WATER AND DEUTERIUM IN PUMICE
FROM THE 1959–60 ERUPTION OF KILAUEA VOLCANO, HAWAII

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Abstract.—Water was extracted from samples of pumice collected during the 1959–60 summit and flank eruptions of Kilauea Volcano, Hawaii, and the amount of H₂O and the relative deuterium content were determined. Water content of the samples from the summit eruption of Kilauea Iki ranged from 0.064 to 0.099 percent, by weight, and showed an inverse relation to relative deuterium content, which ranged from −5.5 to −7.9 percent relative to that of SMOW (standard mean ocean water). The samples collected from the Kapoho flank eruption contained 0.086 to 0.104 percent H₂O, and showed a wide range in deuterium content, from −5.7 to −9.1 percent relative to that of SMOW. These data are discussed in terms of the changing chemistry of the lavas.

The origin of water in rhyolitic glass has been investigated (Friedman and Smith, 1958) using the abundance of deuterium in water dissolved in the glass as a clue to the origin of such water. Rhyolitic glass was used because of its common occurrence and because it remains relatively unaltered for long periods of time. Recently, K. J. Murata, of the U.S. Geological Survey, made available for study a suite of basaltic pumice and lava samples from the 1959–60 eruption of Kilauea that permits a similar investigation to be made of the origin of water in basic rocks. Acknowledgement is made to Mr. Joseph Harris and to Miss Betsy Levin for their aid in some of the experimental work.

The 1959 summit eruption of Kilauea began on November 19, 1959, at Kilauea Iki (fig. 1) and persisted until November 21, when the level of the lava reached the level of the eruptive vent. During the next 4 weeks, 16 additional eruptive events occurred. The last eruptive phase ended on December 20, 1959.

The next outbreak of activity occurred on January 13, 1960, when fountaining began near sea level at Kapoho on the east rift zone of Kilauea. This activity continued until February 19, 1960, when the 1959–60 eruption ended.

ANALYTICAL METHODS

The samples analyzed were coarsely crushed in a diamond mortar, and about 3–5 grams of each sample was immediately weighed into a previously outgassed platinum crucible. The covered crucible was placed in a Vycor tube and connected to a vacuum system. The sample was heated in vacuum to 110°C for 2–12 hours to remove adsorbed water, which was pumped away. It was then slowly heated by means of an induction heater to 1,400°–1,600°C and allowed to remain at that temperature for at least 15 minutes. The evolved water was collected by freezing at liquid-nitrogen temperature. After a check was made for noncondensable gas, the ice was allowed to warm, and the water vapor was reacted with uranium metal at 700°C. The amount of hydrogen gas formed by this reaction was measured volumetrically and provided a quantitative measurement of the amount of water collected from the melted volcanic glass. This measurement is accurate to ±5 percent of the amount of water present. The hydrogen gas was then transferred to a specially constructed mass spectrometer, and the ratio of deuterium to hydrogen in the gas was compared to the ratio of deuterium to hydrogen in a standard sample. Differences in the ratios, between the sample and the standard, of as little as 0.1 percent of the ratio in the standard can be measured. All the deuterium results in this paper are given in relation to SMOW (standard mean ocean water), which has an isotopic composition close to that of average ocean water. Previous results (Friedman and Smith, 1958) were given in relation to a standard Lake Michigan water which has 4.2 percent less deuterium than does SMOW. The technique of water and deuterium determination is described in greater detail in Friedman and Smith (1958).
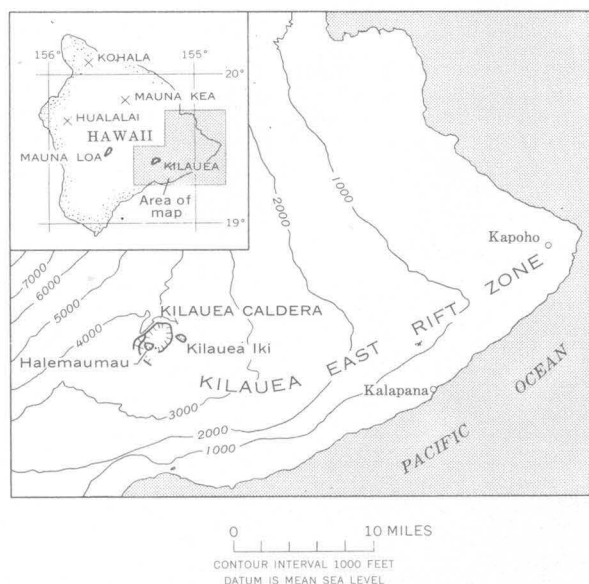
FIGURE 1.—Index map of eastern Hawaii, showing the summit region and east rift of Kilauea Volcano.

All samples were analyzed in duplicate. If satisfactory checks were not obtained on the duplicates, additional pairs were analyzed. Sample selection proved to be very critical. The first group of analyses was made on samples of finely vesicular pumice of density ≈0.3 grams/cubic centimeter that contain few crystals, as determined when the crushed material was immersed in oil and examined with the polarizing microscope. The discussion in this paper is limited to these samples. Samples of coarsely vesicular pumice and of crystallized lavas were also analyzed; however, the results obtained vary widely from one replicate analysis to another, and no correlations of any kind can be made on these samples. During the eruption of these materials, water was lost from the large open vesicles. In addition, various amounts of water also were lost during the partial or total crystallization of the lava as it cooled.

Water extracted from the finely vesicular glassy pumice probably represents water present in the magma just prior to eruption. During eruption, the pressure on the magma was suddenly lowered, and the water that was dissolved in the magma came out of solution in the form of fine bubbles. The large increase in volume of the magma due to this vesiculation undoubtedly aided the ejection of material from the vent. The pumice so ejected was rapidly chilled, freezing in the vesicular structure of largely unconnected bubbles. Water vapor caught in the bubbles rapidly diffused into the cooling lava and was thus trapped. Its cellular nature allowed pumice from the vents at Kapoho to float long distances in the sea,

some of it eventually reaching the island of Kauai, about 350 miles away.

Errors due to the uptake of additional water after the samples were erupted were minimized by the (1) protection afforded by a skin of nonvesicular lava on the surface of the pumice lumps, (2) rapid collection of the material shortly after eruption, and (3) selection of large pieces of pumice for analysis. Again it must be emphasized that the relationships to be discussed hold only for these selected pumice samples. Figure 2 shows photographs of this finely vesicular pumice.

RESULTS

Content of water, deuterium, and selected constituents in the glass

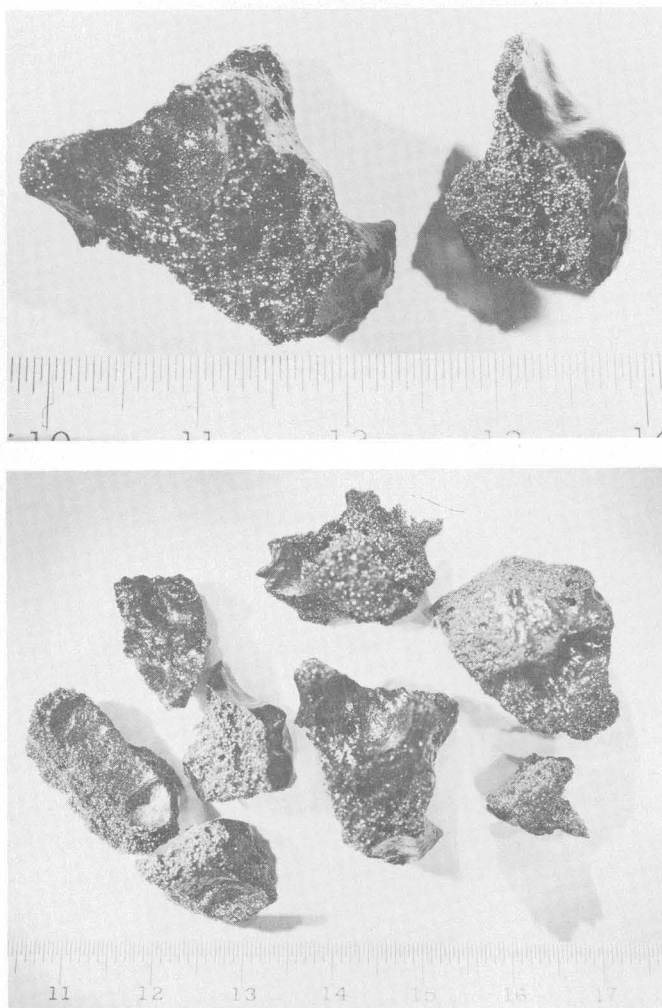Table 1 gives analyses for water and selected constituents from the glass, in weight percent, and the

FIGURE 2.—Pumice fragments of the type used in the study described in this paper. Note finely vesicular nature of the pumice, and outer skin that acted as a shield to inhibit secondary exchange of water with the atmosphere. Scale is in centimeters.

Table 1.—*Content of selected constituents and water, and relative deuterium concentration in the water, in glass erupted from Kilauea Volcano*

Lab. No.	Field No.	Date and time of eruption	Selected constituents and water (weight percent)				D/H [2] (percent)
			SiO_2 [1]	MgO [1]	K_2O [1]	H_2O	
KILAUEA IKI (SUMMIT ERUPTION) 1954 **First phase**							
S-4	3125-9	Nov. 17, 1500	49. 0	11. 5	0. 47	0. 099	−7. 9
S-5	3125-3	Nov. 18, 1700	46. 7	19. 5	. 35	. 064	−6. 6
IK-3	3125-10	Nov. 19, 0800	47. 6	[3] 16. 0	(. 42)	. 073	−7. 0
S-7	3134-6	Nov. 20, 0700	48. 2	13. 7	. 45	. 084	−7. 5
Later phases							
S-3	3125-12	Nov. 29, 2100	49. 4	8. 9	0. 54	0. 090	−7. 5
S-19	3134-1	Dec. 11, 0600	47. 3	16. 6	. 41	. 075	−6. 6
S-21	3134-2	Dec. 14, 1400	46. 7	19. 2	. 41	. 071	−7. 2
S-24	3125-4	Dec. 19, 0615	47. 0	18. 2	. 38	. 068	−6. 9
KAPOHO (FLANK ERUPTION) 1960							
P-2	3134-8	Jan. 15, 1730	50. 6	[3] 6. 5	[3] 0. 65	0. 098	−9. 1
F-3	3125-5	Jan. 17, 1900	50. 6	6. 4	. 65	. 095	−8. 3
F-7	3134-11	Jan. 26, 1900	50. 4	7. 0	. 62	. 086	−5. 7
F-12	3134-13	Feb. 2, 0800	49. 3	10. 6	. 54	. 090	−7. 6
F-13	3134-14	Feb. 4, 1130	48. 9	12. 1	. 50	. 090	−7. 7
F-17	3125-6	Feb. 13, 1900	48. 8	13. 1	. 49	. 087	−6. 0
F-18	3134-15	Feb. 16, 2030	49. 3	11. 1	. 51	. 104	−6. 4
F-19	3125-7	Feb. 18, 1630	48. 9	12. 5	. 48	. 101	−7. 5

[1] Analyses from Murata and Richter (1966).
[2] Relative deuterium concentration in the water extracted from the glass as compared with the concentration of deuterium in SMOW, in percent.

[3] Composition obtained by interpolation (on the basis of the SiO_2 percentage) on the variation diagram given by Murata and Richter (1966).

relative deuterium concentration in the water as compared with that in SMOW, in percent. The chemical analyses for the selected constituents were obtained on conventional finely ground samples of pumice, whereas the water determinations were made on coarsely crushed pieces of the same pumice. Owing to the porphyritic nature of many of the pumice samples, this difference in sample preparation introduces a slight uncertainty as to whether the analytical data for the selected constituents apply exactly for the portions used in determining water. However, the relatively large number of pieces taken (3 to 5 grams) probably minimized this error, as is indicated by the satisfactory agreement obtained on duplicate analyses.

In figure 3, K_2O, H_2O, and relative deuterium content of pumice from the Kilauea Iki summit eruption and from the flank eruption at Kapoho are plotted in separate columns. Magnesia is plotted as the reference constituent along the abscissa, following the practice of Murata and Richter (1966), so that the variations of water and relative deuterium content can be readily correlated with the variations of all other constituents.

Kilauea Iki samples consist principally of varied amounts of olivine phenocrysts set in a frothy matrix

of basaltic glass. The samples represent the first stage of differentiation of the primitive magma, in which the separation and settling of olivine phenocrysts lead to greater concentrations of olivine in the lower part and lesser concentrations in the upper part of the magma body. The primitive magma contains about 10 percent MgO, so samples with less MgO represent olivine-depleted residual magmas, whereas those with more MgO represent olivine-enriched accumulate magmas.

Constituents that are not incorporated in olivine, such as K_2O, Na_2O, TiO_2, and P_2O_5, occur in the melt (glass). In terms of bulk composition these constituents are concentrated in residual magmas and diluted, by olivine, in accumulate magmas. In a quantitative test of these relations, Murata and Richter (1966) show that the preceding 4 constituents uniformly are 1.418 times more concentrated (within the range of 1.411–1.421) in a Kilauea Iki pumice containing 8.0 percent MgO than in one containing 19.0 percent MgO. The inverse relationship between K_2O and MgO is illustrated in figure 3*C*, and this particular type of straight-line variation, due solely to variation in amount of olivine, has been called the "olivine-control line" by Powers (1955). Because H_2O is not incorporated in olivine, it too might be expected to manifest a similar olivine-control line.

The variation of the percentage of H_2O with that of MgO is shown on figure 3B. The dashed line indicates the variation to be expected solely on the basis of olivine control (1.42 times higher concentration of water at 8.0 percent MgO than at 19.0 percent MgO). The solid line represents the trend of all the points more closely, and it suggests an enrichment of water in olivine-depleted magmas over and above that due to olivine control. A line drawn through the points for samples S-4, S-7, IK-3, and S-5, from the first phase of the summit eruption, would indicate the excessive enrichment of water even more strongly. The first eruptive

phase was not complicated by repeated eruption and withdrawal of magma characteristic of the later phases; thus samples from the first phase might be expected to preserve the H_2O-MgO relationship most faithfully. In a column of differentiated summit magma, the upper part, therefore, contains relatively more H_2O than K_2O, Na_2O, and other constituents that concentrate in residual magmas. Such a relationship agrees with Kennedy's hypothesis (1955) regarding the vertical distribution of H_2O in a magma body, but does not support a similar distribution for the alkalies.
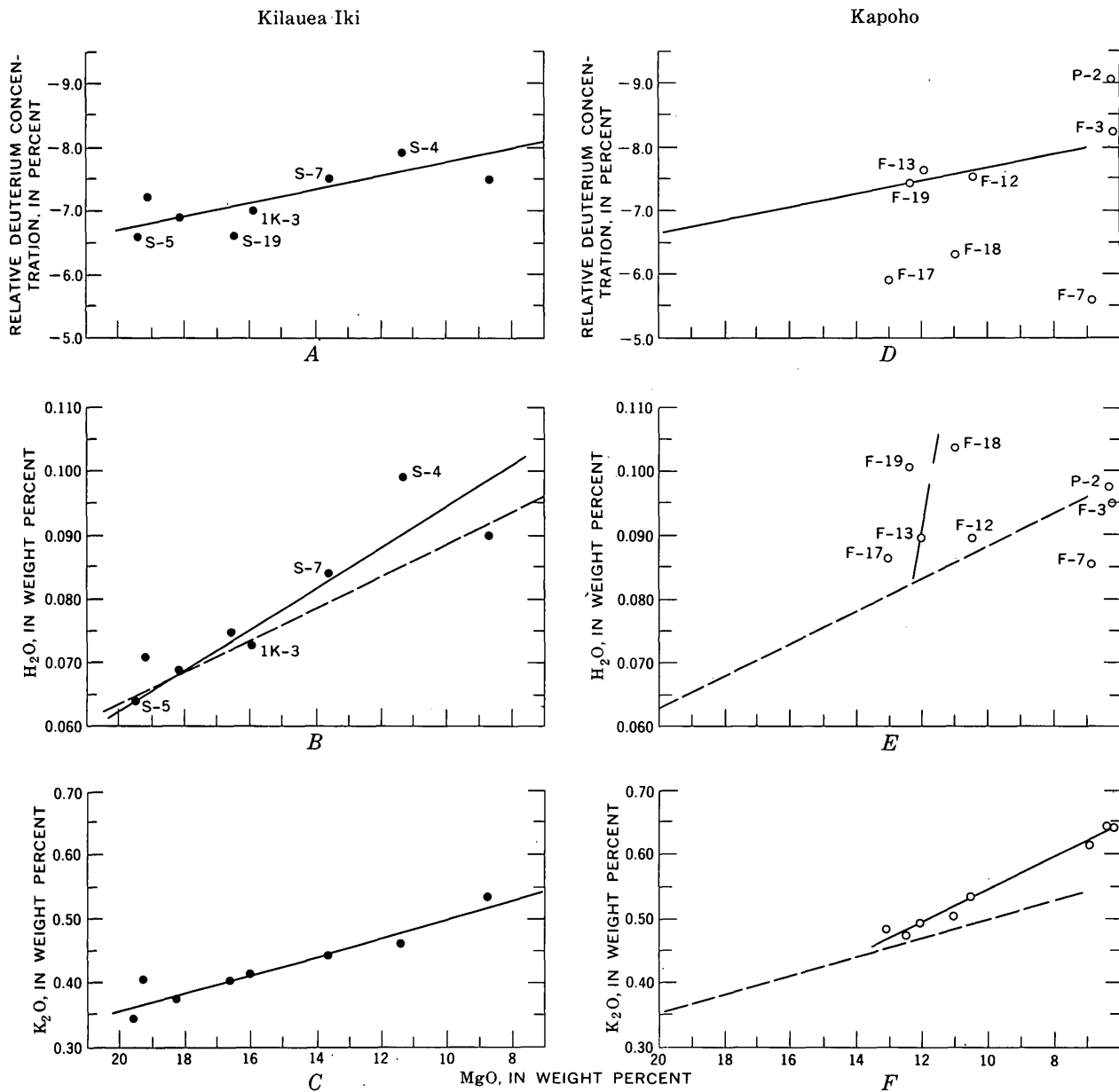

FIGURE 3.—Plots of K_2O, H_2O, and relative deuterium content versus MgO for pumice from the Kilauea Iki and Kapoho phases of the 1959-60 eruption of Kilauea. Numbers refer to samples listed in table 1.

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Figure 3A shows the relationship between relative deuterium content of the H₂O and percentage of MgO. Except for the aberrancy of sample S–19, the results clearly indicate that the H₂O in low-lying accumulate magmas is richer in deuterium (has lower negative deuterium values) than that present in less-magnesian magmas of the upper part of the magma column. This relationship most likely depends somewhat on the previously mentioned nonuniform distribution of H₂O in the magma column, and, like the distribution of H₂O, is most strongly manifested by samples from the first eruptive phase.

The covariance of K₂O and MgO in samples from the flank eruption at Kapoho is shown on figure 3F, and is compared with the trend due to olivine control in Kilauea Iki samples. The Kapoho materials represent more advanced stages of basaltic differentiation than do those from Kilauea Iki, and their uniformly higher content of K₂O (relative to MgO) is due to the continued concentration of K₂O in residual magmas of the later differentiation stages.

The solid curve in figure 3E indicates the H₂O content to be expected in the 1960 Kapoho samples if H₂O were to concentrate in residual magmas at the same rate as K₂O. Only 3 samples (F–12, F–13, and F–17) out of the total of 8 have such a concentration of H₂O. Samples P–2, F–3, and F–7 represent old magma that was not expelled during the 1955 flank eruption; they are greatly deficient in H₂O, suggesting a loss of H₂O from the old magma during its storage within the volcano.

Samples F–12, F–13, and F–17 to F–19 are considered by Murata and Richter (1966) to represent newer magma that migrated, within a month or so prior to eruption, from the summit region to the eruption site at Kapoho. The high H₂O content of samples F–18 and F–19 shows that an excess enrichment (beyond the degree of enrichment of K₂O) occurred in the newer flank magma, just as it did in the summit magma of Kilauea Iki. But the excess enrichment in the Kapoho magma does not correlate with the MgO content. There is a suggestion that the later expelled portions of the magma (samples F–18 and F–19) were richer in H₂O than portions expelled earlier, but no reason for this can be advanced.

As shown on figure 3D samples of the old magma (P–2, F–3, and F–7) have a very wide range of deuterium content, entirely out of proportion to slight differences in chemical composition with respect to K₂O, MgO, and other less mobile constituents. Two factors might have promoted the development of the wide variation in deuterium in the old magma—its long

period of storage within the volcano, and its substantial loss of H₂O (relative to K₂O).

The deuterium content of the newer Kapoho magma (samples F–12, F–13, and F–17 to F–19 of table 1) is not closely related to the H₂O content and, in general, is higher than would be expected. It is evident that the complicated deuterium and H₂O relationships in the old and new magmas of Kapoho cannot be explained satisfactorily at present. However, the independent migration of H₂O relative to the other constituents is clearly evident in the data on these magmas. The following discussion is limited to the relationships established for the primitive magma of Kilauea Iki, whose preeruption history was much shorter and simpler than that of derivative magmas erupted at Kapoho.

Figure 4 is a plot of the relative deuterium content versus H₂O content, in weight percent. It is obvious that, in general, the samples from the flank eruption at Kapoho have a higher H₂O content than do the samples from the summit eruption (Kilauea Iki) (table 1). Also, the samples from the flank eruption have a wider range of deuterium values than the Kilauea Iki summit samples. The summit samples, and to a small extent the flank samples, show an inverse relationship between H₂O content and deuterium content of the H₂O, and the samples with a higher H₂O content contain less deuterium (higher negative deuterium values). These basalt glasses are all enriched in deuterium as compared with rhyolitic glasses. The rhyolitic glasses range in relative deuterium concentration from −9.6 to −17 percent compared with −5.7 to −9.1 percent for the basalt glasses (table 1).

Although there is evidence that sea water was in contact with the molten magma at the beginning of the flank eruption, the H₂O from the glasses of the flank eruption (Kopoho) is no closer in hydrogen isotopic composition to sea water than are the glasses from the summit eruption of Kilauea Iki. If sea water is an
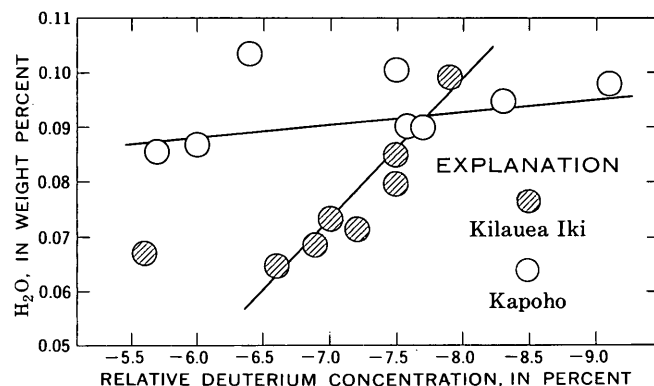
FIGURE 4.—Relative deuterium concentration versus H₂O content in pumice from the Kilauea Iki and Kapoho phases of the 1959–60 eruption of Kilauea.

important contaminant in these Hawaiian magmas, it must have been introduced at depth so that it has an equal influence on both the summit and flank magmas.

Kokubu and others (1961) analyzed two samples of Hawaiian lava and concluded that the H_2O in Hawaiian lava is not entirely a result of contamination, but is in part juvenile. The first sample, listed as an Hawaii volcanic bomb from the 1955 eruption of Kilauea, contained 0.09 percent H_2O having a D/H (relative deuterium concentration in H_2O as compared with that in SMOW) of −8.5 percent. The second, a "Hawaiian glassy spatter" from the 1954 Kilauea eruption, contained 0.09 percent H_2O with a D/H of −7.8 percent.

The data in their paper indicate a range in deuterium content of 3.5 percent, the most concentrated sample being 5.7 percent less concentrated than present-day sea water. Until the effects of fractionation processes on the isotopic composition of H_2O in magmas are better understood, conclusions, such as those made by Kokubu and others seem premature.

Reasons for variation in content of H_2O, selected constituents, and deuterium

The percentage of H_2O, SiO_2, and K_2O, the relative percentage of D/H, and the accumulated amount of lava extruded from Kilauea Iki are all plotted on figure 5 as a function of time for the summit eruption.

The changes in H_2O, SiO_2, and K_2O content of the lavas can be explained if olivine formed near the cooler top of a vertical magma chamber and settled part of the way down the column prior to eruption. However, the mechanism of sinking olivine cannot account for the change in the deuterium content of the H_2O in the lavas.

The variations in deuterium content, which in the samples from the summit correlate with the H_2O, SiO_2, and K_2O contents, may be explained in several ways:

1. Variation in deuterium content is an intrinsic property of the chemical composition or temperature of the magma. This assumes that the bonding of the H_2O to the silicate was a process in which there was an isotope effect, and that this isotopic fractionation of the hydrogen was dependent upon temperature and the structure of the melt. The structure of the melt in turn would depend upon the chemistry of the melt and therefore on its composition.

The foregoing could explain the relations found during the summit eruption, but it does not explain why the flank eruption does not give similar relationships between the deuterium and the K_2O and SiO_2.

2. Another explanation, closely related to the first, is that there is a fractionation of hydrogen isotopes when water is bound to the melt, but this fractionation
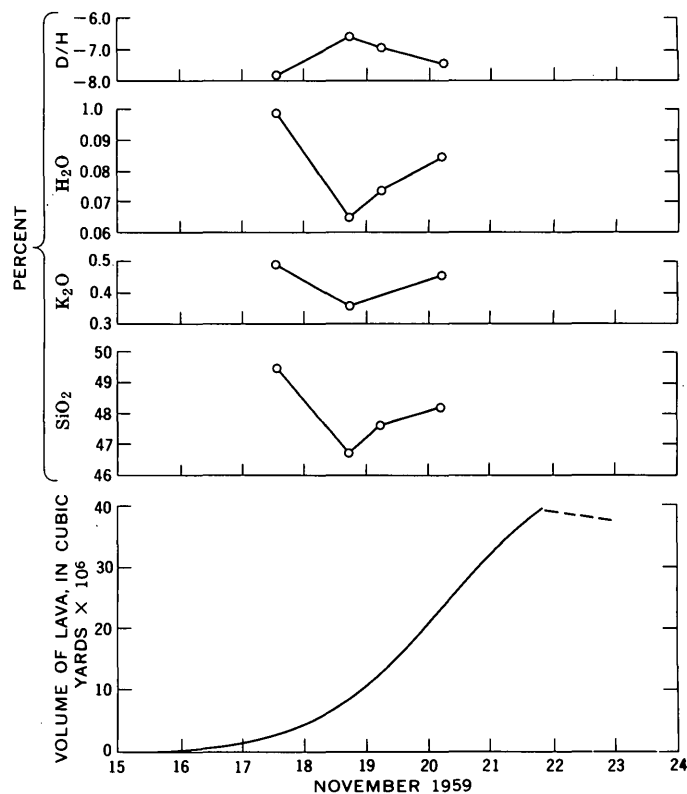

FIGURE 5.—Relative deuterium concentration (D/H); content of H_2O, K_2O, and SiO_2; and accumulated amount of lava extruded from Kilauea Iki, as a function of time for the summit eruption.

is relatively independent of the melt composition. If we then assume that the magma loses H_2O, and that it loses "light" H_2O (H_2O enriched in the light hydrogen isotope) preferentially, the H_2O-versus-deuterium relation can be satisfied. Again, this cannot explain the results of the flank eruption.

3. Explanations based on differential solubility of H_2O in melts of different composition will not explain the data from the flank eruption. In fact any explanation based solely on the intrinsic properties of the magma will fail to explain all the data. Clearly then, we must look to the mechanics of the eruption for at least part of the explanation.

Murata and Richter (1966) are of the opinion that the changes in the major chemistry of the lavas during the first phase of the summit eruption can be caused by (1) settling of olivine in a primary magma chamber, at a depth of perhaps 5 kilometers from the summit, and then (2) tapping of the top of the chamber. During the eruption there will be mixing of the settled magma with primitive magma rising from a depth of 20–30 km. The reversal in the trend of percentage of SiO_2 and

percentage of K_2O that occurred on November 18–19, 1959, might be due to uneven mixing or to the emptying of a reservoir of olivine-rich magma. The first phase of the summit eruption would consist of initially tapping the top of a magma chamber depleted in olivine by crystal settling, with or without primitive magma. This would be followed by tapping a mixture of primitive magma plus an olivine-rich magma containing the olivine that settled from above, with progressively more of the olivine-rich magma, until November 18–19. After that time, the amounts of admixed olivine-rich magma would decrease.

Probably a temperature gradient will be established in the primary magma chamber. The existence of this chamber is based on tilt data that indicate a swelling at about 5 km below the summit months before the summit eruption. If the rate of diffusion of H_2O in the magma is greater than convective mixing of the magma, a deuterium gradient might also be established, resulting in deuterium concentrating in the lower region, which will be the region of the high olivine content and therefore of low K_2O, SiO_2, and H_2O content.

Would storage of the magma, in a magma chamber of large vertical extent having a thermal gradient, concentrate the deuterium at the hotter, bottom end of the chamber? Two processes could possibly act to yield such an isotopic fractionation.

The first process is the fractionation that would occur upon diffusion of H_2O. During such diffusion, the lighter isotope would move more rapidly than the heavier. If H_2O had been diffusing from the hot part of the magma into the cooler, as suggested by Kennedy (1955), a concentration gradient of deuterium would result, the deuterium being more concentrated in the hotter residue and depleted in the H_2O-richer, cooler top.

The second process is thermal diffusion in a column in which separation of isotopes can take place. Unfortunately the process is very complicated, and even the direction of separation cannot be estimated.

The deuterium content obtained for samples from the flank eruption shows as wide a variation as for samples from the summit material (table 1). However, the deuterium content correlates poorly with H_2O, SiO_2, and K_2O content. The deuterium variations can be due to the cause suggested for the variations in the summit material—diffusion of H_2O. This would also explain the slight change of H_2O content with deuterium observed in the samples of the flank eruption.

The flank magma may have been emplaced as early as 1924. Some of this magma was erupted in 1955.

The 1960 lava, then, can represent a sample of magma that has had a long time to differentiate. In addition, it has had to move laterally about 40 km from its probable feeder. The K_2O and H_2O contents of the most primitive 1960 flank material show it to be already highly differentiated compared with the summit lava. However, in contrast with the summit samples, we do not get a total sample of the crystals that have settled from this magma, owing to the fact that they have had time to settle out. Therefore, the K_2O, SiO_2, and H_2O contents are not as low in the flank samples as in the summit samples (see table 1).

The flank magma has a much more complicated history than the summit magma. The long storage time in the rift zone, the long lateral movement within the rift zone, the great size and probable complex shape of the rift-zone storage chamber, and the possible complexity of various exits from the rift-zone chamber tapping different parts of the magma chamber are all factors complicating understanding of the flank lavas. Therefore, it is not surprising that the points representing the flank data show more scatter than do the summit points (figs. 3 and 5).

Other volatiles

The fluorine content of the pumices given by Murata and Richter (1966) ranges from 0.02 to 0.04 percent, a variation not considered significant in view of the precision of these analyses. The average fluorine content is 0.03 ± 0.01 percent.

The CO_2 values in the glass are small; therefore the variations between samples are not considered significant, not only because of the analytical errors, but also because varied amounts of magmatic CO_2 will be retained by the different types of pumice in the vesicles. The average content of CO_2 can be taken as 0.01 ± 0.01 percent.

The chlorine content of $0.02+0.1$ percent appears to be reasonably constant from sample to sample. The low chloride would mean either little incorporation of sea water into the magma, or incorporation of sea water and loss of HCl from the magma due to the low solubility of HCl in the melt (Murata, 1966). Although chlorides are observed in fumerolic deposits, the small amount observed would provide an argument against a major amount of sea water having been incorporated in the magma.

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GEOLOGICAL SURVEY RESEARCH 1967

Chapter B

GEOLOGICAL SURVEY PROFESSIONAL PAPER 575-B

Scientific notes and summaries of investigations in geology, hydrology, and related fields