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VOLATILES IN VOLCANIC GLASSES AND THEIR STABILITY RELATIONS[1]

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ABSTRACT

Previous studies of glassy volcanic materials have indicated the presence of volatiles with different stabilities, one pristine and the other the result of low-temperature hydration. The present study at controlled temperatures has indicated that the hydrated type may be expelled at low temperatures, and then the pristine volatiles determined at fusion temperatures. By this method pristine volatiles have been determined for 37 samples, representing ash-fall, pumice-fall and ash-flow materials. These volatiles are present to the extent of a few tenths of one per cent, and have been retained over such a wide range of time and conditions as to indicate very rigid fixation. The same volatile content seems to characterize ash-flow materials from the time of initial eruption until final fixation in welded tuffs. Obsidians give evidence of having been emplaced with a similar volatile content.

This study has indicated the possibility of the determination of the pristine volatiles, as exemplified by water, in a wide variety of glasses. However, of major importance is the possibility it presents of similar determinations of the rarer volatiles. Determinations of Cl, Fe, S, B, Br, and the oxygen isotopes are urgently needed for the interpretation of volcanism.

INTRODUCTION

Studies of the volatile components in glassy volcanic rocks, including pyroclastic ones, are revealing relationships which contribute to an understanding of volcanic processes. Several lines of studies are being carried forward by members of the U. S. Geological Survey. Ross and Smith (1955) have reported on "Water and other volatiles in volcanic glass," and Friedman and Smith (1958) have discussed "The deuterium content of water in some volcanic glasses." Friedman and Harris (1961) have determined fluorine in volcanic glass, and Powers and Malde (1961) have evaluated "Volcanic ash beds as stratigraphic markers." Ross (1962) has described "Microlites in glassy volcanic rocks."

The studies by Ross and Smith indicated that the volatiles of volcanic rocks were present in two states of combination, with marked differences in stability. One was released on heating at low temperature and was believed to be the result of hydration after deposition, and the other was released on heating at high temperatures and was believed to represent pristine volatiles inherited from the magma. The two forms of water had markedly different effects on the optical properties. The present paper continues these studies, and presents evidence that hydration has taken place without essentially affecting the relations of the pristine volatiles. This suggests that meaningful data on the content of pristine volatiles may be obtained from analyses of pyroclastic materials that are normally hydrated subsequent to deposition.

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METHODS OF STUDY

The present study was initiated by determinations of the stabilities of the volatiles in representative glasses from localities in the Valles Mountains and San Luis Hills of New Mexico. These were tested at controlled temperatures. The obsidian from Obsidian Ridge, with 0.32 percent high-temperature volatiles, lost none of these on heating for 22 days at 600° C. On the other hand, perlite, a hydrated glass, from Arroyo Hondo lost 2.85 per cent volatiles when heated at 400° C., and reached stability in 30 hours. A similar perlite from Tres Piedras, under the same conditions lost 2.54 per cent volatiles and reached stability in 40 hours. These experiments established a marked hiatus in the stabilities of the two types of volatiles. This large difference suggested that the high-temperature volatiles might have remained essentially intact and were only obscured by the presence of the low-temperature volatiles.

The earlier determinations (Ross and Smith, 1955) had been made on specimens composed of perlite (the hydrated glass) enclosing pelletlike nodules of obsidian (marekanite) which had escaped hydration. This relationship had permitted determinations of high-temperature volatiles in the nonhydrated fraction, and the total volatiles (low and high temperature) in the hydrated portion of the same sample. Six such specimens in which the high-temperature volatiles had previously been determined were available for restudy. The perlite portions of these were heated at 400° C. until stability was reached, and then the high-temperature volatiles were determined by fusion at about 1100°C. The results of the tests of six specimens are given in Table 1.

Table 1 shows a very close correspondence in the amounts of the high-temperature volatiles as directly determined on obsidian of the nonhydrated marekanites and as determined on hydrated material (perlite) from the same specimens. This seemed to establish the feasibilty of the heating method for determining the pristine volatiles in hydrated glasses, and provides a method for determining and distinguishing the two types of volatiles in pyroclastic materials, which in general have undergone hydration. This evidence that the pristine volatiles were unaffected by low-temperature hydration is supported by the studies of Friedman and Harris (1961) who state,

> "Our data show that during hydration the fluorine content of the glass remains relatively constant in the samples that we analyzed. From this it may be inferred that the amount of fluorine found in the hydrated glass shards of a bed of volcanic ash represents the original fluorine content of the material. . . . "

The previous study by Ross and Smith (1955) included determinations of high-temperature volatiles in 9 obsidians associated with perlite (hydrated) with a range from 0.09 to 0.35 per cent, and of 10 other obsidians with a range of 0.10 to 0.32 per cent. The present study considers the hydrated pyroclastic materials—pumice, ash, and welded tuffs—since these had not previously been amenable to study.

Determinations of the volatile content in 37 specimens of these materials are presented in three groups—Table 2, air-fall pumice; Table 3, air-fall ash; and Table 4, ash-flow materials.

PROVENIENCE OF MATERIALS

Volcanic events, especially many of those of the past, have erupted immense amounts of ash into the air. Some of this ash had worldwide distribution, and amounts large enough to form conspicuous deposits have fallen hundreds of miles from the source. Here it commonly be-

TABLE 1. HIGH-TEMPERATURE WATER IN HYDRATED GLASSES AND OBSIDIANS

	Determinations on hydrated glasses	Determinations on obsidian	
		Ross and Smith, 1955[1]	New determinations
	(weight per cent) (1)	(weight per cent) (2)	(weight per cent) (3)
1	0.34	0.32	—
2	.39	.35	—
3	.29	.30	—
4	.29	—	0.30
5	.36	.33	—
6	.20	—	.18

1. Arroyo Hondo, Valles Mountains, New Mexico.
2. Obsidian Ridge, Valles Mountains, New Mexico.
3. Cerro No Aqua, near Tres Piedras, New Mexico.
4. Determination was made on another perlite-obsidian specimen from the same locality.
5. Prestahnukur, Iceland.
6. Ammon quadrangle, Idaho. Column 1, perlite-like welded tuff; column 3, nonhydrated obsidian-like welded tuff.

[1] Data from Ross and Smith (1955, Table 1, entries 1a, 3a, 5a, and 6a, respectively). In the previous study the percentages presented here in column (2) were determined on the marekanite fraction which contained only high-temperature volatiles. On the other hand the perlite on which the figures in column (1) were determined contained both low- and high-temperature volatiles. In order to make the results comparable, the low-temperature volatiles were disregarded, and the loss above equilibrium at 400° C. was used in determining the proportion of high-temperature volatiles. The same method was used in presenting the high-temperature volatiles in Tables 2, 3 and 4.

TABLE 2. LOW- AND HIGH-TEMPERATURE VOLATILES IN AIR-FALL PUMICE

	Sample material	Age	Volatile content	
			Low temperature	High temperature
1	Pumice	Pleistocene	2.57%	0.30%
2	Pumice	Pleistocene	4.78	0.32
3	Pumice	Pleistocene	3.66	0.25
4	Pumice	Pliocene	5.17	0.33
5	Pumice	Pleistocene	3.78	0.26
6	Toledo rhyolite pumice	Pleistocene(?)	5.20	0.36
7	Guaje pumice	Pleistocene(?)	3.50	0.38
8	Valles rhyolite pumice	Pleistocene	2.60	0.42
9	Pumice	Recent	3.75	0.22
10	Pumice	Recent	3.78	0.35
	Mean			0.30

1. 1.5 mi. northeast of Battleship Rock, Valles Mountains, New Mexico.
2. El Cajete Crater, 3 miles south of Redondo Peak, Valles Mountains, New Mexico.
3. Del Norte pumice mine, 4 miles north of Bland, Valles Mountains, New Mexico.
4. Lower Peralta Canyon, T. 16 N., R. 5 E., sec. 33, Santa Domingo Pueblo quadrangle, Valles Mountains, New Mexico.
5. Medio Canyon, Santo Domingo Pueblo quadrangle, Valles Mountains, New Mexico.
6. Guaje Canyon, Frijoles quadrangle, Valles Mountains, New Mexico.
7. Kwage Mesa, Frijoles quadrangle, Valles Mountains, New Mexico.
8. 1.5 mi. southwest of Cerros del Abrigo, Jemez Springs quadrangle, Valles Mountains, New Mexico.
9. Passo de Cortes about 75 km. southeast of Mexico, D. F., Mexico. Probably derived from Popocatepetl. Collected by Carl Fries.
10. Lipari Island, Italy.

comes part of a sedimentary section, where it may undergo various vicissitudes. Much of such ash has altered to bentonite, thousands of cubic miles of which characterize the western United States (Ross, 1955). However, some had come into an environment where it persisted for long periods as fresh volcanic ash.

Ash beds are widespread in the Great Plains region of the United States and have been reported from a region extending from Nebraska to Oklahoma and west Texas, those in Kansas having been most carefully studied (Swineford, 1949; Swineford and Frye, 1946). These geologists have suggested that the ash in the Pearlette Ash Member of the Sappa Formation (Pleistocene in age) and possibly the ash in the Ogalalla Formation (Pliocene in age) has been derived from the Valles Mountains, New Mexico. Excellent volcanic ash from the Great Plains region has been supplied by Powers, who has also supplied ash from Oregon and the Snake River Plains of Idaho (Powers and Malde, 1961).

Pumice has in general been blasted into the air as has ash and differs only in the size of the fragments and in being deposited nearer the source. Eight samples of pumice are from the Valles Mountains, New Mexico, one from Mexico, and one from Lipari Island.

Ash-flow materials have been transported by flowage while hot and commonly welded after deposition. Thus they have had a longer and more complicated history than ash-fall materials. Some have remained

TABLE 3. LOW- AND HIGH-TEMPERATURE VOLATILES IN AIR-FALL ASH

	Sample material	Age	Volatile content	
			Low temperature	High temperature
11	Ash	Pliocene(?)	5.09%	0.30%
12	Ash	Pliocene(?)	5.48	.35
13	Ash	Pliocene	5.44	.35
14	Ash	Pliocene	5.04	.33
15	Ash	Pliocene(?)	4.51	.40
16	Ash	Recent	2.00	.40
17	Ash	Recent	2.35	.38
18	Ash	Pliocene	4.54	.38
19	Ash	Pliocene	4.25	.39
20	Ash	Pliocene	5.33	.39
21	Ash	Pleistocene	3.97	.41
22	Ash	Pleistocene	3.63	.41
23	Ash	Pleistocene	3.10	.37
24	Ash	Pleistocene	3.42	.41
	Mean			.376

11. Santa Fe Group, Valles Mountains, New Mexico.
12. Santa Fe Group, near Espanola, Valles Mountains, New Mexico.
13 and 14. Lower Peralta Canyon, T. 17 N., R. 5 E., sec. 33, Santa Domingo Pueblo quadrangle, Valles Mountains, New Mexico.
15. Snake River Plain, 5 miles west of Glenns Ferry, Idaho (Powers and Malde, 1961).
16. Mount Mazama, valley of Franks Creek, Oregon.
17. Mount Mazama, valley of Jonas Creek, Oregon.
18, 19, and 20. Ogalalla Formation near Calvert, Norton County, Kansas.
21. Pearlette Ash Member of Sappa Formation, Cudahy mine, Meade County, Kansas.
22. Pearlette Ash Member of Sappa Formation, Sunday Canyon, Roberts County, Texas.
23. Pearlette Ash Member of Sappa Formation (upper ash), Harlan County, Nebraska.
24. Pearlette Ash Member of Sappa Formation, Wilson Valley, Lincoln County, Kansas.

Nos. 15 to 24 inclusive collected by Howard A. Powers.

TABLE 4. LOW- AND HIGH-TEMPERATURE VOLATILES IN ASH-FLOW MATERIALS

	Sample material	Age	Volatile content	
			Low temperature	High temperature
25	Basal pumice	Pleistocene	2.78%	0.30%
26	Basal pumice	Pleistocene	2.36	.24
27	Basal pumice	Pleistocene	2.60	.34
28	Basal pumice	Pleistocene	3.37	.42
29	Basal pumice	Pleistocene	2.98	.21
30	Welded tuff	Pleistocene	1.76	.20
31	Welded tuff	Pleistocene	3.20	.28
32	Welded tuff	Oligocene	3.44	.15
33	Welded tuff	Pleistocene	2.59	.15
34	Welded tuff	Pleistocene	3.66	.42
35a	Quartz latite	Pleistocene	3.26	.34
35b	Rhyolite	Pleistocene	4.58	.37
36	Welded tuff	Pleistocene	1.76	.30

25 and 26. Bishop Tuff of Gilbert (1938), California.

27. Base of Otowi ash flow, Otowi Mesa, Frijoles quadrangle, Valles Mountains, New Mexico.

28. Tshirege ash flow, Valles Mountains, New Mexico.

29 and 30. Battleship Rock, Valles Mountains, New Mexico.

31. San Miguel, Regala, Hidalgo, about 22.5 km. northeast of Pachuca. Collected by Carl Fries.

32. About 9 km. east of Taxco, State of Guerrero, Mexico. Collected by Carl Fries.

33. Near Ammon, southeastern Idaho. Collected by G. R. Mansfield.

34. Redondo Peak, Valles Mountains, New Mexico.

35. Oro-Tlalpujahua district, Mexico. Collected by Carl Fries. Welded tuff composed of two materials (a) quartz latite and (b) rhyolite.

36. Virilla Canyon, Costa Rica, collected by Gabriel Dengo, described by Howell Williams (1952, p. 173–176).

glassy and amenable for determinations of volatiles, but others underwent devitrification with loss of volatiles.

Much of the material used in this study is from the Valles Mountains, New Mexico, where geologists Ross, Smith and Bailey of the U. S. Geological Survey are engaged in detailed studies of the volcanic history of that region. (See Ross *et al.* 1961). Materials available for study from this region include ash-flow tuffs, pumice, and volcanic ash (Ross and Smith, 1961). The ash flows (commonly containing some pumice material) extended as far as 16 miles from their source. Local deposits of direct fall material were deposited at various distances from the sources and conspicuous beds occur in the Rio Grande Valley east of the volcanic area. A number of very excellent specimens from Mexico have been supplied by Carl Fries.

Determinations of the petrographic character of a representative number of pyroclastic materials will serve to illustrate their range in composition. Those of the Valles Mountain region are all rhyolites, with a SiO_2 range of 72 to 77 per cent. The Kansas ash as reported by Swineford and Frye (1946) ranges from 72 to 74 per cent SiO_2. The Narrows ash of the Snake River Plain is rhyolite 72.18 per cent SiO_2, and the Peters Gulch 69.82 per cent SiO_2 (Powers and Malde, 1961). The Bishop Tuff is rhyolite (Gilbert, 1938). The Lapari pumice is rhyolite, 74.37 per cent SiO_2 (Washington, 1917). The welded tuff of the Oro-Tlalpujahua district, Mexico is composed of rhyolite 67.61 per cent SiO_2, and quartz latite 62.09 per cent and SiO_2 and the Popocatepetl pumice, is latite, SiO_2 61.90 per cent (Carl Fries, written communication). The Mazama ash as derived from Crater Lake is dacite about 70 per cent SiO_2 (Williams, 1942).

Geologic Age

The volcanic rocks of the Valles Mountains range in age from Pliocene, probably middle Pliocene, to late Pleistocene. The ash-flow materials are Pleistocene but the ash and pumice of Peralta Canyon are Pliocene and the ash from the Rio Grande Valley is probably Pliocene. Detailed studies of the Kansas ash beds by Kansas geologists (Swineford and Frye, 1949; Caney *et al.* 1952) have shown that the Ogalalla ash is Pliocene and the Pearlette ash is Pleistocene in age. The ash from Passo de Cortes, Mexico, is probably Recent, as is the pumice from Lipari, Italy, and the ash derived from Mount Mazama. The Bishop Tuff of California is Pleistocene in age (Gilbert, 1938). The welded tuff from near Taxco, Mexico, is reported by Carl Fries to be Oligocene in age, and that from the Tlalpujahua district, Mexico, is reported by Fries (written communication) to be "not more recent than middle Pleistocene."

Discussion of Determinations

Tables 2, 3, and 4 give determinations of low-temperature and pristine volatiles for 37 specimens. The volcanic history of pumice and ash (Tables 2, 3) was abruptly ended by eruption into the air, but the ash-flow materials (Table 4) had a more complex, and a longer history.

The water of hydration (low-temperature water) of ash, pumice, and glassy tuffs ranges from 2 to 5.35 per cent but commonly ranges from 2.50 to 5.00 per cent. Various factors which control hydration are only partly known, and their relative effect is difficult to evaluate and need not be discussed in a paper devoted to high-temperature volatiles.

Ten samples of pumice (Table 2) show a high-temperature volatile content ranging from 0.20 to 0.38 per cent with a mean of 0.297 per cent. The high-temperature volatile content of 14 samples of ash-fall material (Table 3) ranges from 0.30 to 0.41 per cent with a mean of 0.376 per cent. This mean value is higher than that for pumice due to the number of high-volatile glasses included from the Great Plains region.

Two types of ash-flow materials are represented in Table 4. Those with the simplest history are the pumice fragments which form the nonwelded basal portion of many ash flows and which are represented in specimens 25 to 29. These have a pristine volatile content ranging from 0.21 to 0.42 per cent, and a mean of 0.302 per cent. This group of materials, which were transported by flowage while hot, have essentially the same range and mean volatile composition as the pumice which was blasted into the air and quickly chilled.

The eight welded tuffs, Nos. 30 to 36, including 35a,b have a range of 0.15 to 0.42 per cent and mean of 0.274; No. 31 is only slightly indurated and might be grouped with the nonwelded pumice group. The others are densely welded and two of these show only 0.15 per cent of high-temperature volatiles and make the range of this group unusually large.

An interesting pair of determinations is presented by ash-flow materials from Battleship Rock. No. 29 was pumice from the nonwelded basal portion and No. 30 was from the densely welded central portion of the same geologic section. These contained essentially the same volatile content (0.21 and 0.20 per cent), and welding had not affected the content of high-temperature volatiles.

A large number of determinations of the volatile content of densely welded ash-flow tuffs, and especially pairs of determinations as in Nos. 29 and 30 are desirable. However, welding seems to have had little, if any, effect on the content of high-temperature volatiles.

The volatile contents presented in Tables 2, 3 and 4 indicate that a large proportion of the determinations lie between 0.25 and 0.38 per cent, with the greatest concentration in the range around 0.35 per cent (between 0.33 and 0.37 per cent).

Glass-Volatile Relations

At the time of an explosive volcanic eruption, there was a partition of volatiles; part of them was explosively released into the air or was retained in the interstices of vesiculated pumice, and part remained in solution in the glass. The vesiculation that accompanied partition no doubt occurred during relief of pressure, in the throat of the volcanic vent. Partition therefore took place in an atmosphere of the released volatiles, but their concentration and pressures are problematical. The temperature at the time of vesiculation was probably essentially that of the magma. The mechanism of partition implies the establishment of an equilibrium between glass and volatiles at the time of eruption at temperatures probably of the order of 800° to 900° C.

The initial eruptive process was essentially the same for the ash-fall and ash-flow materials. Both were vesiculated, probably in the throat of the volcanic vent, and they show no observable difference in the physical form of the ash or pumice fragments. Ash-fall material was airborne, and much of it traveled long distances. On the other hand, the ash-flow material was transported as an ash-gas system, and in general, it retained essential amounts of heat during flowage and also for a long period after emplacement.

The resulting material assumed the form of indurated tuffs, welded tuffs, and devitrified tuffs. Many of the tuffs became densely welded after traveling many miles from their source, implying a long cooling history. Ash flows, even those with densely welded horizons, are commonly characterized by a basal horizon of nonwelded ash or pumice. These show the same volatile content as the direct-fall materials which have been quickly chilled. This indicates that distance and mechanism of travel had not affected the volatile content.

The content of pristine volatiles in glassy pyroclastic materials from a large variety of environments, from many regions, and from periods of time measured by some millions of years have been presented. The results indicate a remarkable stability of volatiles in glass, and a narrow range in their weight per cent.

The stability of high-temperature volatiles is confirmed by experiments on the typical glass from Obsidian Ridge. This glass lost no volatiles on heating for 22 days at 600° C., lost volatiles slowly at 800° to 900° C., and became plastic enough to bend but without vesiculation at 950° C. The loss of volatiles is so slow that the exact temperature of initial instability is doubtful, but an order of 750° is indicated.

These experiments were made at 600° C. or above and involved an essentially anhydrous atmosphere. On the other hand, if they had been made in a volatile-rich one the stability relations would have been more nearly analogous to those in a volcanic vent.

The determinations of the amount and stability of volatiles retained during flowage and emplacement of ash-flow tuffs has a bearing on theories about the mechanism of flowage. Fenner (1923, p. 72) remarks: "I would, therefore, stress the remarkable character imparted to the dust-and-gas mixture by a continuous evolution of gas . . . [during the progress of the sand flow]." Perret (1937, p. 48) has also remarked: "It [the nuée ardente] possesses two essential characteristics: an extremely rapid transport of crater material in a horizontal direction to considerable distances, and a lava in itself highly explosive and continuing to discharge gas throughout its mass as long as the temperature remains sufficiently high." Ross and Smith (1961, p. 40) observe, " . . . they [the volatiles] are partly released from solution in the glass shards during flowage." However, it was pointed out that a nonhydrated welded tuff still retained 0.15 per cent of H_2O, and it is stated, "Moreover, the physical effects of volatiles is greatly disproportional to their amount." Smith (1960) minimizes the amount of volatiles and remarks (p. 810), "If the amount given off by diffusion were only a few hundredths of a per cent by weight, the volume at eruptive temperatures would be impressive and would provide an adequate lubricant." The trend of thought has been to minimize the estimates of the weight per cent of volatiles directly released from solution in the glass. The validity of this reasoning is confirmed by the evidence that there was no appreciable loss of pristine volatiles at temperatures at least higher than 600° C., and by the stability relations. Smith (p. 810) mentions the " . . . escape of gas that was trapped by the sheer bulk of the ash and pumice, but which had been released by vesiculation before the flow formed" and the "rupture during flowage of vesicles that contain partly expanded gas. . . . " It seems not improbable that these two sources of gas are adequated for flowage at the elevated temperatures of emplacement.

TABLE 5. VOLUME RATIO OF WATER VAPOR (1%) TO GLASS AT VARIOUS TEMPERATURES AND PRESSURES

Temperature (° C.)	Glass volume	Steam volumes		
		15 psi	50 psi	100 psi
500	1	81	24	12
700	1	103	30	15
900	1	123	36	18
1200	1	155	46	23

VOLATILE-VOLUME RELATIONS

The volatiles retained in glass at the time of initial eruption provide no clue to the water content of the original magma. Estimates have been made, but the assumptions on which these have been based have been exceedingly precarious. Another approach is to consider the volatiles which would be adequate for the explosive effects of a volcanic eruption. The extreme violence of some eruptions suggests a large volume of volatiles, but what would this be expressed as weight per cent?

The calculations in Table 5 may help to answer that question. For this study we are concerned with the volume of steam at different temperatures and pressure, which would be released from solution in the glass. The data for such calculations are provided by the standard steam pressure tables (Keenan and Keyes, 1946). The data in these tables are given in cubic feet, pounds pressure, and Fahrenheit temperatures. However, the calculation of the ratios of steam volume to rock volume (the source of the steam) is independent of the units of measurement. The temperatures, however, have been recalculated from Fahrenheit to Centrigrade. Table 5 gives the volume ratio of water vapor to glass assuming one per cent of water by weight. To illustrate—one per cent of water by weight at atmospheric pressure and 900° C. will occupy a volume 123 times greater than that of the glass from which it is released.

These figures, which show the very large ratios between water vapor and glass, may help to visualize the potentialities of volatiles rather than to actually evaluate their amount. However, it seems that 1 or at most 2 per cent of H_2O would be ample for even the most violent explosions, and ash-flow eruptions which seem to have been less violent may have required even less.

This study of the volatiles of glassy pyroclastic rocks has primarily concerned those volatiles retained in the glass at the time of eruption, but those which escaped into the air also escaped direct determination. Thus the total volatiles of the magma are not directly known. The consideration of steam volume relations indicates that small amounts of volatiles would be adequate for violently explosive eruptions, but this also leaves the specific amount questionable.

Relationships of Glassy Flow Rocks

Pyroclastic rocks are the dominant type of glassy volcanic materials, but glassy flow rocks (obsidian) also contribute information about volatile relationships. An earlier paper by Ross and Smith (1955) presented data on the volatiles in two groups of glassy flow materials. One of these (Table 1) represented glass (marekanite) which had escaped hydration although associated with hydrated perlite. One of these glasses, with 0.9 per cent H_2O is believed to have been hydrated under pressure. The others contained volatiles ranging from 0.22 to 0.35 per cent and hence do not differ materially from the values in the pyroclastic glasses.

The other group (Table 3) included typical lava-flow obsidians. Of these, one contained 0.20 and another 0.32 per cent volatiles, not essentially unlike pyroclastic materials. The volatiles in eight specimens ranged from 0.08 to 0.12 per cent which corresponds to about one-third the normal volatile content. These will be discussed below.

The significant feature of obsidians is that many are without vesiculation and even when there is vesiculation the weight per cent of released volatiles if very small. In some obsidians there is vesiculation in the upper few inches. Thus no appreciable amount of volatiles was lost from the obsidians subsequent to their emplacement.

The volcanic center at Xalpazquillo Puebla, Mexico, presents some very significant relations. A mass of obsidian 50 meters or more in diameter was thoroughly brecciated during extrusion. This brecciation must have occurred in an extremely viscous medium for the fractures are partly healed by welding after extrusion. The obsidian shows no evidence of vesiculation during emplacement, brecciation and welding. That is, there is no evidence of volatiles other than the 0.32 to 0.34 per cent now present in the glass.

Two samples from 13 km. east of Pachuca, Hidalgo, Mexico, collected by Carl Fries, illustrate obsidian relationships. One of these has vesiculated with the production of 0.87 per cent of pore space and 0.09 per cent of pristine volatiles, and a nonvesiculated phase of the same obsidian contains 0.12 per cent pristine volatiles. Both are without low-temperature volatiles. The volatile content of the two phases of this obsidian is not essentially different and illustrates vesiculation relations in a glass with a very low volatile content. Both types are without any microlite crystal material.

Microlites (minute crystals) characterize many glassy volcanic rocks and their identity and relationships have been described by Ross (1962), and this provides a background for a consideration of the relationships between microlites and volatiles and their bearing on volcanic processes. A few obsidians with 0.10 to 0.12 per cent of volatiles contain microlites, but most of those within that range seem to be in general without them. As is well known, magnetite as an early exsolution product is ubiquitous in nearly all types of volcanic rocks and seems to have no particular significance. Later-formed magnetite may have. In the course of this study the volatiles from two groups of obsidian have been determined. Specimens from Bearhead, Vales Mountains, which were essentially without microlites contained 0.37 and 0.39 per cent of volatiles, and a group from Xalpazquillo, Mexico, with 0.32 to 0.34 per cent of volatiles contained abundant feldspar microlites, but most low-volatile obsidians are without them. Eight other obsidians examined by Ross (1962, Table 1) were without observable microlites. The glasses with 0.10 to 0.12 per cent of volatiles would have a very much higher viscosity than those with the order of 0.35 per cent, and this would tend to inhibit the transfer of material necessary for crystal development. Thus a low volatile content seems to be a factor affecting microlite formation, although clearly not the only one. Also some obsidians like that from Bearhead are anomalous.

The foregoing studies present evidence that obsidians may be emplaced in the presence of a very small content of volatiles. At the time of explosive eruption of pyroclastic materials, volatiles to the extent of a few tenths of one per cent are retained in the glassy shards, and this content seems to remain essentially constant during flowage, emplacement and welding. Thus both obsidians and ash-flow materials present evidence of the very rigid retention of volatiles under changing environments, and this has significant geologic implications.

This study has been concerned with the quantitative relations between volatiles and some of the events of volcanism. These events have included explosive volcanic eruptions, some of which have strewn immense volumes of ash over world-wide areas; the flowage, emplacement, welding and devitrification of ash flows, with volumes ranging up to hundreds and even thousands of cubic miles; and the less violent eruption of viscous glass flows forming obsidians, commonly with minor vesiculation, and some with brecciation and welding and the development of microlites. It seeems that these volcanic events have in general been actuated by relatively small proportions of volatiles—grotesquely small compared with their effects and the amount of volcanic materials produced during eruption.

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