to belong to another pillow.

The pillow is weakly plagioclase and olivine phyric with 1% or less of each. Three generations of plagioclase crystals are present in most specimens: sparse, rounded and corroded, zoned plagioclase xenocrysts as much as 3 mm long; elongate, euhedral plagioclase phenocrysts 1-2 mm long, and skeletal groundmass plagioclase, generally less than 1 mm long. Olivine as both phenocrysts and groundmass forms less than 2% of the rock. Rare, partly altered megaphenocrysts of olivine as much as 3.5 mm across are present in the lower half of the pillow where they may have settled. These are possibly also xenocrysts.

Skeletal plagioclase forms the framework of the groundmass. The interstices are filled with sheaves of radiating, fibrous pyroxene interleaved with plagioclase and dark brown mesostasis, all charged with minute crystals of iron-titanium oxide.

The glassy rind of the pillow (335-6-1, 47-49 cm) is complexly transected by veins of carbonate and zeolites bordered by zones of banded palagonite. The palagonite appears to be related to an earlier set of fractures that must have guided the carbonate-zeolite veins for it is generally not symmetrically disposed about the veins and is locally crosscut by them. Relict patches of clear sideromelane, forming about 25% of the sample, contain sparse microphenocrysts of plagioclase and olivine and globular plagioclase-pyroxene nucleii 0.1 to 0.5 mm in diameter. The latter have a core of skeletal plagioclase encircled by a thick, fibrous fringe of intergrown pyroxene and plagioclase. Inward from the pillow rim, the globules multiply and presumably coalesce to form the crystalline groundmass of the pillow interior.

Amygdules decrease in size and quantity from just below the glassy rind (0.5-1.5 mm diameter, 5%-8%) to the interior of the pillow (0.1-0.5 mm diameter, 0.5%-1.0%). They are filled with magmatic residue, beige and waxy yellow-green to brown or reddish-brown smectites, and carbonates. Rarely they are empty or partially empty.

Alteration is most pronounced adjacent to veins. Unfortunately from the point of view of determining the variation in alteration inward from a pillow surface, which was one of our objectives, the pillow sampled is cut longitudinally to the core by one or more veins and transverse fractures. The vein filling is foram-bearing nanno ooze which indicates that the veins were open to the pillow surface. Adjoining the veins for distances of 3 to 10 mm the alteration comprises reddish-brown radiating bundles, reminiscent of plagioclase-pyroxene intergrowths, patches of yellow to brownish smectites filling the interstices, and scattered carbonate crystals stained brownish-red with hydrous iron oxide. The bundles, on the basis of probe analyses and optic properties, are interpreted as mixtures of pyroxene-plagioclase intergrowths and secondary hydrous iron oxide. Beyond the halos attending the veins, alteration is limited to sparse green and yellow or brown smectites in the interstices of the groundmass. On the average, alteration products constitute 20% to 30% of the samples examined.

Miscellaneous Samples

Of the remaining samples, 335-10-1, 145-147 cm and the set 332A-7-1, 125-127 cm and 332A-7-1, 132-134 cm are of special interest. One of the oldest samples of the

collection, 335-10-1, 145-147 cm, is also the freshest. Seventy-five percent of the sample is clear sideromelane and only 5% is composed of secondary minerals. The remainder consists of plagioclase and olivine phenocrysts and megacrysts (5%) and plagioclase-pyroxene nucleii. The set, 332A-7-1, 125 cm and 332A-7-1, 132 cm, represent the rim and interior, respectively, of a single pillow. Both are aphanitic basalts with sparse plagioclase phenocrysts set in a groundmass of skeletal plagioclase and finely fibrous pyroxene-plagioclase fronds. A brownish mesostasis forming 10% to 20% of the rock contains essentially the only alteration minerals present. From the rim to the interior of the pillow the alteration minerals appear to change from predominantly reddish-brown to predominantly pale yellow smectites. This is consistent with the difference in chemical composition for the two samples and with the compositions determined in other samples for smectites of similar coloring.

MINERAL CHEMISTRY

Hole 332B, Upper Set

Analyses (100) of plagioclase in six samples show that the sparse phenocrysts have cores of An_{84-70}, with zoned mantles of An_{80-44}, and that the groundmass compositions are An_{72-47} (Figure 2a). In the two rind sections, all plagioclase is within the range An_{85-70}. The FeO content of the plagioclase can be related to the core, mantle, and groundmass compositions (Figure 2a), and the variation is comparable to that reported by Keil et al. (1972) and Smith (1974). Pyroxene compositions (Figure 3a) range from $Wo_{46}En_{37}Fs_{17}$ to $Wo_{10}En_{52}Fs_{38}$, with the majority plotting within a broad augite field but with an apparent projection towards ferroaugite. Olivine shows a generally restricted range of composition (Fo_{85-84}), (Table 1), with zoning (Fo_{80-70}) limited to Sample 25-3, 83-85 cm. Primary opaque minerals were analyzed semiquantitatively; aside from rare chromite, pyrrhotite, and native Cu, the oxide phases are titanomagnetite in the upper unit and titaniferous magnetite in the lower unit of the set. Representative carbonate analyses are given in Table 1, and aside from the aragonite (confirmed by XRD) analyzed in Sample 25-2, 127 cm, all are magnesian calcite, with manganiferous varieties limited to the centers of amygdules and void fillings. Available data suggest a trend of decreasing Mg down the section from Samples 25-2, 91-93 cm to 25-3, 116-118 cm. Supplementary X-ray determinations identified aragonite in Sample 25-3, 12-14 cm. Of other elements, strontium was only detected in the aragonite up to a value of 1.2% Sr. Members of the smectite group, confirmed by X-ray diffraction of analyzed grains, occur in most sections. Representative analyses, Table 1, show that the beige to pale brown varieties are Mg-rich, and that the greenish-yellow type in Sample 25-3, 83-85 cm is Fe and K rich. Also, most sections contain amorphous (by XRD) dark red to opaque granules, which take a good polish, and which have a silicon-rich hydrous iron oxide composition (Table 1). A Na-K zeolite (Table 1) occurs as crystal sprays on void surfaces in Sample 25-3, 116-118 cm.

Site 335

Analyses (209) of plagioclase in six sections group into three populations: (1) xenocrysts, An_{86-78}, (2) phenocryst cores, An_{76-72}, and (3) rims on xenocrysts and phenocrysts, and groundmass grains, An_{72-61} (Figure 2b). Pyroxene compositions from four crystalline samples are shown in Figure 3b, and representative analyses are given in Table 1. The augites are pres-
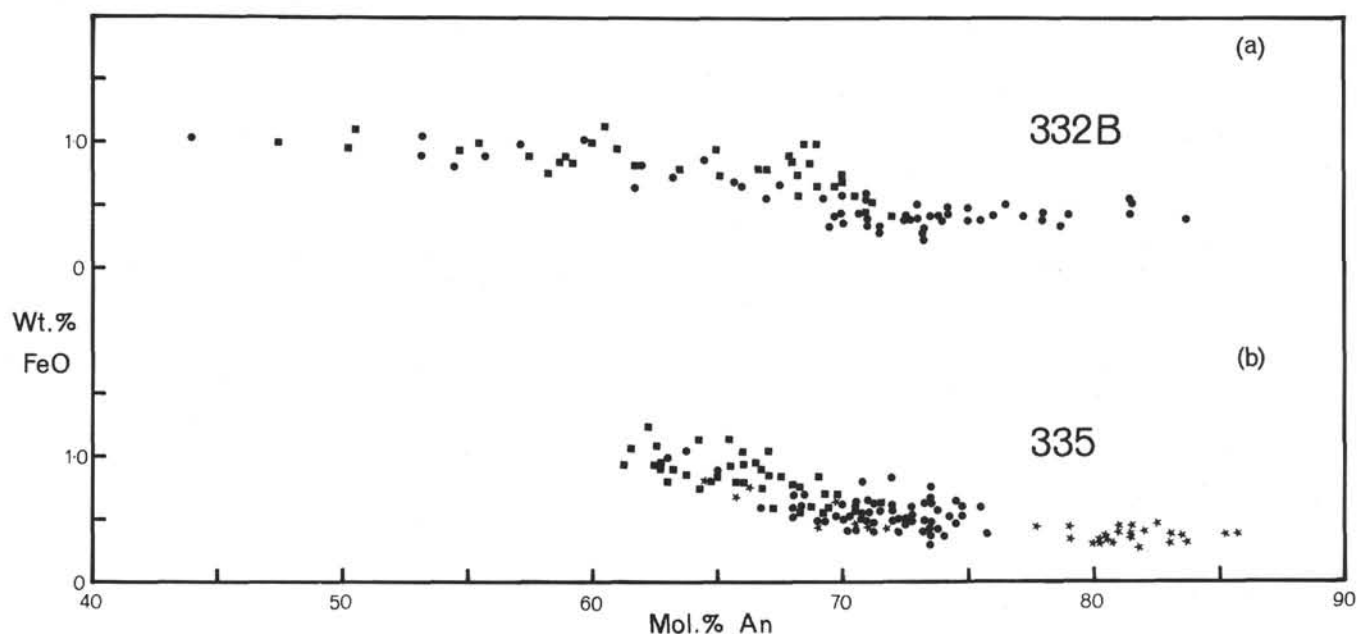

Figure 2. *Weight percent FeO plotted against molecular percent An for plagioclases in selected crystalline samples. (a) Hole 332B; (b) Site 335. Xenocrysts-stars, phenocrysts-filled circles, groundmass plagioclase-filled squares.*
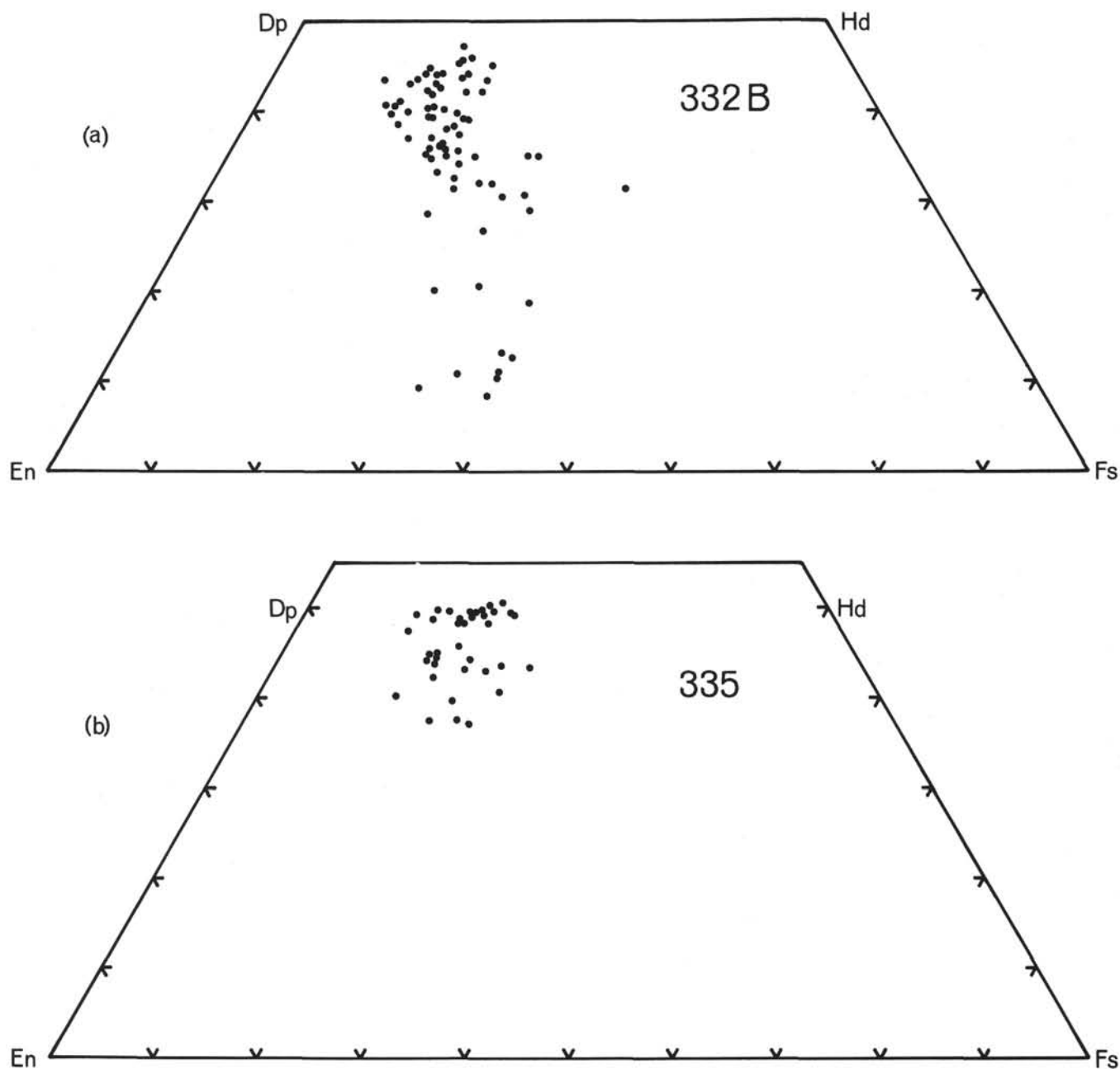
Figure 3. *Pyroxene variation for selected samples. (a) Hole 332B (b) Site 335.*

ent in all sections in fine-grained feathery intergrowth with plagioclase, while the salites occur only in the coarser grained center of the pillow as prismatic grains analyzed in Sample 6-1, 105-107 cm. Olivine compositions (Table 1) correspond with four petrographic populations, viz. megacryst core (Fo_{89-88}), megacryst margin (Fo_{88-85}), phenocryst core (Fo_{88-85}), and phenocryst margin and groundmass (Fo_{85-84}). The megacryst margin was observed only in Sample 10-1, 145 cm, where the unaltered megacryst is within sideromelane. Carbonate compositions are listed in Table 1; as in 332B, most are magnesian calcite, with manganiferous varieties occurring in the centers of amygdules and void fillings (0.07%-1.89% $MnCO_3$) and within altered olivine megacrysts (6.28%-7.20% $MnCO_3$). Aragonite

(confirmed by XRD) was found only in Sample 6-1, 105-107 cm as void fillings with a coarse, platy texture and with a strontium content as high as 0.9% Sr. Members of the smectite group occur in all rock samples, and are divided here into two groups. (1) A Mg-rich type that has only limited compositional variation and is pale colored in shades of beige and brown. Average compositions for each sample are listed in Table 1. In Sample 6-1, 129-131 cm, a texturally distinct Mg-smectite occurs as pale brown fibrous aggregates replacing olivine; the mean of five analyses is listed in Table 1. (2) An Fe-rich group which shows considerable compositional variation (based on 29 analyses); particularly MgO (4%-17%) and K_2O (7%-1.4%). Members of this group are highly colored in red-

brown through olive to yellow-green, and are waxy both in appearance and consistency. Representative analyses are given in Table 1. Most sections contain goethite, identified by X-ray diffraction of analyzed grains. These occur as reticular networks replacing olivine and as dark red granules. Two mean analyses (Table 1) show the high Si value and significant Mg with minor Al, Cr, Mn, and Ca. A Na-K zeolite occurs in Samples 6-1, 47-49 cm and 10-1, 145-147 cm as veins and in 6-1, 129 cm as an amygdule and thin vein. Average compositions are listed in Table 1, and include the two variants occurring in Sample 6-1, 47-49 cm, where they grade into each other over 10-20 μm. X-ray powder diffraction patterns of both types are analogous to the hydrothermal products K-H and $K_{72}Na_{28}$-H of Taylor and Roy (1964) that were produced by treatment of synthetic members of the phillipsite group. Banded palagonite is developed along fractures in sideromelane in the rind sections. Compared with the mean glass composition, K, Fe, Ti, and the volatiles show significant increase in the palagonite, though they display minor variations within the bands. In contrast, Na, Mg, and Ca all decrease within the palagonite. Representative analyses are listed in Table 1.

CHEMISTRY

Hole 332B

Analyzed samples from the upper set of Hole 332B are classed as tholeiitic basalts (Figure 4) on the basis of both major (Irvine and Baragar, 1967) and minor elements (Miyashiro and Shido, 1975). Their division into two flow units, previously postulated on the basis of petrography, is also evident in the chemistry. The main difference is in the titanium content. The upper unit contains titanomagnetite and has a mean TiO_2

content of 0.91%, whereas the lower unit contains titaniferous magnetite and has a mean TiO_2 content of 0.71%.

The analyzed samples from the lower set of Hole 332B are from the picritic flow noted previously. Predictably, they are distinguished by much higher MgO, Cr, and Ni, higher MnO, and lower Fe_2O_3, Na_2O, and P_2O_5 than the other basalts. Variations of elements within the flow have a bilateral symmetry with respect to its center: Ga, V, Sr, and Sc increase towards the boundaries whereas MgO and Ni decrease. These variations reflect the original olivine distribution within the flow. The higher CO_2 and water content and iron oxidation ratio, evident near the flow boundaries, are indicative of the greater degree of alteration which the exteriors of the flow have undergone.

Site 335

Samples of the pillow in this hole are also of tholeiitic basalt. Within the pillow, systematic chemical variation is limited to F, Na_2O, and possibly SiO_2, of which, the latter two increase towards the center and F increases toward the margins (Figure 5). Possibly other elements had similar systematic trends but were obscured by the alteration effects associated with the veins and fractures which transect the pillow. The F, Na_2O, and SiO_2 variations are not readily explained by minerals recognized in the rock. Whether or not they can be attributed to interaction with seawater is not wholly clear.

A correlation matrix was derived from all the analyses of the pillow to determine what elements may be correlative with obvious indicators of alteration such as H_2O, Fe_2O_3, and Cl. Pairs which show significant (P>0.01) positive correlations are: Cl-S, Cl-Sr, H_2O^--S, Fe_2O_3-K_2O, and H_2O_T-CaO. Pairs which show significant negative correlations are Fe_2O_3-Cr, Fe_2O_3-Al_2O_3, and H_2O_T-SiO_2. The implications of these correlations are not fully understood. Some may be attributed to seawater alteration. For example, the Cl-Sr correlation can reasonably be attributed to precipitation of aragonite, a rich source of Sr, from seawater. On the other hand, S is known to be high in the primary glass of the pillow rim where alteration is also severe.

General

All analyses of our sample collection are plotted on the AMF diagram of Figure 4. They form essentially two groups; the picrites and the others. Together they form an iron-enrichment, tholeiitic trend which is greatly extended by the magma residue contained in the interstices and amygdules of some of the lavas. Compositions of these latter were obtained by broad beam microprobe analysis (Chapters 2 and 5, this volume).

A comparison of analyses between the two holes shows that TiO_2, K_2O, Na_2O, and H_2O_T are more abundant in Site 335 samples. Whether the increase in K_2O is attributable to original differences in lava composition or to a longer exposure to seawater in the case of Site 335 is difficult to ascertain. Normally Na_2O is lost and K_2O gained during weathering on the ocean floor whereas in these samples from deeper levels they
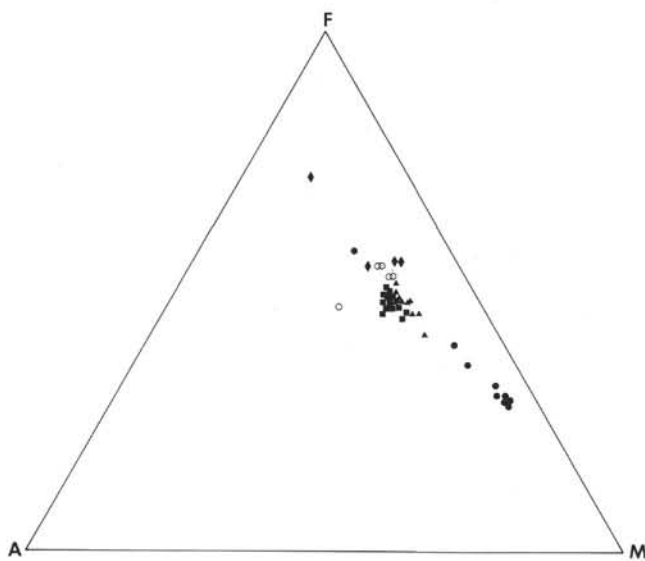

Figure 4. *AFM diagram showing all samples. Picrite-filled circles; upper part of Hole 332B-filled triangles; pillow of Site 335-filled squares; miscellaneous samples of pillow rinds-open circles; late magmatic residue in amygdules and intersticies-filled diamonds.*
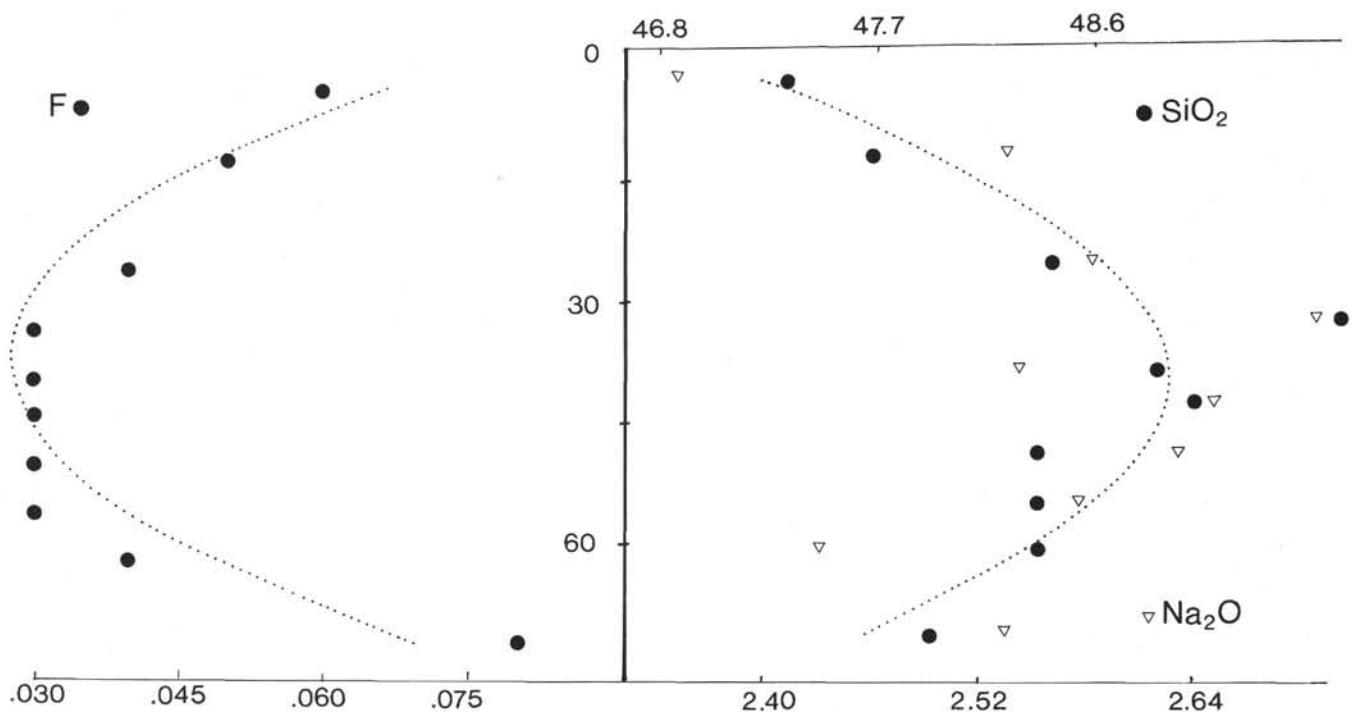
Figure 5. *Systematic chemical changes in the pillow of Site 335. Dotted lines are best-fit parabolas for each set of analyses. The vertical scale is in cm; all quantities are in percent.*

follow one another. K-bearing smectites seem more abundant in the pillow of Site 335 than in samples of Hole 332B in harmony with the higher water content. This would be consistent with a higher degree of weathering for the pillow, but there is little other supporting evidence for this view.

H_2O_T and ($Fe_2O_3/FeO + Fe_2O_3$) from all the samples are positively correlated. When an alteration index $\sqrt{(H_2O)^2 + (5x[Fe_2O_3/FeO + Fe_2O_3])^2}$ is plotted (Figure 6) against elements that commonly increase during submarine weathering, such as K_2O, Rb, Li, Ba, and Cs no correlation is evident. The alteration index and K_2O of Site 335 are slightly higher than Hole 332B, but as previously noted this could result from a primary difference in composition. In view of this lack of correlation of elements usually identified with submarine weathering, one cannot conclude on the basis of our data that there has been significant net gain or loss of metals from the sea.

SUMMARY AND DISCUSSION

1) Sequential samples spanning three flow units show no systematic differences in composition that can be unequivocally attributed to alteration.

2) Systematic chemical differences in the picrite flow of Hole 332B can be related to concentration of olivine phenocrysts in the flow interior.

3) Secondary material developed in glassy pillow rinds is chiefly palagonite, and in crystalline lavas is smectites, carbonate, and goethite (or amorphous hydrous iron oxide).

4) Smectites group into Mg-rich and Fe-rich varieties; the latter are generally potash-rich.

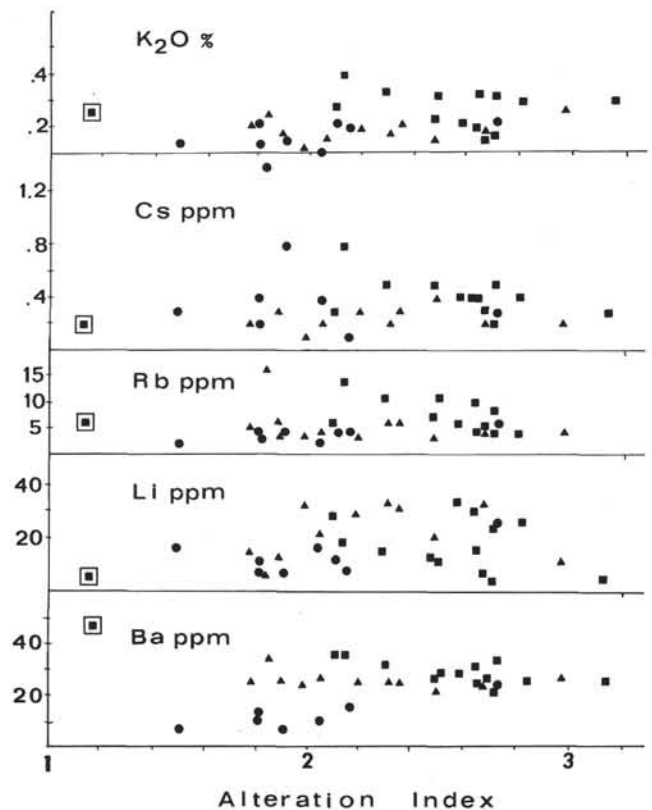5) Iron oxide ratio ($Fe_2O_3/FeO + Fe_2O_3$) and water

Figure 6. *Plot of K_2O, Cs, Rb, Li, and Ba against an alteration index $\sqrt{(H_2O)^2 + [5x(Fe_2O_3/FeO + Fe_2O_3)]2}$. Upper part of Hole 332B-filled triangles; picrite of Hole 332B-circles; pillow of Site 335-squares. Boxed square is Sample 335-10-1, 145 cm, a glassy pillow rind with the least alteration of any of the samples.*

contents are positively correlated and vary directly with degree of alteration. No correlation is evident between these parameters and elements normally affected by weathering at the ocean floor.

The most puzzling aspect of these results is the lack of positive evidence for systematic exchange of elements between seawater and the volcanic rocks. Many authors (Matthews, 1971; Hart, 1969; Melson, 1973; and Thompson, 1973) have demonstrated the changes of composition to be expected with alteration by seawater; most notably gains in K, Rb, and Ba and losses in Ca, Mg, and Fe. Individual samples from the rim and interior of a pillow in our collection show most of the expected changes and samples from the oldest site (335) are certainly higher in K than those of the youngest site (Hole 332B). However, taken together the samples show no systematic change in element composition with increasing alteration. The reason for this can only be speculative at present but possibly relates to the removal of the basalt from contact with the ocean water. Instead, small quantities of entrapped or descending salt water might be expected to equilibrate with the vastly greater bulk of basalts with little resulting chemical change in the latter. The variety of smectites, carbonates, zeolites, and amorphous hydrous iron and silicic mineraloids are products of this interaction and may serve to fix the exchangeable elements close to their original site.

REFERENCES

Abbey, S., Lee, N.J., and Bouvier, J.L., 1974. Analysis of rocks and minerals using an atomic absorption spectrophotometer. Part 5. An improved lithium-fluoroborate scheme for fourteen elements: Geol. Surv. Canada, Paper 74-19.

Hart, S.R., 1969. K, Rb, Cs contents and K/Rb, K/Cs ratios of fresh and altered submarine basalts: Earth Planet. Sci. Lett., v. 6, p. 295-303.

Irvine, T.N. and Baragar, W.R.A., 1971. A guide to the chemical classification of the common volcanic rocks: Canadian J. Earth Sci., v. 8, p. 523-548.

Keil, K., Fodor, R.V., and Bunch, T.E., 1972. Contributions to the mineral chemistry of Hawaiian Rocks II. Feldspars and interstitial material in rocks from Haleakala and West Maui Volcanoes, Maui, Hawaii: Contrib. Mineral. Petrol., v. 37, p. 253-276.

Matthews, D.H., 1971. Altered basalts from Swallow Bank, an abyssal hill in the NE Atlantic; and from a nearby sea mount: Phil. Trans. Roy. Soc. London, Ser. A, v. 268, p. 551-571.

Melson, W.G., 1973. Basaltic glasses from the Deep Sea Drilling Project, chemical characteristics, compositions of alteration products, and fission track "ages": Eos Trans. AGU, v. 54, p. 1011-1014.

Miyashiro, A. and Shido, F., 1975. Tholeiitic and calc-alkali series in relation to the behaviour of titanium, vanadium, chromium, and nickel: Am. J. Sci., v. 275, p. 265-277.

Plant, A.G. and Lachance, G.R., 1973. Quantitative electron microprobe analysis using an energy dispersive spectrometer; Proc. Eighth Nat. Conf. on Electron Probe Analysis (New Orleans), Paper 13.

Smith, J.V., 1974. Feldspar minerals, Vol. 2, Chemical and textural properties: Heidelberg (Springer Verlag).

Taylor, A.M. and Roy, R., 1964. Zeolite studies IV: Na-P zeolites and the ion-exchanged derivatives of tetragonal Na-P: Am. Mineralogist, v. 49, p. 656-682.

Thompson, G., 1973. A geochemical study of the low-temperature interaction of sea water and oceanic igneous rocks; Eos Trans. AGU, v. 54, p. 1015-1018.