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INITIAL SUBMARINE ALTERATION OF BASALTIC PILLOW LAVAS: A MICROPROBE STUDY

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ABSTRACT. Rapidly quenched glass rims of very young rift valley deep sea pillow basalt have a pristine magma chemistry, but compositions of the interiors of the same pillows are appreciably altered by both low and high temperature processes. Low temperature exchange with seawater has added significant amounts of K to the largely crystalline pillow interiors by seawater penetration into radial cooling cracks and diffusion along crystal boundaries. However, the small amount of residual glass in the interior is not K-rich enough to account for all the K increase; additional K is present in secondary alteration pockets lining cracks and vesicles. Mg abundances are essentially constant in whole rock analyses, but residual glasses show a Mg decrease with increasing crystallinity reflecting crystal fractionation. The Fe decrease in the pillow interior probably represents a high-temperature deuteric or seawater reaction that removes transition metals. Both Fe and Mn are locally redistributed in secondary metal oxide-rich crack filling material.

INTRODUCTION

The physical process of pillow formation during submarine extrusion and the ensuing thermal history of the cooling lavas should control the chemical exchange between seawater and the pristine magma. The formation of pillow lavas has been described recently by Moore (1975). In brief, pillow lavas are formed when basaltic lava is erupted subaqueously, flowing within conduits of cooled and solidified lava to form elongate lobes. These lobes extend themselves by rupture and spreading of the weak, thin, quenched margins near lobe fronts. The thermal history of the pillow is recorded by the progressive increase in degree of crystallization and size of crystals from a completely glassy rim to a nearly holocrystalline center of the pillow; these textures have been summarized by Bryan (1972). A decrease in volume occurs because of the cooling of the solid phases; sets of cracks develop and are thought to allow seawater to penetrate into the hotter interior. Reaction between seawater and the rock occurs at elevated temperatures during the brief period of cooling (Corliss, 1971; Humphris, 1975) and then continues for a long time at low temperatures after cooling has ceased.

There are numerous studies of the low temperature chemical exchange between seawater and basaltic lavas. Roger Hart's (1970) investigation concentrated upon the increase in hydration, oxidation, and alkalinity of basalt during alteration with increasing age of the ocean crust. A similar increase in U with increase in alteration has been found by Aumento (1971) where alteration increased with age of the ocean crust. Miyashiro, Shido, and Ewing (1969) showed that the degree of hydration is greater on the pillow rim compared to the core of extensively altered pillows. Matthews (1971) found both cores and rims to be extensively altered in basalts from older portions of the Atlantic at Swallow Bank. Stanley Hart (1969) showed that large increases of alkali ions (Cs, Rb, K) occur

in altered rims compared to the interior. Melson (1973) noted chemical alteration related to palagonitization of glasses in contrast to relatively fresh interiors. These results generally led to the conclusion that low temperature weathering (halmyrolysis) rather than high temperature alteration was the alteration mechanism and that the rims were more highly affected than cores. In these cases, the glassy rims showed visible signs of alteration.

Other researchers have made the highly contrasting conclusion that the pillow glassy rims are fresher than the pillow interiors. For example, Poldervaart and Green (1965) found pillow interiors that were more oxidized and more K-rich than *fresh* glass rims. In his dissertation, Paster (ms) found a hydrated glass rim but more extensive alteration and secondary mineralization along joints and fractures in the interior. Dymond (1970) and Funkhouser, Fisher, and Bonatti (1968) found an excess of ^{40}Ar within the pillow glass, whereas the crystalline interior has lost appreciable quantities of excess ^{40}Ar. Corliss (1971) noted that the interior portions of pillows and flows are depleted in several elements relative to fresh flow margins. Three zones in pillows are distinguished by Thompson (1973), an altered layer of outermost glass (palagonitized), a fresh layer of glass, and an altered interior. The outermost layer of palagonite was found to contain the highest U content, the underlying fresh glass and the gray crystalline pillow interior the lowest U content, and a yellowish-brown crystalline zone between the fresh glass and the gray interior an intermediate U content (Macdougall, 1973). Also, glass rims have higher precious metal contents and higher S contents than do pillow interiors (Keays and Scott, 1976; Scott and Frank, 1974). Although two mechanisms are called for during alteration (mostly high temperature by Paster (ms) and Corliss (1971) and low temperature alteration by Thompson (1973)), there is general agreement that the most nearly pristine sample of the original magma chemistry is found in the rapidly quenched glass rim that shows no evidence of palagonitization. Shido, Miyashiro, and Ewing (1974) concluded that fresh pillows have a fresh glass exterior and an altered interior, but highly weathered pillows have a highly altered exterior and a less altered interior. Below depths of 2 km where the confining pressure is sufficient to prevent vesiculation, the glass on fresh pillow rims retains volatiles, but the crystalline interior loses significant volatiles (Moore and Schilling, 1973). Thompson (1973) expresses the prevalent philosophy: when magma extrudes in a deep subaqueous environment, the outer rim of pillows quench to form a glass that, initially, acts as a closed chemical system; however, the more slowly clooed and more crystalline pillow interiors are exposed to alteration. Several mechanisms may contribute to this alteration of pillow interiors. (1) Deuteric alteration may occur toward the end of crystallization as the original volatiles in the magma become concentrated in residual fluids; this would be a very short-lived phenomenon. (2) Radiating cooling cracks allow seawater to penetrate the still hot interior; the localized chloride-

rich hydrothermal fluids would migrate along crystal boundaries, form complexes with transition metals, and exchange with exterior seawater as suggested by Corliss (1971); this too would be a short-lived phenomenon related to lava cooling alone. (3) After cooling of the pillows, the radial cooling cracks would continue to allow seawater to penetrate; then low temperature alteration of the crystalline interior would be accompanied by low temperature alteration of the glassy rim. However, this long-term phenomenon does not equally affect the exterior and interior of pillows, as pointed out by Thompson (1973). Hydration and palagonitization alter the glass rims, whereas the crystalline interiors are altered to clay minerals and zeolites. Because the rates of palagonitization are more rapid that those operating on pillow interiors, after several millions of years the glass entirely alters to a palagonite and parts of the interior removed from radiating cooling fractures are still *relatively* fresh. Thus young pillow basalts can be expected to have fresh glassy rims and slightly altered interiors, whereas old pillow basalts have highly altered, palagonitized rims and less altered interiors.

The types of alteration mechanisms discussed above certainly do not include all forms of alteration of oceanic basalts. As fairly rapid extrusion progresses, the leading front of a pillow lava builds steep forset beds (Moore, 1975); these quenched pillow-like lobes have fragments of spalled glass accumulated in their interstices from up-slope pillow formation, and this complex is subsequently covered by new lava lobes trapping seawater between fragments and irregular lobe edges. Such trapped seawater becomes heated and reacts with surrounding glass causing much higher rates of palagonitization than that at ambient seawater temperatures. A second common form of oceanic crustal alteration is hydrous metamorphism or hydrothermal alteration superimposed upon rocks where fracture systems allow deep circulation of seawater within the newly formed hot lithosphere (Miyashiro, Shido, and Ewing, 1971; Melson, Thompson, and van Andel, 1968; Tómasson and Kristmannsdóttir, 1972).

A summary of the reported chemical trends for both low temperature and high temperature alteration is presented in table 1; the net effects on the basalt chemistry are given to compare high and low temperature trends. A summary of consistent changes in low temperature environments includes a net addition of K, Rb, Cs, Fe^{+3}, H_2O, U, B, and Li, and a net loss of Ca, Mg, and Si from the basalt exteriors or interiors depending upon the degree and duration of alteration. High temperature alteration shows a loss of metals from pillow interiors, principally Mn, Fe, Co, Au, Ag, S, Ca, K, and Si and an addition of H_2O and Mg to pillow interiors. These trends are closely paralleled by experimental hydrothermal alteration where Mg, Na, and H_2O are added to the rock but Ca, K, Fe, Mn, Si, and some transition metals are lost. These phenomena may be superimposed, and distinction between them can be difficut. The clearest contrast between low temperature alteration and high

temperature deuteric or hydrothermal alteration is shown by Mg and K exchange trends.

Several questions remain: Can the high temperature alteration by deuteric and hydrothermal fluids be distinguished? Deuteric alteration by volatiles indigeneous to the magma should contrast significantly from hydrothermal alteration by seawater. Do unambiguous criteria for distinction between deuteric and hydrothermal alteration exist? How do the alteration trends of glasses interstitial to crystals differ from whole rock alteration trends? Can the effects of crystal fractionation upon these glasses be distinguished from the effects of alteration? Can high and low temperature alteration be distinguished in the glasses? Are the secondary fillings in cracks or veinlets a result of a closed system redistribution of the internal composition during high or low temperature alteration? Or are these veinlets the results of an open system influx of seawater during or after cooling? Are all pillows affected by at least some high temperature alteration?

A detailed microprobe study of glass in young rift valley lavas has been carried out to distinguish among the effects of (1) low temperature alteration, (2) high temperature alteration, and (3) crystal fractionation and to attempt to answer other questions above. Glassy rims, glass interstitial to quench crystals, phenocrysts, microphenocrysts, quench crystals, and secondary filling in cracks in these pillows were analyzed. In modeling the alteration process, it will be assumed that the glass rims with no visible alteration and no quench crystals represent the chemistry of the original magma feeding the lavas.

The basalts selected for study were dredged from the rift valley walls of the Mid-Atlantic Ridge between 25 and 30°N during the Trans-Atlantic Geotraverse project conducted by the National Oceanic and Atmospheric Administration in 1971 and 1972. From spreading velocities based upon magnetic anomalies (McGregor and Rona, 1975), a *maximum* age of 0.4 m.y. is indicated for these pillows. Because the rocks were dredged from depths greater than 2.5 km, volatile escape should not be a factor that affected glassy margins.

METHOD OF STUDY

Distributions of K, Fe, Mn, and Mg were chosen to characterize the nature of chemical variations in these glasses, and these elements were determined by electron-beam microanalyzer (microprobe). The methods of microprobe analysis are similar to those discussed in Scott (1971) and the same instrument at Kline Geology Laboratory, Yale University was used. A 15 KV potential, a low sample beam current of 5 nano-amps, and a 10 micron diameter electron beam did not create vaporization pits in basaltic glass, and no loss of K was recorded with time. The elements that were chosen for analysis identify either the nature or degree of alteration mechanisms. Because of the initial low K content of tholeiitic mid-ocean ridge basalts and the relatively high K content of seawater, K should serve as a sensitive indicator of alteration. Mg should also be a

TABLE 1

Low temperature alteration (halmyrolysis)

Study	Net addition to basalt	Net loss from basalt	Interpretation
R. Hart (1970)	K Fe Ti P Mn (slight)	Si Ca Mg Na	Submarine weathering increases with age.
Aumento (1971)	U		Submarine weathering increases with age.
Miyashiro, Shido, and Ewing (1969)	Mn Ti Fe Fe P H_2O K (in pillows)	Si Fe^{+2} Mg Ca	More altered rim than core.
Philpotts, Schnetzler, and Hart (1969)	K		Low temperature alteration, little effect on rare-earth elements.
Scott and Frank (1974)		S	Rim has original high S content, interior altered.
Hart and Nalwalk (1970)	H_2O Fe^{+3}	Ca Si	Either deuteric or low temperature.
S. Hart (1969)	K Rb Cs		Altered rims, fresh interior.
Melson (1973)	K Fe Ti	Ca Mg P Na Mn	Palagonitized glass more altered than rims.
Thompson (1973)	H_2O K B Li Fe^{+3} Rb Sr V Zr Pb P	Ca Mg Si Co	Generally the degree of alteration of the outer glass is greater than the interior; fresh glass occurs in young pillows just beneath the altered glass.
Shido, Miyashiro, and Ewing (1974)	K Fe^{+3}	Fe Mg	Fresh pillows have altered interior and fresh glass rim.
	Fe Fe^{+3} Ti P H_2O	Ca	Weathered pillows have glass rims that are highly altered relative to less altered interiors.

TABLE 1 (continued)

Study	Net addition to basalt	Net loss from basalt	Interpretation
High temperature alteration (including deuteric and hydrothermal alteration)			
Keays and Scott (1976)		Au Ag S Si Mn Fe	Fresh glass exterior of young pillows, but deuteric alteration of interior; K added to interior by low temperature alteration.
Superimposed hydrothermal or hydrous metamorphic alteration (natural)			
Miyashiro, Shido, and Ewing (1971)	H_2O	Ca	
Tómasson and Kristmannsdóttir (1972)	Mg	Ca K Si	Hot seawater reaction with basalts.
R. Hart (1973)	K Mg Na	Si Ca Fe Mn	Both metamorphism and low temperature formation of smectites; K added by low temperature alteration.
Humphris (1975)	Mg H_2O	Si Ca	Fe^{+2}/Fe^{+3} and Na behavior differ with different types of metamorphism.
Experimental hydrothermal alteration			
Hajash (1975)	Mg Na H_2O	Ca K Fe Mn Si Cu	Experiments at 200° to 500°C, 500-800 bars, natural seawater and oceanic basalt. Two week duration of experiments.
Mottl, Corr, and Holland (1974)	Mg Na H_2O	Ca K Fe Mn	Experiments under nearly same conditions as Hajash (1975) but several months duration.
Bischoff and Dickson (1975)	Mg	Si Ca Fe Mn Cu Ni	Experiments at 200°C, 500 bars, and 4752 hrs.

sensitive test of crystal fractionation. Fe and Mn were picked, because they play important roles in the formation of metalliferous sediments on ridge crests (Dymond and others, 1973) and because hydrothermal Mn deposits are found on the rift wall of the Mid-Atlantic Ridge at 26°N (M. Scott and others, 1974; R. Scott and others, 1974) with abnormally abundant weak-acid-soluble Fe and Mn particulate matter suspended in the overlying water column (Betzer and others, 1974). Whole rocks were also analyzed to compare net chemical variations with glass variations within pillows; these analyses were done by a Model 306 Perkin-Elmer atomic absorption spectrophotometer. A spectrophotometric molybdate blue method was used for silicon determinations. Water analyses on whole rock samples were determined by weight additions to magnesium perchlorate from vapors produced by heating rocks to 1000°C. The Texas A&M University TRIGA reactor was used for rare-earth element analyses of glass rims by instrumental neutron activation analysis following methods described by Corliss (ms) and Gordon and others (1968).

RESULTS

Although the extensive evidence outlined in the introduction indicates that young pillow basalts can have quenched glass rims that act temporarily as closed chemical systems, the pristine chemical character of the rims of pillows used in this study must be established before comparisons with altered portions of pillows can be used to determine the degree and nature of alteration. Large lithophile ions behave in a similar manner in processes of melting within the mantle; they are partitioned strongly toward the melt phase (Hubbard, and Gast, 1970). Thus a comparison of two large ion variations that have drastically different behaviors during alteration should be a good measure of the presence or absence of alteration. One of the most sensitive indicators of alteration that can be readily measured is the K content, and some of the least mobile ions during *initial* alteration are the rare-earth elements. The La/Sm ratio covaries with K_2O wt percent in glass rims with no visible alteration (fig. 1). Because the relative abundance of larger rare earth elements increases with K, it is concluded that both the La/Sm ratio and K variations are related to original magma chemistries (Scott and others, 1973). Only highly altered rock registers significant changes in La/Sm ratios (Thompson, 1973).

Chemical Zonation in Pillows

This study concentrates upon a comparison of the chemical variations within the pillow interior with the fresh glass rim; the outermost and most altered zone of Thompson (1973), the palagonitized glass, is very thin or essentially absent in many of these young pillows (Hekinian and Hoffert, 1975). One palagonite was investigated by microprobe, and the chemical variation between the botryoidal Liesegang-like zonations within the palagonite were so extreme that detailed explanations were

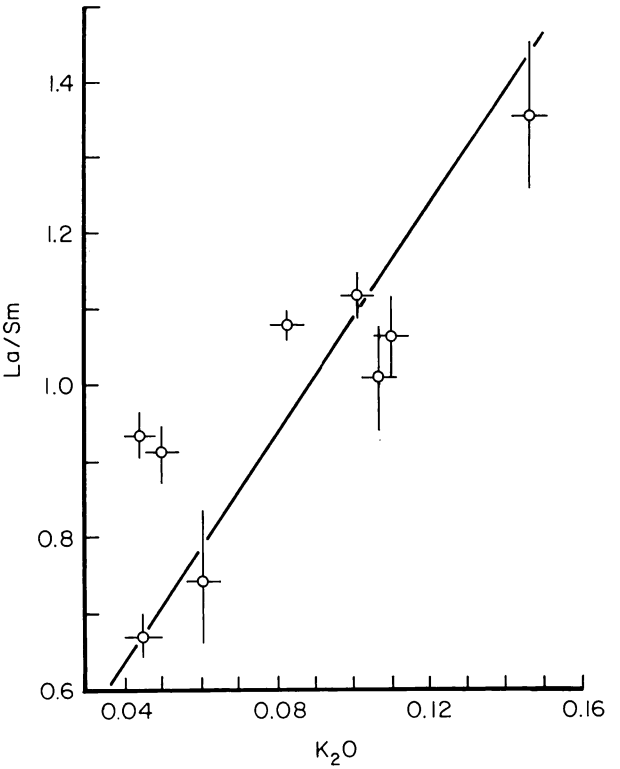

Fig. 1. Plot of La/Sm ratios versus K_2O wt percent in fresh glass margins. Bars indicate one standard deviation. Other chemical data for these pillows are listed in table 3 from T3-72D254-16-15 through T3-72D249-7A4. This covariance suggests that abundances of the large ions K and La are related to original magma chemistries and that the K abundances in the fresh glass margins have not been appreciably affected by reaction with seawater.

difficult (unpub. data). The altered interior zone recognized by Thompson was studied in detail.

In one phenocryst-poor pillow (10C19), seven zones were recognized by visual criteria and were separated for whole rock analysis. Four interior zones, distinguished by microscopic textural or coloration differences, were analyzed by microprobe. From the rim to the interior, visible zones include (1) a fresh glass rim, (2) a transition zone between fresh glass to a variolitic zone containing patches of feathery, cross-hatched, skeletal olivines, (3) a gray variolitic zone where variolites coalesce, (4) a yellowish variolitic zone, (5) a largely microcrystalline gray zone without variolitic textures, (6) a distinct dark gray band aligned parallel to the pillow exterior and to radial cracks within the pillow, and (7) the seemingly unaffected, crack-free interior portions (fig. 2). The interior of phenocryst-poor pillows consists of texturally homogenous skeletal intergrowths of "lantern-shaped" olivine, "belt-buckle-shaped" chains of plagioclase, plu-

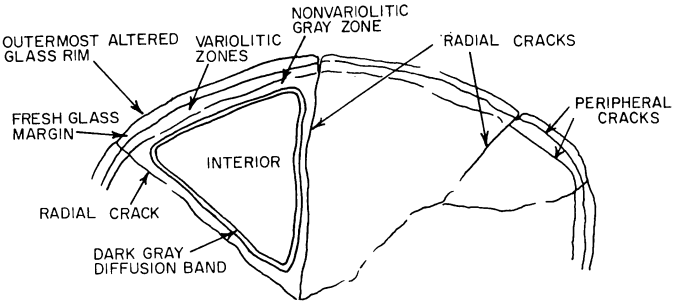

Fig. 2. Typical zones and cracks in a pillow. The pillow diameters are typically 0.5 to 1 m. The thickness of the peripheral zones are exaggerated for clarity; in most cases, they are only a few centimeters thick.

mose intergrowths of plagioclase and pyroxene, and skeletal magnetite with only a little interstitial isotropic glassy material. Zones 1 through 5 concentrically ring the pillow margin and are obviously texturally related to progressive crystal growth during cooling of the pillow. Small concentric cracks commonly separate these zones into thin layers; other cracks radiate from the pillow interior (fig. 2). The gray non-variolitic zone extends along these radial cracks into the pillow interior. The dark gray zone forms a Liesegang-like inner sheath within uncracked pillow interiors; this concentric arrangement of zones suggests a diffusion origin for zones 5 and 6 and probably postdates cooling and crystallization.

Phenocryst-rich pillows, such as 10C4 of table 2 are less distinctively zoned, although the quenched textures are similar to those described for phenocryst-poor pillows. These phenocryst-rich pillows have abundant cracks that extend from phenocryst to phenocryst and make a three-dimensional network of cracks rather than a simple pattern of radiating cracks as sketched in figure 2. Therefore, this study concentrated upon the phenocryst-poor examples (10C19 in table 2 and all the pillows listed in table 3).

Whole rock analyses of zones.—The most conspicuous changes in chemistry are K variations from low values at the fresh margin to very high values in the dark gray band and intermediate values in the interior portion that has no obvious visible signs of alteration (fig. 3, tables 2 and 3). The degree of K enrichment in the interior ranges between 1.3 to 2.8 and averages 1.7 times the content in the glass margin, and the degree of K enrichment in the dark gray band varies between 1.5 to 4.5 and averages 2.7 times the content in the margin. Although this is significantly higher than the enrichment in the interior, the volume of the dark gray band is calculated to be less than 3 percent of the volume of the interior. Although Fe generally varies less than a factor of 1.1, in contrast to the factor of 3 to 4.5 variation of K, the Fe variations are significant; an average of 0.5 wt percent FeO decrease occurs in the interiors with five of the eight pillows showing a decrease between 0.4 and 1.2,

TABLE 2

Sample number	SiO_2	Al_2O_3	FeO_T	MnO	MgO	CaO	Na_2O	K_2O	H_2O^+	H_2O^-	Description of zone and distance from pillow margin	
T3-71D159-10C19-1	48.8	14.0	10.7	0.207	9.9	10.4	2.72	0.050	0.35	0.29	freshest glass with no visible alteration	0-1 cm
2	49.2	14.0	10.4	0.204	9.9	10.6	2.63	0.059	0.50	0.09	transition to gray variolitic zone	1-2 cm
3	48.7	14.1	10.3	0.207	9.8	10.3	2.63	0.071	0.77	0.52	gray variolitic zone	2-3 cm
4	49.1	14.5	10.5	0.204	9.2	10.4	2.72	0.062	0.74	0.16	yellow variolitic zone	3-4 cm
5	48.1	14.6	11.0	0.201	9.7	10.8	2.67	0.076	0.57	0.10	gray nonvariolitic zone	4-6 cm
6	48.2	14.1	11.1	0.207	9.8	10.4	2.63	0.227	0.77	0.08	dark gray diffusion band along cracks	6-7 cm
7	49.4	14.6	10.1	0.197	9.8	10.8	2.67	0.142	0.36	0.04	interior, uniform	7-50 cm
Pillow position and location: 29°47′N, 42°44′W, between 2750 and 1920 m depth, on eastern wall of median valley												
T3-71D159-10C4-1	49.3	14.2	10.0	0.175	10.8	10.2	2.41	0.044	0.27	0.06	freshest glass with no visible alteration	0-1.5 cm
2	47.5	14.2	10.4	0.182	11.2	10.6	2.42	0.032	0.61	0.22	brown variolitic zone	1.5-3 cm
3	49.2	14.3	9.9	0.192	12.0	10.6	2.26	0.064	0.29	0.04	dark gray diffusion band along cracks	3-4 cm
4	49.5	15.0	9.0	0.154	11.1	10.9	2.17	0.076	0.67	0.12	interior of uncracked regions	4-- cm
Pillow position and location: 29°47′N, 42°44′W, between 2750 and 1920 m depth, on eastern wall of median valley												
One standard deviation (error)	±0.5	±0.4	±0.2	±0.005	±0.1	±0.2	±0.04	±0.005	±0.02	±0.005		

Wt percent of oxides. FeO is total iron. Al_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O were determined by atomic absorption spectrophotometry. SiO_2 was determined by the molybdate blue spectrophotometric method. H_2O^- was determined by wt loss at 110°C. Total H_2O was determined by wt addition to magnesium perchlorate from rock vapors produced by heating rock to 1000°C.

two showing no significant change, and one showing a 0.3 wt percent increase. The trend in Mn is not as distinct: of eight pillows analyzed, five show decreases and three show increases in the interior relative to glassy margins ranging between −0.021 and +0.005, averaging −0.007 wt percent MnO, a net decrease of Mn. Because the MnO analyses have a precision of ±0.005 wt percent, this apparent decrease cannot be taken as significant.

Microprobe analyses of glass in zones.—Two pillows, 10C19 and 10C4, were studied by microprobe to identify small scale variations of K, Fe, Mn, and Mg in interstitial glass and in secondary crack filling material. Chips and polished thin sections from most of the zones listed in table 2 were used in this microprobe study.

Figure 4 summarizes the wt percent variations in MgO, FeO, and K_2O in glass from zones of pillow 10C19. The principal departures from

TABLE 3

Sample number	FeO	MnO wt %	K_2O	Description of zone
T3-72D254-16-3A	9.2	0.168	0.106	fresh glass at margin
16-3B	8.7	0.164	0.160	interior
16-3C	9.4	0.156	0.269	dark gray diffusion band
T3-72D254-16-5A	9.0	0.160	0.099	fresh glass at margin
16-5B	8.4	0.156	0.184	interior
16-5C	8.7	0.142	0.219	dark gray diffusion band
T3-72D254-16-6A	8.9	0.162	0.106	fresh glass at margin
16-6B	8.7	0.164	0.182	interior
T3-72D254-16-7A	9.0	0.161	0.096	fresh glass at margin
16-7B	9.3	0.164	0.138	interior
T3-72D254-16-8A	9.6	0.165	0.102	fresh glass at margin
16-8B	8.4	0.156	0.136	interior
16-8C	9.3	0.159	0.289	dark gray diffusion band
T3-72D254-16-11B	9.0	0.161	0.110	fresh glass at margin
16-11B	9.0	0.166	0.181	interior
T3-72D254-16-15	9.6	0.175	0.122	fresh glass at margin
Dredge position and location: 26°30.1′N, 44°34.6′W, depth 3468 m, east wall of median valley, six pillows at dredge site 16 listed.				
T3-72D254-17-26	7.7	0.151	0.061	fresh glass at margin
Pillow position and location: 26°44.5′N, 44°37.2′W, depth 3486 m, west wall of median valley.				
T3-72D251-12-74	9.0	0.175	0.101	fresh glass at margin
Pillow position and location: 25°45.9′N, 45°9.8′W, depth 4304 m, west wall of median valley.				
T3-72D253-13-7	9.0	0.182	0.138	fresh glass at margin
Pillow position and location: 26°8.0′N, 44°45.0′W, depth 2994 m, east wall of median valley.				
T3-72D251-10-24	9.5	0.179	0.083	fresh glass at margin
Pillow position and location: 25°40.5′N, 45°4.6′W, depth 4327m, east wall of median valley.				
T3-72D249-7A4	9.7	0.185	0.107	fresh glass at margin
Pillow position and location: 25°18.2′N, 45°18.4′W, depth 3618 m, east wall of median valley.				

Use table 1 explanation.

the glass rim are (1) an order of magnitude decrease in MgO content in the interior, (2) two orders of magnitude increase in K_2O in the dark gray band and a factor of 4 increase in the interior, (3) a factor of 3 increase in FeO in the dark gray band and a factor of 1.4 increase in the interior, and (4) no significant MnO change. In pillow 10C4 similar but less dramatic changes in glass composition are found (fig. 5).

Sets of polished thin sections through pillow 10C19 were analyzed (fig. 6) in considerably greater detail and show very similar trends that include: (1) a MgO decrease by a factor of 2.5 at intermediate zones and 1.7 in the interior, (2) a K_2O increase by a factor of 5 in the interior, (3) an FeO decrease by a factor of 1.4 at intermediate zones and increase by 1.2 in the interior, and (4) a MnO decrease by a factor of 2 only in the intermediate zones.

Crack filling material.—Most cracks studied in polished sections did not contain secondary filling material and showed no visible evidence of alteration along the walls except for local oxidation of iron in residual glass; even skeletal and phenocryst olivine appear to be unaltered. Several cracks in pillow 10C19, containing secondary alteration products in cracks between probe positions 10 and 13 in figure 6, show yellowish-brown, reddish-brown, dark brown, and almost opaque black amorphous patches along cracks. These patches are unusually rich in Fe, Mn, and K; in general, brown correlates with higher Fe content and black with higher Mn content; the K abundance seems to be independent of color or Fe and Mn abundances. Table 4 summarizes the chemistry of the largely isotopic, crack-filling material. The MnO and FeO contents exceed 50

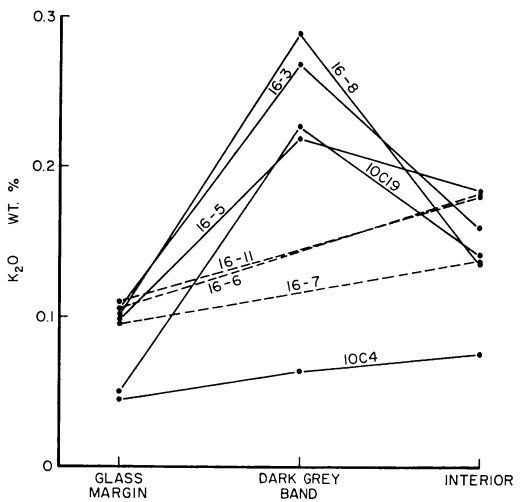

Fig. 3. Whole rock K_2O wt percent of fresh glass margins, the dark gray band, and the interiors of pillows. The numbers refer to the dredge sites and specimen numbers of samples in tables 2 and 3. Dashed lines are used for pillows where no diffusion bands were analyzed.

wt percent, and K_2O values reach 3.5 wt percent. The range in composition along any one crack may cover the extremes listed in table 3.

DISCUSSION

The validity of this study is based upon the explicit assumption that the glass margin has effectively acted as a closed system to K, Mn, Fe, and Mg. Evidence summarized in figure 1 and accompanying text support this assumption for these pillows, and other researchers find no exceptions for young deepsea pillows that have glassy rims with no visible signs of alteration (table 1).

Because the chemical exchange between seawater and rock is a function of the degree of penetration of seawater into the pillow interior and the thermal state of the pillow during penetration, the physical

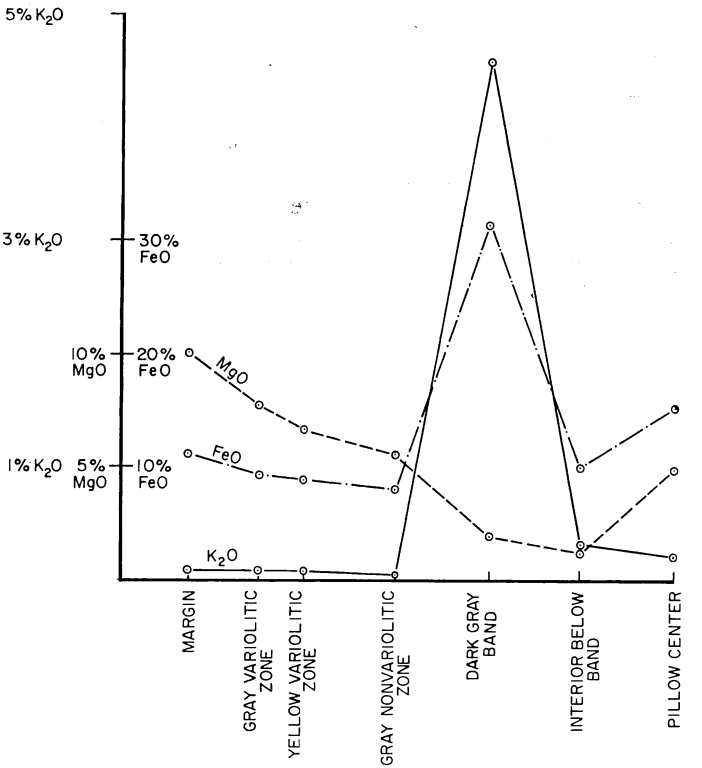

Fig. 4. Microprobe analyses of glass chips from zones in pillow 10C19. The horizontal axis indicates the relative position in the pillow and is not drawn to scale; the vertical axis has different scales for MgO, FeO, and K_2O wt percent. Solid line = K_2O, dashed line = MgO, dash-dot line = FeO. MnO variations are insignificant and are not shown. Distances of analyzed positions from the margin are listed and given in table 2 except for the "interior below band" position (9 cm below the margin) and "pillow center" position (50 cm below the margin). All four elements were measured simultaneously.

events during cooling of the pillows should be reviewed. The process of cooling from an extrusion temperature of about 1200°C to ambient seafloor temperatures of 2°C can be subdivided into four categories of density increases: (1) as the molten phase quenches to a glass and cools from 1200° to 1100°C, (2) during cooling of the glass from 1100° to 2°C, (3) during crystallization of olivine, plagioclase, and pyroxene at about 1100°C, and (4) during cooling of crystalline phases from about 1100° to 2°C. These density changes are calculated from thermal expansion data (Skinner, 1966) and density data (Daly, Manger, and Clark, 1966) to be (1) 1.2 percent, (2) 2.7 percent, (3) 5.5 percent, and (4) 2.7 percent. This means that the outer glass rim undergoes a total density increase or volume decrease of about 3.9 percent, but the nearly crystalline interior undergoes about a 9.4 percent decrease. However, these volume decreases must be considered sequentially to follow the development of cooling cracks. Initial quenching of the glass rim about a molten interior creates sets of radially aligned cracks that migrate inward with retreating isotherms as the exterior skin volume decreases. Thus, seawater has an avenue of penetration to the cooling molten front. However, when the more slowly cooling interior begins to crystallize, the volume of the solid phases decreases considerably, and the rigid skin of the pillow retains the pre-crystallization volume of the entire pillow. One response to this condition is the formation of concentric cracks at the boundary between glass and crystalline interior. Another related feature is the occurrence of irregular voids in the pillow interiors. Seawater or possibly deuteric fluids probably occupy these voids.

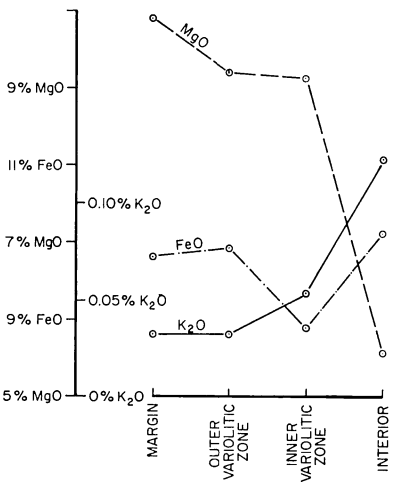

Fig. 5. Microprobe analyses of glass chips from zones of pillow 10C4 described in table 2. The horizontal axis indicates relative position in the pillow, and the vertical axis has different scales for MgO, FeO, and K_2O wt percent. MnO variations are insignificant and are not shown. Solid line = K_2O, dashed line = MgO, dash-dot line = FeO. All four elements were measured simultaneously.

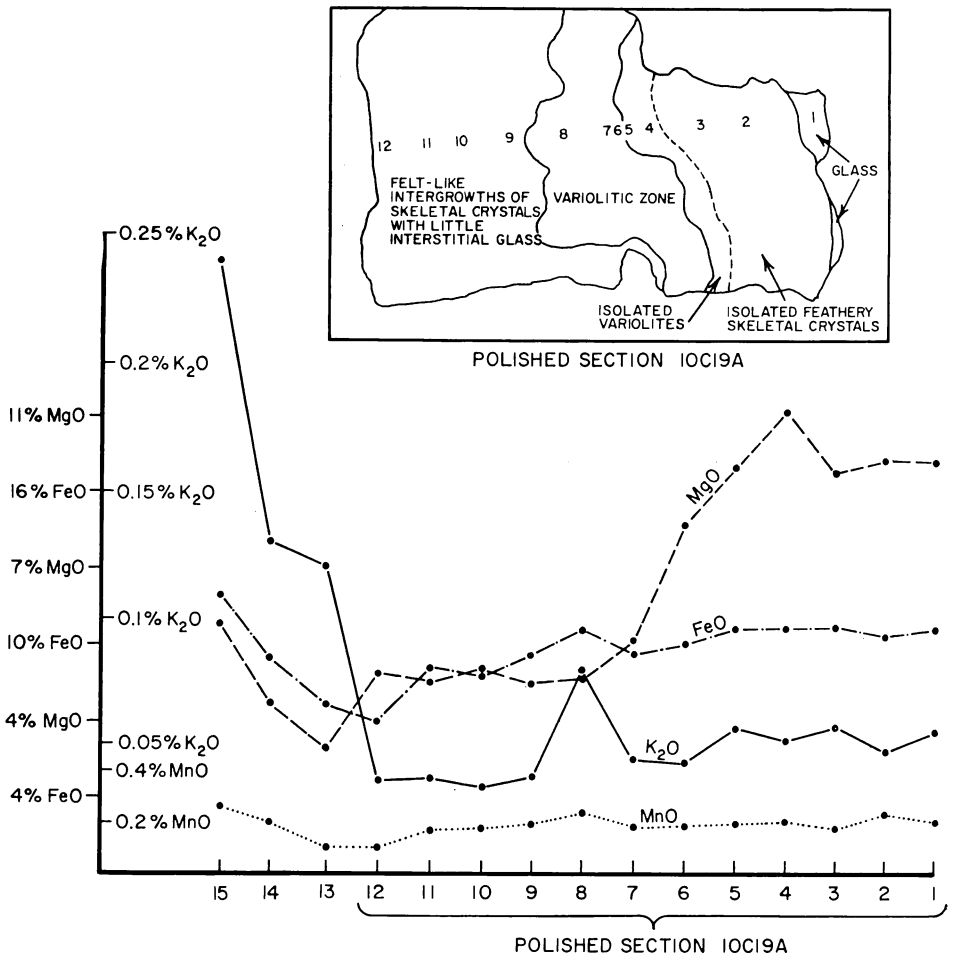

Fig. 6. Microprobe analyses of glass within polished thin sections from pillow 10C19. The sketched section 10C19A is 24 by 46 mm and covers zones from the glass margin on the right into the interior. The numbers mark the position of analyzed interstitial glass; these correspond to the numbers on the horizontal axis of the plot of MnO, K_2O, MgO, and FeO wt percent versus relative position in the pillow. The vertical axis has four scales. Solid line = K_2O, dashed line = MgO, dash-dot line = FeO, dotted line = MnO. Position 13 on the horizontal axis marks the relative position of a relatively fine-grained skeletal crystal zone about 6 cm from the pillow margin from polished section 10C19B1, position 14 is from a coarser-grained zone about 8 cm from the margin from polished section 10C19B2, and position 15 is close to the center of the pillow about 50 cm from the margin from polished section 10C19D. All four elements were measured simultaneously.

Crystal fractionation will produce changes in the composition of residual glass that should increase with increasing crystallinity of the pillow interior. This effect may be modified and superimposed by (1) high temperature exchange of seawater with the cooling pillow, (2) reaction between the aqueous fluids concentrated and segregated during crystal fractionation and the cooling glasses and crystalline phases (that is, deuteric alteration) and (3) low temperature exchange of seawater with the cool pillow.

K variations.—A distinct net addition of K from seawater to the interior of the pillows is required by the data shown in figure 2. Experiments at high temperatures (Hajash, 1975; Mottl, Corr, and Holland, 1974; Bischoff and Dickson, 1975) and natural alteration reactions at high temperatures (Tómasson and Kristmannsdóttir, 1972) indicate that K is removed from the solid phases to seawater. On the other hand natural alteration (Thompson, 1973) and experiments at low temperatures (Scott, Burkett, and Leaird, 1970) indicate that K is added to solid phase. Therefore, the relatively slow exchange of K at low temperature must be the dominate process in the pillow selected for this study. It is possible that the temperature dependence of the direction of alkali exchange between seawater and basaltic glass may be similar to K exchange between alkali feldspars and alkali-bearing solutions (Orville, 1963) in which K-rich solid phases are favored at low temperatures and a relatively K-rich aqueous phase is favored at higher temperatures. The increase of K in the interior does not indicate an absence of high temperature reactions; it simply means that the net effect of low temperature reactions was larger. Apparently, the glass margin is bypassed by flow of seawater along radial cracks to the largely crystalline interior where relatively rapid penetration occurs along crystal boundaries. Diffusion

TABLE 4

Position	FeO	MnO	K_2O	Description
11* in 10C19 A	27.6	11.8	3.56	brown amorphous patch
11 in 10C19 A	17.1	1.03	0.28	pale brown discolored regions along same fracture
11 in 10C19 A	53.4	0.26	0.01	rich brown alteration patch
12 in 10C19 A	30.7	8.05	2.97	brown amorphous patch
12 in 10C19 A	33.0	0.26	3.53	yellowish brown patch along same fracture
12 in 10C19 A	24.1	18.8	2.93	dark brown patch along same fracture
12 in 10C19 A	1.17	53.8	1.14	black opaque patch along same fracture
12 in 10C19 A	1.31	55.4	0.29	another black opaque patch along same fracture
13 in 10C19 B	17.9	0.37	0.00	dark rim around a vesicle

* Approximate microprobe position number shown in figure 6.

of large ions through glass is much slower (Moore, 1966; Hekinian and Hoffert, 1975), and, therefore, alteration of the glass lags behind the interior during initial alteration.

In whole rock samples from the interior of 10C19 the K values are 2.8 times the glass rim values, but microprobe values of the residual glass in the interior are 5 times glass rim values (figs. 4, 5, and 6); in other words, the interior glass is 1.8 times more K-rich than the interior whole rock. Since conservative estimates of the degree of crystallization in the interior leave less than 10 percent residual glass, the glass should be far richer in K than observed if all the excess K resides in interstitial glass. In fact, if the whole rock value for K were the same as the rim (with no secondary K influx and only fractional crystallization concentration of the K in the remaining glass) the interior glass should have at least 0.44 wt percent K_2O rather than the 0.25 percent K_2O observed. (This calculation includes the measured 0.013 percent K_2O that exists in the 45 volume percent plagioclase present.) To take into account the addition of K necessary to have a whole rock value of 0.142 percent K_2O in the pillow 10C19 interior, with a minimum of 90 percent crystallization, the K_2O content of the interior glass should be about 1.36 percent K_2O. Thus, the dilemma is not the abundance of K but the low values in the glass. Where then does the excess K reside? The possibility of some late-stage K bearing phase crystallizing from deuteric fluids is considered unlikely, because extensive scanning by microprobe failed to reveal its existence. Also, no evidence was found to suggest that K was concentrated along grain boundaries. Probably, this K occurs in the amorphous material locally filling cracks and coating vesicle walls formed during low temperature alteration. As shown in table 4 some of this material contains 3.5 wt percent K_2O. Nearly 3 percent of the interior would have to consist of altered regions, fracture fillings, and vesicle linings to account for this amount of K. There may well be this much secondary alteration material present, but a quantitative measure of such dispersed material would take a study far more extensive than this one. The dark gray bands have the highest Fe, K, and H_2O in the whole rock (fig. 3) and the highest Fe and K values in the glass (fig. 4). Because the dark gray bands have a Liesegang-like concentrically banded geometry to both radial and peripheral cracks, their origin probably is the same as Liesegang rings, that is, a diffusion origin. The fact that ions as similar as K^+ and H_3O^+ (?) migrate together is not surprising, but the correlation with Fe is more puzzling. The answer may lie in the observation of abundant fine-grained opaque material (iron oxides?) in the dark gray band. The presence of the dark gray band, of apparent diffusion origin, creates an additional problem. The K values in the interior zone, deeper within the pillow than the dark gray band, are higher in K than the glassy margin, as discussed above. Then how does the K diffusion that permeates the pillow interior differ from the K, Fe, and H_2O diffusion that only penetrates to the dark gray band? Probably two mechanisms of

diffusion are necessary to explain the K abundances, because the dark gray band represents a sharp discontinuity in K distribution. A simple diffusion gradient based upon the proximity of seawater along the cracks can explain the K and water-rich dark gray band, but the uniform 4-fold increase of K in the interior must have occurred at a greater rate without significant penetration by water. Detailed knowledge of the ionic species and complexes involved in crystal boundary diffusion should provide an answer. Knowledge of the controls of K variations should also be of value in interpretation of ^{40}Ar dating (Seidemann, 1973).

Mg variations.—Because there is no significant trend in the whole rock MgO values from the margin to the interior (table 2), the pronounced decrease in MgO content of residual glasses in the interior is interpreted as a fractional crystallization trend. Although some loss of Mg in the interior glass may be related to a low temperature loss (table 1), it is highly improbable that relatively fresh appearing glasses have lost 50 percent of their Mg by such exchanges. In a qualitative measure, the reduction of MgO can be correlated with increasing crystallinity supporting the conclusion that crystal fractionation is the primary cause of this trend.

Fe and Mn variations.—The variations of Fe and Mn within these pillows are more difficult to explain than K variations. Although whole rock evidence (tables 2 and 3) makes a good case for a net loss of Fe from pillow interiors, the microprobe data shown in figures 4, 5, and 6 suggest that the FeO values in residual glass in the interior are about 2 wt percent higher than in the margin glass. A partial explanation for this increase probably is simple crystal fractionation creating Fe enrichment in residual glass. It is also possible that some low temperature addition of Fe is involved, as demonstrated for the dark gray band. In contrast, no consistent and significant additions or losses of Mn were detected in the interior by whole rock analysis or in the pillow center by microprobe studies. From microprobe studies of pillow 10C19, there is a definite decrease in both Fe and Mn in residual glass in the intermediate zones between analyzed positions 8 and 14 shown in figure 6. Cracks occur within zones that are locally filled with amorphous Fe- and Mn-rich material. Calculations suggest that this loss of iron can be accounted for quite reasonably by local solution and reprecipitation within these cracks without a net loss of Fe or Mn from the pillow. The amount of Mn lost from these zones, assuming a perfect spherical shape to the 50 cm radius pillow 10C19 is about 20 g. Only 0.013 wt percent of the zone between analyzed positions 10 and 13 would have to consist of amorphous manganese-rich patch-filling fractures (50 wt percent MnO, table 4) to account for all Mn lost from these zones.

Pillow 10C19 also shows a loss of about 625 g of Fe from the glass between analyzed positions 8 and 14. In this case about 0.35 wt percent of the rock between these positions must consist of Fe-rich patches (50 wt percent FeO, table 4) to account for Fe redistribution without a

net loss of Fe from the pillow. If these secondary enrichment patches are scattered within the entire pillow, only 0.11 wt percent of the pillow would have to consist of secondary patches. Again, the net loss of an average of 4.5 percent of the Fe in whole rock pillow interiors is supported by whole rock analyses reported here.

Thus, two Fe trends have to be explained: a net whole rock decrease toward the center but a local increase in the residual glass in the center. Presumably, the net loss of iron observed in the pillows can be attributed to the superimposition of smaller effects of some additive process and larger effects of some subtractive process. The small additive process may be the redistribution of Fe during crystal fractionation enriching residual glass or a net addition of iron by low temperature influx of seawater-carried Fe (Miyashiro, Shido, and Ewing, 1969; R. Hart, 1970; Moore, 1966). This second possibility is considered unlikely, because the rocks that have gained Fe by low temperature alteration are generally more extensively altered than the rocks studied here. The large subtractive process probably occurred at elevated temperatures during initial cooling of pillows. During the initial cooling stage, gradients of decreasing oxygen fugacity and increasing temperature gradients probably exist toward the pillow center. Because oxidation-reduction boundary curves have positive oxygen fugacity versus temperature slopes, the solution of Fe^{+2} is favored at high temperatures, and net Fe loss from the interior may occur by loss of Fe-rich fluids by a mechanism similar to that suggested by Corliss (1971).

CONCLUSIONS

From the study of these pillow lavas, we conclude that significant alteration occurs within young petrographically "fresh" pillows which are dredged from rift valley walls only a few kilometers from the median valley axis. The glass rim near the pillow margin is confirmed to be a pristine unaltered, chemically closed, reference system. K diffusion into pillow interiors during low temperature alteration (or submarine weathering) has caused a net increase in the K values to nearly twice those of the unaffected margin. Penetration of this K occurred by diffusion along radial cracks into the more crystalline interior where crystal boundaries were probably used for diffusion paths. Enrichment of residual glass cannot account for all the K added; appreciable K must exist in secondary crack filling pockets. Although there is an average net loss of Fe from the pillow interiors, the residual glasses have somewhat higher Fe contents than do the glass margins; the net loss is attributed to high temperature reactions during cooling and crystallization. The higher residual glass values may reflect Fe-enrichment by crystal fractionation. Some Fe and Mn, originally in residual glass from intermediate zones within the pillows, appear to have been redistributed as secondary fracture filling patches. The decrease of Mg values in glass from the interior but constant Mg values throughout the whole rock pillow suggest that crystal fractionation was the principal cause of Mg variations in glass in these

pillows. No unambiguous criteria to distinguish between deuteric and high temperature hydrothermal alterations were found. The ambiguities and uncertainties that still remain, particularly in regard to the Fe and Mn make us appreciate Mark Twain's comment, "The researches of many commentators have already thrown much darkness on this subject, and it is probable that, if they continue, we shall soon know nothing at all about it."

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REFERENCES

Aumento, F., 1971, Uranium content of mid-ocean basalts: Earth Planetary Sci. Letters, v. 11, p. 90-94.

Betzer, P. R., Bolger, W. G., McGregor, B. A., and Rona, P. A., 1974, The Mid-Atlantic Ridge and its effect on the composition of particulate matter in the deep ocean [abs.]: Am. Geophys. Union Trans., v. 55, p. 293.

Bischoff, J. L., and Dickson, F. W., 1975, Seawater-basalt interaction at 200°C and 500 bars: implications for origin of sea-floor heavy-metal deposits and regulation of seawater chemistry: Earth Planetary Sci. Letters, v. 25, p. 385-387.

Bryan, W. B., 1972, Morphology of quench crystals in submarine basalts: Jour. Geophys. Research, v. 77, p. 5812-5819.

Corliss, J. B., ms, 1970, Mid-ocean ridge basalts: Ph.D. dissert. Univ. California, San Diego, 148 p.

———— 1971, The origin of metal-bearing submarine hydrothermal solutions: Jour. Geophys. Research, v. 76, p. 8128-8138.

Daly, R. A., Manger, G. E., and Clark, S. P., 1966, Density of rocks, *in* Clark, S. P., ed., Handbook of Physical Constants, revised ed.: Geol. Soc. America Mem. 97, p. 19-26.

Dymond, J., 1970, Excess argon in submarine basalt pillows: Geol. Soc. America Bull., v. 81, p. 1229-1232.

Dymond, J., Corliss, J. B., Heath, G. R., Field, C. W., Dasch, E. J., and Veeh, H. H., 1973, Origin of metalliferous sediments from the Pacific Ocean: Geol. Soc. America Bull., v. 94, p. 3355-3372.

Funkhouser, J. G., Fisher, D. E., and Bonatti, E., 1968, Excess argon in deep-sea: Earth Planetary Sci. Letters, v. 5, p. 95-100.

Gordon, G. E., Randle, K., Goles, G. G., Corliss, J. B., Beeson, M. H., and Oxley, S. S., 1968, Instrumental activation analysis of standard rocks with high resolution X-ray detectors: Geochim. et Cosmochim. Acta, v. 32, p. 364-396.

Hajash, Andrew, 1975, Hydrothermal processes along mid-ocean ridges: an experimental investigation: Contr. Mineralogy Petrology, v. 53, p. 205-226.

Hart, Roger, 1970, Chemical exchange between sea water and deep ocean basalts: Earth Planetary Sci. Letters, v. 9, p. 269-279.

Hart, S. R., 1973, A model for chemical exchange in the basalt-seawater system of oceanic layer II: Canadian Jour. Earth Sci., v. 10, p. 199-816.

———— 1969, K, Rb, Cs contents and K/Rb, K/Cs ratios of fresh and altered submarine basalts: Earth Planetary Sci. Letters, v. 6, p. 295-303.

Hart, S. R., and Nalwalk, A. J., 1970, K, Rb, Cs, and Sr Relationships in submarine basalts from the Puerto Rico trench: Geochim. et Cosmochim. Acta, v. 34, p. 145-155.

Hekinian, R., and Hoffert, 1975, Rate of palagonitization and managanese coating on basaltic rocks from the rift valley in the Atlantic Ocean near 36°50'N: Marine Geology, v. 19, p. 91-109.

Humphris, S. E., 1975, Elemental fluxes during hydrothermal alteration of basalts [abs.]: EOS Am. Geophys. Union Trans., v. 56, p. 469.

Kay, Robert, Hubbard, N. J., and Gast, P. W., 1970, Chemical characteristics and origin of ocean ridge volcanic rocks: Jour. Geophys. Research, v. 75, p. 1585-1613.

Keays, R. R., and Scott, R. B., 1976, Precious metals in ocean-ridge basalts: implications for basalts as source rocks for gold mineralization: Econ. Geology, in press.

Macdougall, D., 1973, Uranium distribution in weathered marine basalts: EOS Am. Geophys. Union Trans., v. 54, p. 988.

Matthews, D. H., 1971, Altered basalts from Swallow Bank, an abyssal hill in the NE Atlantic and from a nearby seamount: Royal Soc. London Philos. Trans. A., v. 268, p. 551-571.

McGregor, B. A., and Rona, P. A., 1975, Crest of Mid-Atlantic Ridge at 26°N: Jour. Geophys. Research, v. 55, p. 740-742.

Melson, W. G., 1973, Basaltic glasses from the Deep Sea Drilling project. Chemical characteristics, compositions of alteration products, and fission track "ages": EOS Am. Geophys. Union Trans., v. 54, p. 1011-1014.

Melson, W. G., Thompson, G., and van Andel, Tj.-H., 1968, Volcanism and metamorphism in the Mid-Atlantic Ridge, 22°N Latitude: Jour. Geophys. Research, v. 73, p. 5925-5941.

Miyashiro, A. F., Shido, F., and Ewing, M., 1969, Diversity and origin of abyssal tholeiite from the Mid-Atlantic Ridge near 24° and 30° North Latitude: Contr. Mineralogy Petrology, v. 23, p. 38-52.

———— 1971, Metamorphism in the Mid-Atlantic Ridge near 24° and 30°N: Royal Soc. London Philos. Trans. A, v. 268, p. 589-603.

Moore, J. G., 1966, Rate of palagonitization of submarine basalt adjacent to Hawaii: U.S. Geol. Survey Prof. Paper 550-D, D163-D171.

———— 1975, Mechanism of formation of pillow lava: Am. Scientist, v. 63, p. 269-276.

Moore, J. G., and Schilling, J.-G., 1973, Vesicles, water, and sulfur in Reykjanes Ridge basalts: Contr. Mineralogy Petrology, v. 41, p. 105-118.

Mottl, M. J., Corr, R. F., and Holland, H. D., 1974, Chemical exchange between seawater and mid-ocean ridge basalt during hydrothermal alteration: an experimental study: Geol. Soc. America Abs. with Program, v. 6, p. 879.

Orville, P. M., 1963, Alkali-ion exchange between vapor and feldspar phases: Am. Jour. Sci., v. 264, p. 273-288.

Paster, T. P., ms, 1968, Petrologic variation within submarine basalt pillows of the South Pacific-Antarctic Ocean: Ph.D. thesis, Florida State Univ.

Philpotts, J. A., Schnetzler, C. C., and Hart, S. R., 1969, Submarine basalts: some K, Rb, Sr, Ba, rare-earth, H_2O and CO_2 data bearing on their alteration, modification by plagioclase, and possible source materials: Earth Planetary Sci. Letters, v. 7, p. 298-299.

Poldervaart, Arie, and Green, J., 1965, Chemical analysis of submarine basalts: Am. Mineralogy, v. 50, p. 1723-1728.

Scott, M. R., Scott, R. B., Rona, P. A., Butler, L. W., and Nalwalk, A. J., 1974, Rapidly accumulating manganese deposit from median valley of the Mid-Atlantic Ridge: Geophys. Research Letters, v. 1, p. 355-358.

Scott, R. B., 1971, Chemical variations in glass shards and interstitial dust of ignimbrite cooling units: Am. Jour. Sci., v. 270, p. 166-173.

Scott, R. B., Burkett, D. H., and Leaird, J. D., 1970, Experimental alteration of basaltic glass in low temperature aqueous environments: Geol. Soc. America Abs. with Program, v. 2, p. 509.

Scott, R. B., and Frank, J., 1974, Distribution of sulfur in the ocean crust: Geol. Soc. America Abs. with Program, v. 6, p. 945.

Scott, R. B., Hajash, A., Kuykendall, W. K., Rona, P. A., Butler, L. W., and Nalwalk, A. J., 1973, Petrological and structural significant of the Mid-Atlantic Ridge between 24°N and 30°N: Am. Geophys. Union Trans., v. 54, p. 249.

Scott, R. B., Rona, P. A., McGregor, B. A., and Scott, M. R., 1974, The TAG hydrothermal field: Nature, v. 251, p. 301-302.

Seidemann, D. E., 1973, Ar^{40}/Ar^{39} studies of deep-sea rocks: EOS Am. Geophys. Union Trans., v. 54, p. 990-991.

Shido, F., Miyashiro, A., and Ewing, M., 1974, Compositional variations in pillow lavas from the Mid-Atlantic Ridge: Marine Geology, v. 16, p. 177-190.

Skinner, B. J., 1966, Thermal expansion, *in* Clark, S. P., ed., Handbook of Physical Constants, revised ed.: Geol. Soc. America Mem. 97, p. 75-96.

Thompson, G., 1973, A geochemical study of the low-temperature interaction of sea-water and oceanic igneous rocks: EOS Am. Geophys. Union Trans., v. 54, p. 1015-1019.

Tómasson, J., and Kristmannsdóttir, 1972, High temperature alteration minerals and thermal brines, Reykjanes, Iceland: Cont. Mineralogy Petrology, v. 36, p. 123-134.