

## Water Content of Basalt Erupted on the Ocean Floor\*

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*Abstract.* Deep sea pillow basalts dredged from the ocean floor show that vesicularity changes with composition as well as with depth. Alkalic basalts are more vesicular than tholeiitic basalts erupted at the same depth. The vesicularity data, when related to experimentally determined solubility of water in basalt, indicate that K-poor oceanic tholeiites originally contained about 0.25 percent water, Hawaiian tholeiites of intermediate K-content, about 0.5 percent water, and alkali-rich basalts, about 0.9 percent water. Analyses of fresh basalt pillows show a systematic increase of  $H_2O^+$  as the rocks become more alkalic. K-poor oceanic tholeiites contain 0.06—0.42 percent  $H_2O^+$ , Hawaiian tholeiites, 0.31—0.60 percent  $H_2O^+$ , and alkali rich basalts 0.49—0.98 percent  $H_2O^+$ . The contents of  $K_2O$ ,  $P_2O_5$ , F, and Cl increase directly with an increase in  $H_2O^+$  content such that at 1.0 weight percent  $H_2O^+$ ,  $K_2O$  is 1.58 percent,  $P_2O_5$  is 0.55 percent, F is 0.07 percent, and Cl is 0.1 percent. The measured weight percent of deuterium on the rim of one Hawaiian pillow is  $-6.0$  (relative to SMOW); this value, which is similar to other indications of magmatic water, suggests that no appreciable sea water was absorbed by the pillow during or subsequent to eruption on the ocean floor.

Concentrations of volatile constituents in the alkali basalt melts relative to tholeiitic melts can be explained by varying degrees of partial melting of mantle material or by fractional crystallization of a magma batch.

### Introduction

Primary water content of juvenile basaltic melts originating from the earth's mantle is of interest not only because water vapor is the most abundant gas liberated during volcanic activity, but also because original water content may provide some clues to the physical-chemical mechanisms by which basalt magma is generated in the mantle.

Most water is exsolved and lost during subaerial volcanic eruptions due to the drastic reduction in confining pressure upon extrusion. The  $H_2O^+$  content of fresh lava is very low; 18 samples of tholeiitic basalt pumice and spatter from the August 1963 eruption of Kilauea volcano in Hawaii contain an average of 0.05 weight percent (Peck *et al.*, 1966). Older lavas tend to absorb meteoric water so water content increases in Hawaiian rocks of progressively greater age.

Likewise the water content of intrusions of basaltic magma are not representative of original water contents because even though water may not have been lost through vesiculation at the time of intrusion, it may have been lost during slow cooling and crystallization of anhydrous mineral phases. Moreover, during the long time required for erosion to expose basaltic intrusions, mineral alteration may grossly modify original water content.

Analysis of very young basaltic pillow lavas erupted on the ocean floor is probably the best means of determining original water content in basalt. These

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rocks have been drastically quenched to glass on their outer surfaces, and the water content has been little affected by crystallization processes. Also, such rocks can be collected directly from an environment where confining pressure is relatively high compared to surface conditions and where exsolution of volatiles is inhibited. Finally, dredging techniques enable collection of rock intruded under several thousand meters of cover while it is still fresh, a procedure impossible in other intrusive conditions.

Pillow basalts from the Hawaiian region and the Revillagigedo Islands region were collected by ships of the U. S. Coast and Geodetic Survey, those from the Juan de Fuca Ridge by the research vessel *Thomas G. Thompson* operated by the University of Washington, those from the Reykjanes Ridge by the research vessel *Trident* operated by the University of Rhode Island. The author is grateful to the scientists and crews of these ships for their efforts in dredging and making samples available. Frank C. Dodge and Donald E. White critically reviewed the manuscript.

### Vesicle Data

The volume percent of vesicles in a pillow basalt is a measure of the volatile content which was exsolved from the original melt and trapped in the rock in the short time between eruption and quenching on the ocean floor. Vesicularity of pillow basalts collected from the submarine extension of the east rift zone of Kilauea volcano decreases systematically with depth (Moore, 1965); however, basalt pillows dredged from other regions show different vesicularity depth curves (Fig. 1). Basalts from the Revillagigedo Islands region, which are dominantly alkalic (Moore, in press), are much more vesicular than basalts collected elsewhere from (and presumably erupted at) the same depths. K-poor tholeiitic basalts from the Juan de Fuca Ridge (Table) and from the Reykjanes Ridge south of Iceland define a third curve since they are less vesicular for a given depth than are the Kilauean lavas. These relations indicate that the more alkalic lavas have a higher

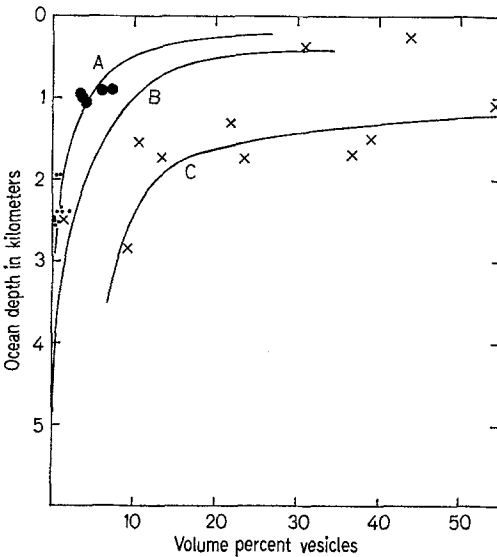


Fig. 1. Vesicularity as a function of depth for three types of submarine basalt. Curve A, K-poor oceanic tholeiites; small dots, Juan de Fuca Ridge samples; large dots, Reykjanes Ridge samples. Curve B, averaged data from submarine part of east rift zone of Kilauea volcano, Hawaii (Moore, 1965). Curve C and crosses, Revillagigedo Island region, Mexico. Chemical analyses of Juan de Fuca rocks are shown in the Table, and those of the Revillagigedo Islands are from Moore, in press

volatile, and presumably, water content when initially erupted on the ocean floor than do their tholeiitic counterparts.

**Chemical Data**

Analytical procedures for measuring small amounts of water in rocks are difficult and subject to many errors. Consequently, a broad scatter of values has been

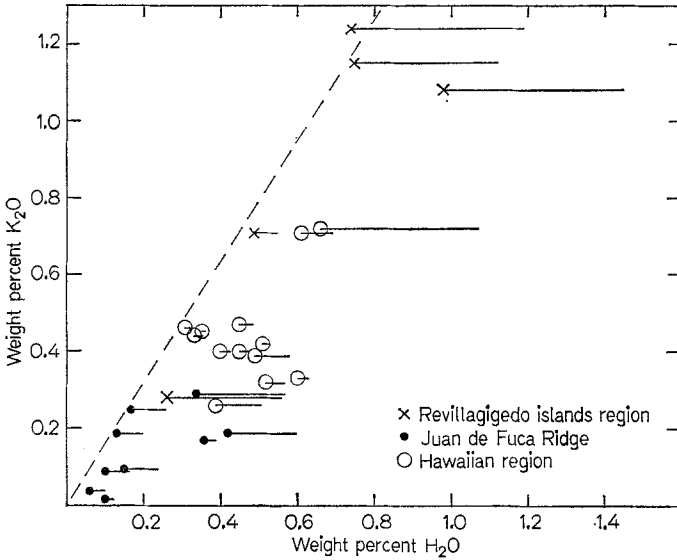


Fig. 2. Water and  $K_2O$  contents of deep-sea basalts from Hawaiian region, Revillagigedo Islands region, and Juan de Fuca Ridge. Symbol represents  $H_2O^+$  content and right-hand end of line is total  $H_2O$  content

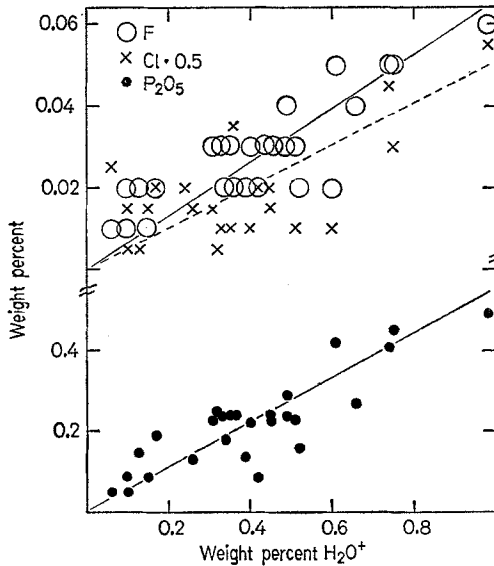


Fig. 3. Weight percent of F, Cl,  $P_2O_5$ , and  $H_2O^+$  in deep-sea basalt from Revillagigedo Islands region, Hawaiian region, and Juan de Fuca Ridge

Table. *Chemical analyses of submarine basalt from the Juan Fuca Ridge area*

(Analyst, Edythe Engelman, Denver Rock Analysis Laboratory, U. S. Geological Survey)

	Chemical analyses								
	9	10	11—12	12—1	12—2	13	14—1	15—3	15—8
SiO <sub>2</sub>	49.74	48.07	46.94	49.43	49.84	47.39	49.45	50.08	49.98
Al <sub>2</sub> O <sub>3</sub>	13.31	20.27	16.12	14.38	14.66	16.72	14.73	15.95	16.09
Fe <sub>2</sub> O <sub>3</sub>	2.12	0.98	1.33	3.55	2.51	2.50	2.10	1.95	1.94
FeO	11.99	6.14	8.46	8.37	8.73	7.78	9.28	7.84	7.71
MgO	6.30	7.90	12.48	6.37	6.30	9.54	7.18	7.10	7.18
CaO	10.17	13.33	10.76	11.44	11.71	11.18	11.92	12.73	12.68
Na <sub>2</sub> O	2.61	2.19	2.45	3.08	3.17	2.67	2.88	2.56	2.51
K <sub>2</sub> O	0.17	0.02	0.04	0.29	0.25	0.19	0.19	0.09	0.09
H <sub>2</sub> O <sup>+</sup>	0.36	0.10	0.06	0.34	0.17	0.42	0.13	0.10	0.15
H <sub>2</sub> O <sup>-</sup>	0.03	0.02	0.04	0.23	0.09	0.18	0.07	0.06	0.09
TiO <sub>2</sub>	2.52	0.75	1.02	2.00	2.02	1.32	1.66	1.29	1.27
P <sub>2</sub> O <sub>5</sub>	0.24	0.05	0.05	0.18	0.19	0.09	0.15	0.09	0.09
MnO	0.27	0.18	0.17	0.21	0.21	0.17	0.21	0.18	0.18
CO <sub>2</sub>	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.01
Cl	0.07	0.01	0.05	0.04	0.04	0.04	0.01	0.03	0.03
F	0.02	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.01
Subtotal	99.94	100.04	99.99	99.95	99.93	100.22	99.99	100.08	100.01
Less 0	0.03	0.00	0.01	0.02	0.02	0.02	0.01	0.02	0.01
Total	99.91	100.04	99.98	99.93	99.91	100.20	99.98	100.06	100.00

9. Trough floor between two ridges or from base of lower flank of eastern ridge. Depth 2,550 m 46° 54.4'N, 129° 19.7'W.

10. Lower flank of eastern ridge. Depth 2,504 m 46° 32'N, 129° 41'W.

11. Near base of ridge along the north side of re-entrant. Depth 2,480 m 46° 22.9'N, 130° 00'W.

12. Lower flank of ridge. Depth 2,400 m 46° 08'N, 130° 04'W.

13. Upper flank of ridge. Depth between 2,400—2,300 m 46° 39'N, 130° 13.2'W.

14. Middle flank of ridge. Depth between 2,000—1,900 m 46° 05.4'N, 129° 55.8'W.

15. Either from floor of trough or base of ridge. Depth between 2,600—2,500 m 46° 17'N, 129° 36.4'W.

reported in the literature for the water content of deep-sea basaltic pillows. Generally fresh pillow basalts have measured values of less than 1.0 weight percent H<sub>2</sub>O<sup>+</sup>. Published analyses of deep-sea pillows show a tendency toward higher water contents in more alkalic rocks (Miyashiro *et al.*, 1969; Muir and Tilley, 1964 and 1966) but it is believed that part of this tendency is masked by analytical uncertainties. The K<sub>2</sub>O and H<sub>2</sub>O contents of deep sea basalts from three areas in the Pacific Ocean are plotted in Fig. 2. All the analyses were made in the Denver Laboratories of the U. S. Geological Survey by the Penfield method described by Peck (1964). H<sub>2</sub>O<sup>-</sup> is determined by weight loss when the sample is heated to 105 ± 5° C. Analyzed deep-sea pillows are from the Hawaiian area (Moore, 1965, 1966), the Juan de Fuca Ridge off the state of Washington (Table), and the Revillagigedo Islands region off the west coast of Mexico (Moore, in press). These analyses show a relationship between the minimum H<sub>2</sub>O<sup>+</sup> and the K<sub>2</sub>O content (which is a measure of the alkalic character of the basalt). Scattering of points

toward higher water content is probably due to absorption of sea water in older samples; thus the  $\text{H}_2\text{O}^-$  content may be, at least in part, a measure of the amount of water added. Those minimum values of  $\text{H}_2\text{O}^+$  which show a linear relationship to the  $\text{K}_2\text{O}$  content are regarded as direct reflections of the water content of the respective melts at the times of eruption.

In addition to  $\text{K}_2\text{O}$  other volatile elements show a fixed relation to the  $\text{H}_2\text{O}^+$  content of young pillows (Fig. 3). F,  $\text{P}_2\text{O}_5$ , and, to a lesser extent, Cl increase with an increase in  $\text{H}_2\text{O}^+$ . At 1.0 weight percent  $\text{H}_2\text{O}^+$ , the average contents are 0.07 percent F, 0.55 percent  $\text{P}_2\text{O}_5$ , and 0.1 percent Cl. The atomic proportions of F:Cl are about 1.1:1. Murata (1966) has shown that the atomic proportion of F in Kilauean lavas exceeds that of Cl even though the F content of volcanic steam condensates and gases is less than that of Cl. He attributes this (page C4) to the reaction of F with wall rocks as the gases migrate to the surface.

### Isotopic Composition of Water

Water analyses were made of several thin slices cut parallel to the rim of a basalt pillow collected at a depth of 4,680 m on the submarine part of the east rift zone of Kilauea volcano (locality 12, Moore, 1965). Analyses of total  $\text{H}_2\text{O}$  as well as deuterium-hydrogen ratios were made by Irving Friedman by heating the sample in vacuum to 1,400—1,600° C, reacting the released  $\text{H}_2\text{O}$  with uranium metal to release  $\text{H}_2$  and measuring the volume of  $\text{H}_2$ . The ratio of deuterium to hydrogen was determined in a mass spectrometer relative to the ratio of standard mean ocean water (SMOW). The results indicate a water content of 0.43 percent on the outermost 1 mm of the pillow decreasing to 0.34 percent at 9—10 mm in from the outer rim. These values compare with 0.33—0.36 percent water determined by the Penfield method (Moore, 1965, Table 2). Isotopic analyses on the slices indicate an increase in deuterium from —6.0% D, SMOW, on the rim to —4.9% 9—10 mm into the pillow. Hence the outer, glassy margin of the pillow shows a gradient, with water content slightly decreasing and the water becoming richer in deuterium toward the center of the pillow.

These results might best be explained by loss of some water, enriched in hydrogen relative to deuterium, from the slower cooling, inner part of the pillow after the rim had quenched, become brittle and fractured. Such a mechanism is in harmony with the fact that original radiogenic argon is trapped in the quenched rim, but lost from the slower cooling interior of Kilauean pillows (Dalrymple and Moore, 1968).  $\text{H}_2\text{O}$  lost by diffusion is likely to be enriched in H because of the smaller mass and therefore higher velocity of H as compared to D. Hence the water in the outer, quenched rind of the pillow may produce the best sample for evaluating original deuterium content. The value of —6.0 percent D, SMOW, compares with —5.53 determined by Arnason and Sigurgeirsson (1968) for water condensed from hot fumaroles at Surtsey volcano, and —5.5 to —7.9 determined by Friedman (1967) for pumice from the 1959 eruption of Kilauea volcano, Hawaii.

### Post-Eruptive Change in Water Content

The volatile content of fresh deep-sea pillows is regarded as representing the volatile content of the basaltic magma as it erupted on the ocean floor. The degree

to which this composition was changed by gain or loss of volatiles as the magma moved upward from its site of formation to the ocean floor is not known. After eruption the volatile content of the pillows could be altered by exchange with sea water during cooling and crystallization, or later as a low temperature process operating during the time from eruption to collection.

Presumably some water escapes from the center of pillows upon cooling and crystallization, whereas it is held in the outer glassy shell as a result of drastic quenching. Hamilton and others (1964) have shown that at a pressure of 0.2 kilobars equivalent to an ocean depth of 2 kilometers, 1.0 percent water is soluble in Columbia River basalt at 1,100° C, and at 4 kilometers depth, 1.5 percent. Hence most of the analyzed pillows plotted on Fig. 2 were probably unsaturated in water at their site of eruption and could probably have included more water had equilibrium been obtained. The fact that they do not have more water suggests that quenching was so rapid that sea water was not dissolved in the basalt melt. Vesicles in the pillows that erupted at depths greater than 1 or 2 kilometers ocean depth are apparently produced by other volatiles less soluble in the melt than water, probably sulfur and carbon gases.

Analyses have shown that several of the Hawaiian samples contain excess  $\text{Ar}^{40}$  in their outer glassy margins and consequently have a calculated radiogenic age that is much greater than is geologically reasonable (Dalrymple and Moore, 1968). The presence of excess  $\text{Ar}^{40}$  is an indication that the melt has not degassed completely as is assumed for recent subaerially-erupted volcanic glasses of zero age which have lost their previously accumulated  $\text{Ar}^{40}$ .

The one pillow analyzed in slices inward from its outer margin shows a small increase in water toward the outer rim. This same sample (Dalrymple and Moore, 1968, locality 12) has a large excess of  $\text{Ar}^{40}$  in its outermost 1 mm. This suggests that the volatile content of the outer margin of the pillow was little modified and that the small decrease in water content inward was caused by loss of water from the slower cooling interior, rather than gain of water by outer zones.

Basalt glass in contact with water hydrates to produce palagonite, and, within general limits, the rate of palagonitization is known (Moore, 1966). Microscopically, the boundary between palagonite and unaltered sideromelane glass is sharp. Palagonite has been removed from all of the analyzed materials utilized in Fig. 1 and hence addition of secondary water is probably not important.

Thicknesses of palagonite (and hydrous iron-manganese oxide) crusts on the samples varies widely. Generally the Revillagigedo samples are coated with 60—1,300 microns of palagonite, the Hawaiian samples with from 5—700 microns, and the Juan de Fuca samples with from 50—600 microns. Hence the trends of Figs. 2 and 3 cannot be related to the thickness of palagonite on the samples and, consequently, to age.

Miyashiro and others (1969) have shown that  $\text{K}_2\text{O}$  increases from the rim inward in pillows from the Mid-Atlantic Ridge. Unpublished analyses of Juan de Fuca pillows indicate the same relation and suggest that it results from post-eruptive leaching of  $\text{K}_2\text{O}$  from the outer part of the pillows. However, because  $\text{P}_2\text{O}_5$  as well as  $\text{K}_2\text{O}$  shows a direct relationship to  $\text{H}_2\text{O}^+$  content in bulk analyses of pillows (Fig. 3), and because  $\text{P}_2\text{O}_5$  does not change from rim to core of pillows (Miyashiro and others, 1969, Table 4), the change in  $\text{K}_2\text{O}$  is probably small.

Perhaps all the analyzed rock contained a slightly higher  $K_2O$  content at the instant of eruption.

### Discussion

Data plotted in Figs. 2 and 3 indicate that deep-sea alkalic basalts rich in  $K_2O$  contain larger amounts of  $H_2O^+$  as well as F, Cl, and  $P_2O_5$  than do tholeiitic basalts. The ratio of these volatile elements remains rather constant such that at 1.0 weight percent  $H_2O^+$ ,  $K_2O$  is 1.57 percent, F is 0.07 percent, Cl is 0.1 percent, and  $P_2O_5$  is 0.55 percent. Also, the change in vesicularity of basalt pillows with increasing depth indicates that the volume of exsolved volatiles trapped in alkalic pillows is greater than in tholeiitic pillows.

Even though not previously demonstrated by direct analyses, several lines of evidence have indicated that alkalic basalts are richer in both water and other volatiles than are tholeiitic basalts. Macdonald and Katsura (1964, p. 92) point out that the late stage alkalic basalts capping Hawaiian volcanoes commonly contain more abundant interbedded pyroclastic layers and were therefore erupted more explosively than the underlying tholeiitic lavas. Hydrous minerals such as phlogopite and amphibole are found in alkalic basalts and associated xenoliths (Macdonald and Katsura, 1964, p. 98; Mason, 1968; Flower, 1969; Kushiro *et al.*, 1967), yet are rare or absent in tholeiitic basalts and their xenoliths, indicating higher water content of alkalic basalts. Kuno (1968, p. 663) suggests that the higher  $Fe_2O_3/FeO$  ratios of alkalic basalts and the common presence of porphyritic magnetite indicates a higher oxygen pressure of formation as compared to that of tholeiitic rocks. He suggests that this may be due to high original water contents, which, in turn, could also account for the deuteric alteration that is commoner in alkalic rocks. Engel and Engel (1966, p. D108) mention an apparent higher vesicularity of alkali-rich basalts as compared with tholeiitic basalt dredged southwest of Hawaii and suggest that this difference is due to a greater volatile content of the alkali basalt magmas.

The relatively fixed ratio of the volatile constituents  $H_2O^+$ ,  $K_2O$ ,  $P_2O_5$ , Cl, and F to one another (Figs. 2 and 3) suggests that a uniformly acting process enriches all of these constituents along with the change from tholeiitic to alkalic affinities. As these elements are concentrated in the first liquid to melt and the last liquid to crystallize in magma, varying degrees of partial melting of mantle material or of fractional crystallization of a magma batch could enrich the first and last liquids respectively in these elements. The greatest enrichment would be produced in the case of the smallest liquid/solid ratio. The apparent great excess of tholeiitic over alkalic basalts in ocean basins (Engel *et al.*, 1965) is in agreement with this concept.

On Fig. 2 an attempt has been made to estimate curves of vesicularity with respect to depth for the three groups of oceanic basalts. Each of these curves shows a prominent change in slope which occurs progressively deeper for the more alkali-rich groups. The change in slope for the K-poor tholeiites is at a depth of about 500 m, for the Kilauean tholeiites at a depth of about 800 m (Moore, 1965, p. 51), and for the alkali-rich Revillagigedo basalts at a depth of about 1,800 m. These depths may represent the confining pressure at which water-dominated gases become saturated in the melt and exsolve to form abundant vesicles. If so, gases in the vesicles at greater depth may be dominated by sulfur and carbon.

Extrapolation to lower pressures of the data of Hamilton *et al.*, 1964, for solubility of water in Columbia River basalt at 1,100° C (see Moore, 1965, p. 49) permits estimation of the water content of each of the groups of basalt that would cause saturation at the ocean depths mentioned above. These values are roughly 0.25 percent water for K-poor tholeiites, 0.5 percent water for Kilauean tholeiites, and 0.9 percent water for alkali-rich basalts. These water contents are in general agreement with the average measured content of  $H_2O^+$  for each of the three groups of basalts (Fig. 2).

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