

# WATER AND OTHER VOLATILES IN VOLCANIC GLASSES\*

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## ABSTRACT

The two phases of volcanic glass, represented by obsidian enclosed in perlite, provide a key to origin and relations not available where either one occurs alone. The perlite has formed through the hydration of obsidian after emplacement. The H<sub>2</sub>O content of obsidian is commonly a few tenths of one per cent, and that of perlite 2 to 5 per cent. The H<sub>2</sub>O in these two types of glass is in such a different state of combination that the proportional effect in increasing the index of refraction is several times as great in obsidian as in perlite. This provides a method for determining the different modes of origin of volcanic glasses. The index of refraction before and after dehydration is determined and the difference divided by the water content. The resulting ratio provides definite criteria.

The studies of Shepherd indicate that the hydration resulting in the development of perlite at the expense of obsidian has tended to flush magmatic types of volatiles out of the system. These relationships indicate that the water and other volatiles in obsidian are pristine, being derived from the parent magma, whereas the water of perlite is the result of a later episode.

## INTRODUCTION

Volcanic glasses have long interested geologists, as they represent a chilled phase of original magma and commonly contain volatile constituents that are believed to represent, at least in part, pristine magmatic materials. The water content of glasses and the wide variation in its proportion have been a subject of much study, and some work has been done on the relation of water to physical properties. However, the full significance of the relationship between physical properties and variations in the volatile content of volcanic glasses presents a fruitful field of research.

Volcanic glasses occur abundantly in the Valles Mountain region of northern New Mexico, and an investigation of some of these was begun as a part of the study of that volcanic region by Ross and Smith. Early in the study it became evident that volcanic glasses presented relationships, some of which had not previously been recognized. This encouraged extending the study to include selected samples from other regions in the belief that this would provide pertinent information about some of the problems of volcanology.

Also it was evident that the mass spectrograph offered a new approach to the study of volatiles in glasses and could aid the general study of glassy rocks. Irving Friedman of the Geological Survey had become interested in the deuterium content of such glasses, and it seemed that

\* Publication authorized by the Director, U. S. Geological Survey.

both these modes of approach would be benefited by an integrated study. Thus, there has been a close coordination of the two methods of investigating volcanic glasses. However, it has seemed advisable to present the results of the index of refraction-water relationships in this paper, and those of the deuterium-hydrogen relationships in a second paper, which will appear in a later issue of this journal.

As commonly happens, new problems have arisen along with new information, and the present paper cannot attempt to follow through all of the avenues suggested. Nor is this the place to discuss possible geologic applications. However, a stage has been reached which seems to justify a presentation of the results that have been attained.

The present study applies only to rhyolitic, dacitic, and related glasses and the conclusions reached apply only to them. Basaltic and andesitic glasses seem to constitute a distinct and somewhat different problem, but data on a few such glasses are included for purposes of comparison.

#### ACKNOWLEDGMENTS

The study of volcanic glasses has been aided by the hearty cooperation of others interested in the problems presented. A number of the samples were received from the U. S. National Museum. Mr. Charles W. Chesterman of the California Division of Mines is engaged in a detailed study of the perlite and obsidian deposits of California and has been very helpful in contributing several sets of specimens of perlite-obsidian from that state. Dr. Tómas Tryggvason of the University Research Institute, Reykjavik, Iceland, sent us several specimens of perlite and one of perlite-obsidian. Professor Tom F. W. Barth has provided obsidian from Hekla, Iceland, and Robert G. Schmidt has provided perlite from Mojave, California, and "vitrophyre" from Saipan, western Pacific. Mr. J. J. Reed, New Zealand Geological Survey, kindly sent us a very useful set of specimens from that country. Joseph J. Fahey of the Geological Survey has been of great assistance in making dehydration tests of glasses and determining specific gravities.

#### PERLITE-OBSIDIAN PAIRS

##### *General description*

In many occurrences of glassy rhyolitic rocks, two types of glass have developed. One is typical obsidian and the other typical perlite, the perlite normally being the dominant material. The obsidian commonly occurs as small pellets enclosed in perlite as illustrated in Plate 1, Fig. *a*. In thin section the obsidian pellets occur as cores surrounded by the concentrically cracked perlite as illustrated in Plate 1, Fig. *b*. These ob-

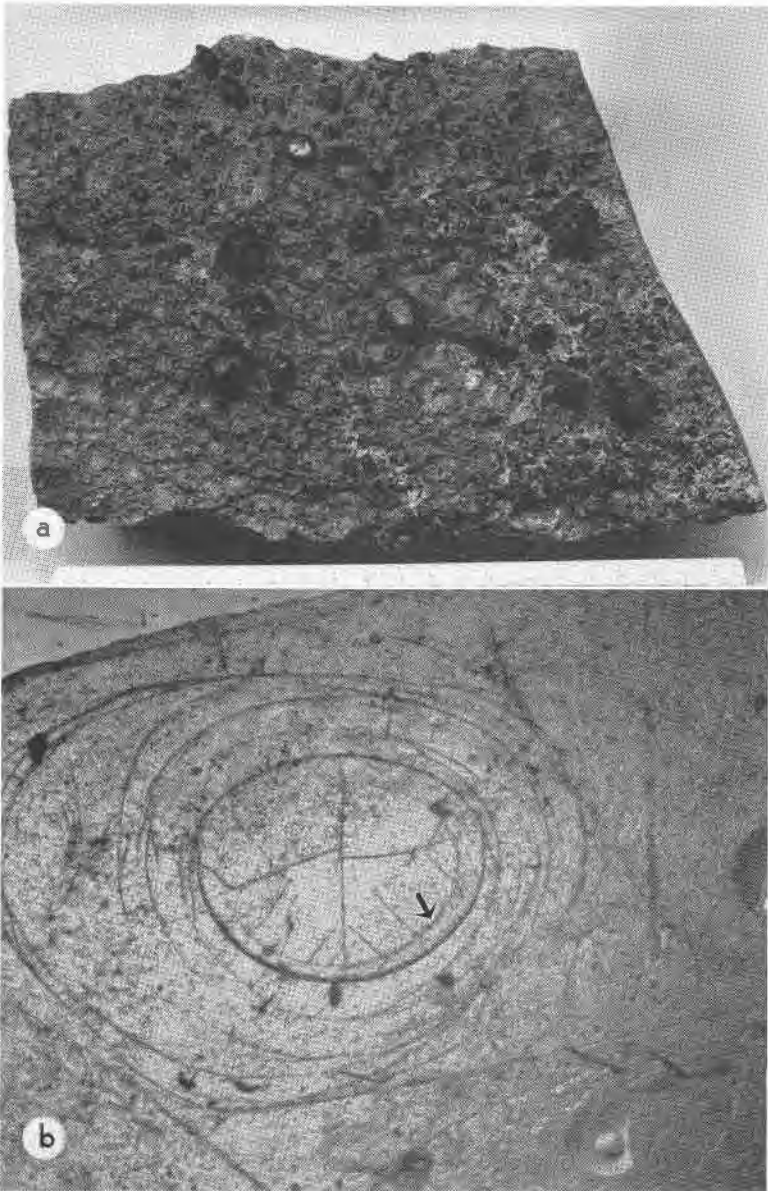


PLATE 1

FIG. *a*. Hand specimen from 1½ miles west of Polvadera Peak, Valles Mountains region, New Mexico. Collected by Smith. Illustrates obsidian cores (dark) enclosed in perlite (gray). Numerous pits represent places where cores have broken out. ½ natural size.

FIG. *b*. Thin section showing perlite with perlitic cracks, enclosing non-hydrated core. The arrow marks the boundary between the core with a much lower index of refraction than the enclosing perlite. The fractures within this core formed on the release of strain during grinding. From Arroyo Hondo, Valles Mountains region, New Mexico. Magnification  $\times 30$ .

sidian cores have been called *marekañite* (Judd, 1886, p. 241-248), and their origin has long been a subject of speculation.

The occurrence of two types of glass occurring in pairs presents evidence about their genetic history that is lacking when either obsidian or perlite is considered alone. In these occurrences there is a sharp boundary between perlite and obsidian, giving direct evidence of a sequence in their formation. The only interpretation that seems possible is that the entire mass was originally obsidian and the perlite was formed as a result of some secondary process. Thus the pairs provide a key which permits the development of criteria for the differentiation of these distinct phases and brings into contrast the differences in their physical and chemical properties.

In hand specimens obsidian is usually black, but much of that from the Valles Mountains region of New Mexico is perfectly transparent in plates up to 3 millimeters thick and with only a slight smoky color. Where trichites are unusually abundant the obsidian may be gray. In general the obsidian contrasts strongly with the light-colored perlite. However, the obsidian also occurs as very small cores in perlite as illustrated in Plate 2, Fig. *a* and these tend to merge in color with the perlite.

The writers have examined perlite-obsidian pairs from 8 different occurrences; four from the Valles Mountains region, New Mexico, one from Cerro No Agua, New Mexico, one each near Olancha and Clear Lake, California, and one from Iceland, and one pumice from Mono craters, California.

A hand specimen from about  $1\frac{1}{2}$  miles west of Polvadera Peak, Valles Mountains region, New Mexico, shows the relation between perlite and obsidian cores. In the Arroyo Hondo locality of the same region, the cores range up to 8 cm. in diameter, those about 15 mm. in diameter being most abundant. The material from this locality is unusually low in the minute trichites which characterize most volcanic glass, the obsidian is remarkably transparent, and the relationships are representative of perlite and obsidian in general. For this reason many of our more detailed experiments have been based on this material.

The other occurrences of volcanic glass need no detailed description. All the obsidians studied are similar to those discussed in connection with the obsidian-perlite pairs. So-called pitchstones seem to include several types of glass. Some are a dull gray due to the development of an unusually large proportion of trichites, and do not differ essentially from other obsidians, which also commonly contain trichites. Some, especially those with a greenish color, have undergone alteration and do not form a part of this study. The larger cores are also characterized by a hydrated film, although this is not as obvious as in those that can be

examined under the microscope. However, this hydrated film is shown by the development of a vesiculated film on heating the cores.

In Table 3 a group of hydrated glasses is listed. This includes typical perlites, pumices, and rocks which would commonly be described as flow rocks, but which are also characterized by perlitic structures. Many of these contain varying proportions of phenocrysts, and in a few the phenocrysts were removed by heavy solutions before study.

#### *Microscopic relations*

In addition to the cores that are so conspicuous in the hand specimen, the perlite from several localities contains smaller but similar cores which are observable only under the microscope. Selected grains of such material from Arroyo Hondo, New Mexico, are illustrated in Plate 2, Fig. *a*. These vary in size to as little as about 0.04 mm. in diameter, those about 0.15 mm. being most characteristic. In this material the outer zone has a water content of about 3.5 per cent and the cores about 0.3 per cent. The index of refraction of the cores is about 1.486 and that of the enclosing perlite about 1.497. This large difference results in the strong contrast illustrated in Plate 2, Fig. *a*. The perlites from Prestahnukur, and Cerro No Agua, contain cores similar to those from Arroyo Hondo.

This sharp boundary is of especial interest, as it might be expected that diffusion of  $H_2O$  into the glass would result in a transitional boundary between the two phases. However no such transitional boundary is observable in any of the specimens studied, even with very high magnifications.

Plate 2, Fig. *b* illustrates the same cores as Plate 2, Fig. *a* under crossed nicols, and shows the strain birefringence which is observable in almost all such cores. This strain birefringence has been described by Judd (1886, p. 241–248) as a part of his study of the “marekanites” from near Okhotsk, Siberia.

There appear to be two types of strain represented in the cores in Plate 2, Fig. *b*. The conspicuous outer zone, which is white in the photomicrograph, is probably related to the hydration of the outer rims. The inner part shows a fainter, more shadowy birefringence that seems to be independent of the narrow outer zone. This is especially conspicuous in grains up to 10–15 mm. in diameter, although it seems to be absent in very large ones. It is questionable whether the formation of a hydrated film 0.03 to 0.05 mm. in thickness would develop strain throughout the core and for a distance several hundred times as great as the thickness of the hydrated border. The outer birefringence disappears on heating, while the inner one persists.

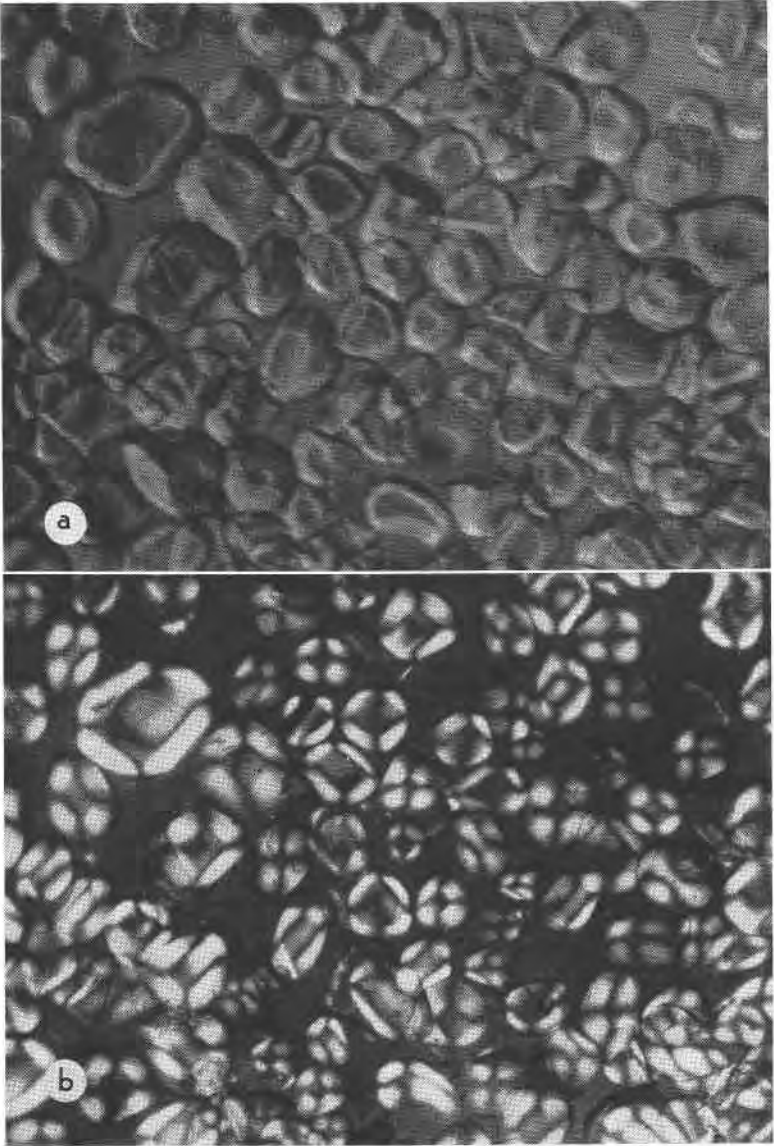


PLATE 2

FIG. *a*. Glassy beads from Arroyo Hondo. Two phases of glass composed of inner cores of low-water glass (0.3% H<sub>2</sub>O) enclosed by hydrated glass (3.5% H<sub>2</sub>O). The contrast between the two is due to the difference in the indices of refraction. Cores  $n=1.486$ , rims (perlite)  $n=1.496$ . Magnification  $\times 27$ .

FIG. *b*. The same glass grains under crossed nicols, showing strain birefringence. The stronger birefringence on the border, coincides with the hydrated outer rim. The inner part shows a weaker birefringence.

The glass surrounding the obsidian cores shows the characteristic perlite structure, but there are great differences in the perfection of its development. An unusually good example of an area of perlite with onion-like structure surrounding a nonhydrated core, is illustrated in Plate 1, Fig. *b*.

#### *Chemical composition*

All the glasses considered in this paper are rhyolitic in character. Most of those for which chemical analyses are available have a silica content from 75 to nearly 78 per cent (water free). One of the least silicic glasses included in this study is that from Little Glass Mountain, California (Shepherd 1938, p. 328), with  $\text{SiO}_2 = 73.59$  per cent.

The  $\text{H}_2\text{O}$  content of the obsidian ranges from about 0.1 to 0.9 per cent in 19 specimens available for study. Most commonly the  $\text{H}_2\text{O}$  content is of the order of a few tenths of a per cent. The hydrated glasses, of which 23 were studied, range from around 2 to about 5 per cent  $\text{H}_2\text{O}$ . A very large proportion have between 3 and 4 per cent  $\text{H}_2\text{O}$ . A further discussion of volatiles is included below.

#### *Methods of study*

The study of volcanic glasses has involved two distinct methods of approach. One of these has been a determination of the differences in amount of the  $\text{H}_2\text{O}$  and a correlation of this with the physical properties of the glass and in particular with the indices of refraction. The other approach has been the determination of the deuterium-hydrogen ratio of the water in solution in the glass.

#### *Index of refraction determinations*

The problems involved seemed to demand very exact determinations of the indices of refraction, especially for the low-water obsidians with their small differences in these indices. For most of the obsidians it was possible to grind and polish surfaces and measure indices of refraction on a refractometer using sodium light. Some glasses gave an optically perfect line of total reflection. In others the line was somewhat hazy and the mean of several readings was used.

The indices of refraction of perlite, pumice, and dehydrated glasses were determined in index oils. The accurate results desired made advisable the use of the double inclined illumination method developed by Saylor (1953). This accentuates contrasts until differences of index of refraction in the 4th decimal place are observable. For this study a special set of index oils with very small intermediate steps was prepared and checked at frequent intervals. Further refinement was obtained by

mixing these oils, drop by drop, and by repeated checks. Temperatures were kept within close limits. Close checks between refractometer and index oil determinations were obtained. It is believed that these methods and the checks gave results significant in the 4th decimal place for much of the glass. Some of the glasses were slightly variable and results significant only in the 3rd decimal place were obtained.

#### *Determinations of volatiles*

Two methods have been used in the determination of the volatiles in glasses. One involves weighing, heating to thorough fusion (about 1050° C. in most glasses), and reweighing. The other involves the direct weighing of the H<sub>2</sub>O as a part of the deuterium-hydrogen determinations. The first method gives the total volatiles, whereas the second gives the H<sub>2</sub>O content directly. Only small differences in the results of the two methods were observable in the study of rhyolitic glasses.

Most of the rhyolitic glasses are so low in ferrous iron that the oxidation of any part of this would have no material effect on the loss of weight on heating. This was confirmed by the method of direct weighing.

Preliminary experiments indicated that most of the H<sub>2</sub>O in glass, and in particular that above a few tenths of a per cent, seems not to be held under equilibrium conditions. However, loss of H<sub>2</sub>O at successive temperatures between 200° and 1050° C. and for uniform periods of heating was determined on representative samples. These experiments showed that loss of H<sub>2</sub>O was far more dependent on length of heating at successive steps than upon actual temperatures. The dehydration curves based on these data seemed to provide no essential information and therefore have not been reproduced. However, it is significant that in our experiments all but about 0.3 per cent of the H<sub>2</sub>O of perlite can be driven off by continued heating at temperatures below 600° C., whereas that above that figure is held with much greater tenacity. The tenacity with which water in perlite is held at different temperatures has been studied by King, Todd, and Kelley (1948).

More significant data on the relation of H<sub>2</sub>O content to indices of refraction were obtained by determining the water loss on representative samples (those from Arroyo Hondo), at closely spaced intervals of water loss. At each successive stage in H<sub>2</sub>O loss, material was removed for index of refraction determinations. The results are presented in Table 4, and the relation indicated by the curves in Fig. 1.

The studies of the escape of volatiles from glasses and the vesiculation at fusion temperatures have presented some interesting relationships which probably have bearings on some aspects of volcanism. However, these need not be considered here.



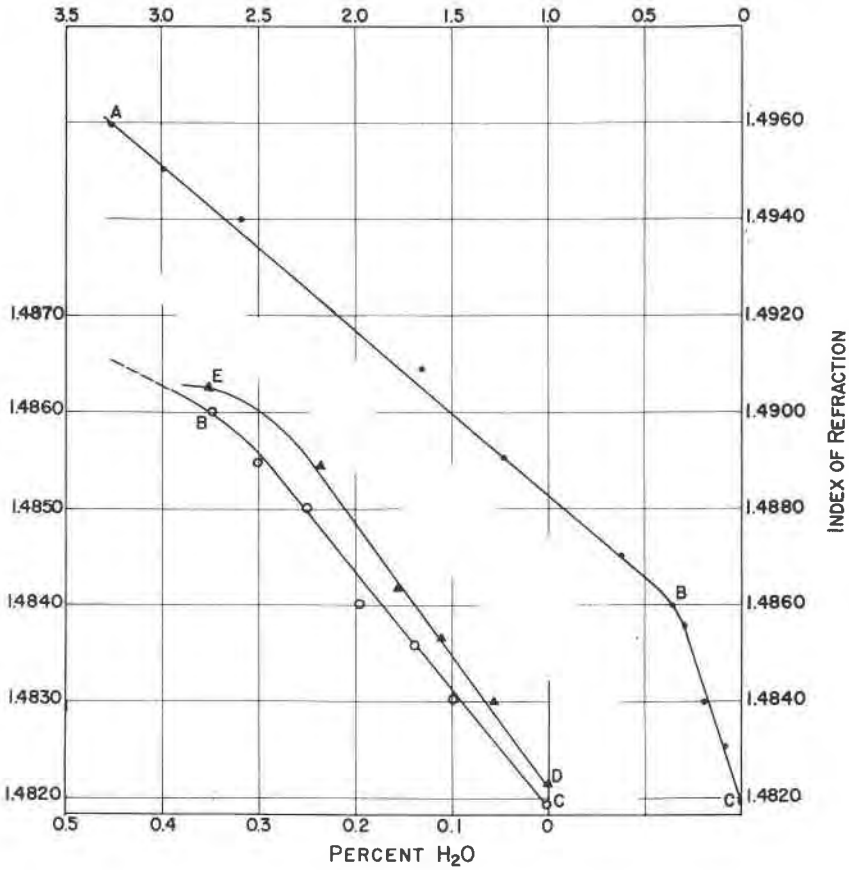


Fig. 1. Relationships between water content and indices of refraction for Arroyo Hondo glasses. The upper curve represents the relationship for perlite. The lowest of the three curves represents that part of the curve for perlite lying between the points B and C plotted on the larger scale. The third curve E-D presents the same relationships for the obsidian plotted on the same scale.

Tilley (1922) points out that the indices of refraction of rhyolitic glasses rise with increasing water content.

*Specific gravity*

The specific gravity of the obsidian from Arroyo Hondo is 2.34. On dehydration the weight loss equaled the water loss. Most of the perlite and all of the pumice contain vesicular cavities which prevent meaningful specific gravity determinations. However, the specific gravity of the perlite from Arroyo Hondo is 2.37 as against 2.34 for the obsidian from

which it was derived. About 3.5 per cent of  $H_2O$  has been added without a corresponding change in specific gravity—that is, with only a small change in volume. The marked birefringence illustrated in Plate 2, Fig. *b*, which has developed as a result of hydration, is no doubt related to this addition of water without a corresponding change in volume. The rise in the index of refraction with the addition of water of hydration is no doubt a part of the same relationship.

#### *Discussion of observations*

The large obsidian inclusions (marekanites) in perlite have long been recognized, but the small ones (Plate 2, Fig. *a*) recognizable only under the microscope are more informative. In these the sharpness of the contact between the two glass phases is shown. It is evident that the high-water rims immediately around the cores have been formed at their expense. Successive outer shells all have similar relations, and it seems evident that all the perlite (i.e., all the high-water glass) has formed from obsidian. This addition of water (hydration) evidently occurred after emplacement of the original glass.

#### *Relation of indices of refraction to water content*

Eight occurrences with two phases of glass present as obsidian and perlite and one of pumice and obsidian have been available for study. The relation between  $H_2O$  content and indices of refraction are presented in Table 1. The indices of refraction before and after dehydration ( $n_h$  and  $n_e$ ) are given; the difference between these is listed and also ( $w$ ) the  $H_2O$  loss in per cent. The difference in the numerical value of the two indices of refraction was divided by water content of the glass. This gives a ratio, shown in the last column of the table, which represents the relative effect of water on the index of refraction of the glass. The same relationship is presented for a group of obsidians in Table 2 and for a group of hydrated glasses in Table 3.

In the perlite of the perlite-obsidian pairs represented in Table 1 the  $H_2O$  content ranges from about 3 to 3.5 per cent, or about 10 times that in the obsidian cores. In some of the hydrated glasses of Table 3,  $H_2O$  content is as much as 5 per cent, and some of the obsidians of Table 2 contain 0.1 per cent  $H_2O$  or less.

These tables show that the relationship of water to index of refraction is surprisingly consistent. Of course, it is best for the high-water glasses where plus or minus errors in determinations of  $H_2O$  content or of indices of refraction have a minor effect on the resulting ratio. In the group represented in Table 1, only in *7b* (representing a pumice from Mono Craters) is the ratio materially out of line. This is probably due to the fact that

TABLE 1. RELATIONS BETWEEN WATER CONTENT AND INDICES OF REFRACTION OF PERLITE-OBSIDIAN GLASSES

No.	Character	Indices of Refraction			Water loss	$\frac{n_h - n_e}{w}$
		$n_h$	$n_e$	$n_h - n_e$	in per cent $w$	
1a	Obsidian*	1.4860*	1.4820*	0.0040	0.32	0.0125
1b	Perlite	1.4957	1.4818	0.0139	3.21	.0043
2a	Obsidian	1.4860*	1.4817	0.0043	0.33	.0130
2b	Perlite	1.4962	1.4821	0.0141	3.22	.0044
3a	Obsidian	1.4862*	1.4817	0.0045	0.35	.0128
3b	Perlite	1.4976	1.4818	0.0158	3.20	.0049
4a	Obsidian	1.4865*	1.4825	0.0040	0.35	.0114
4b	Perlite	1.4985	1.4824	0.0161	3.45	.0047
5a	Obsidian	1.4854*	1.4820	0.0034	0.30	.0113
5b	Perlite	1.4963	1.4821	0.0142	3.45	.0041
6a	Obsidian	1.4860*	1.4821	0.0039	0.33	.0118
6b	Perlite	1.4980	1.4821	0.0159	3.40	.0047
7a	Obsidian	1.4863	1.4818	0.0045	0.35	.0129
7b	Pumice	1.494	1.482	0.012	1.9	.0063
8a	Obsidian	1.4885	1.4858	0.0027	0.22	.0123
8b	Perlite	1.498	1.485	0.013	3.5	.0038
9a	Obsidian	1.488	1.477	0.011	0.9	.0122
9b	Perlite	1.495	1.479	0.016	3.5	.0045

\*. Measured on refractometer.

## LOCALITIES OF PERLITE-OBSIDIAN GLASSES

1a, 1b—Arroyo Hondo, Valles Mountains region, New Mexico, upper glass horizon.

2a, 2b—Arroyo Hondo, Valles Mountains region, New Mexico, lower glass horizon.

3a, 3b—Obsidian Ridge, Valles Mountains region, New Mexico.

4a, 4b—1 mile SW of Bear Springs, Valles Mountains region, New Mexico.

5a, 5b—Cerro No Agua, near Tres Piedras, New Mexico.

Nos. 1a, 1b to 5a, 5b, collected by Ross and Smith.

6a, 6b—Prestahnukur, Iceland. Received from Dr. Tómas Tryggvason, Reykjavik, Iceland.

7a, 7b—Mono Craters, Calif. Collected by Irving Friedman.

8a, 8b—Near Lower Lake, California

9a, 9b—Near Olancho, California.

} Contributed by Charles W. Chesterman.

Mono Craters are very young and the pumice is only partly hydrated.

In Table 2, No. 7, the obsidian from Mayor Island, New Zealand, gives a ratio that is low compared with the other members of the group. However, the numerical figures are so small that an error of 0.01 per cent in determination of the  $H_2O$ , or of 0.0002 in the indices of refraction would explain the discrepancy. The value 0.0075 is still such as to align the Mayor Island glass with other obsidians. Other members of the

TABLE 2. INDEX OF REFRACTION-WATER RELATIONS OF OBSIDIANS

No.	Indices of Refraction			Water loss in per cent $w$	$\frac{n_h - n_e}{w}$
	$n_h$	$n_e$	$n_h - n_e$		
1	1.4843*	1.4827	0.0016	0.11	0.0145
2	1.4832*	1.4815	0.0017	0.11	.0155
3	1.4842*	1.4820	0.0022	0.20	.0110
4	1.4850*	1.4805	0.0045	0.32	.0141
5	1.4883*	1.4867	0.0021	0.19	.0110
6	1.4946*	1.4934	0.0012	0.10	.0120
7	1.4878*	1.4872	0.0006	0.08	.0075
8	1.4905*	1.4893	0.0012	0.10	.0120
9	1.4910*	1.4898	0.0012	0.10	.0120
10	1.4834*	1.4820	0.0014	0.12	.0117

\* Measured on refractometer.

## OBSIDIAN LOCALITIES

- 1 mile NW of the Puerto de Abrigo, Valle Toledo quad., Valles Mountains region, New Mexico.
- Obsidian Knob,  $1\frac{1}{2}$  mi. S.W. of Polvadera Peak, Valles Mountains region, New Mexico. Nos. 1 and 2 collected by Ross and Smith.
- Ascension Island, South Atlantic. Received from U. S. National Museum, Museum No. 36281.
- Norwikakat River, Alaska. Received from U. S. National Museum, Museum No. 6384.
- Mt. Hekla, Iceland. Received from Prof. Tom F. W. Barth.
- Harfintinnuhyggur, Iceland. Received from U. S. National Museum, Museum No. 88428.
- Mayor Island, New Zealand. Received from U. S. National Museum, Museum No. 70345.
- Little Glass Mountain, Calif. Received from Donald E. White.
- Big Glass Mountain, Calif. Received from Donald E. White.
- Osidian Cliff, Yellowstone National Park. Collected by Irving Friedman.

group with about 0.10 per cent  $H_2O$  fall into line with those with 0.30 per cent  $H_2O$ .

The outstanding relationship shown in Tables 1, 2 and 3, is the very large difference in the effect of water, in its several forms, upon the indices of refraction of the two types of glass. The ratio  $(n_h - n_e)/w$  for 9 obsidians of Table 1 ranges from 0.0113 to 0.0130, with a mean of 0.0122. For 8 perlites (omitting the partly hydrated pumice), this ranges from 0.0038 to 0.0049, with a mean of 0.0044. The effect of  $H_2O$  in raising the index of refraction is over  $2\frac{1}{2}$  times as great in obsidian as in perlite. This large difference must be due to the way in which  $H_2O$  is held in the two glasses. The obsidians of Table 2, and perlites and pumices of Table 3

TABLE 3. INDEX OF REFRACTION-WATER RELATIONS OF HYDRATED GLASSES

No.	Character	$n_h$	$n_e$	$n_h - n_e$	Water loss in per cent $w$	$\frac{n_h - n_e}{w}$
1	Perlite	1.4957	1.4789	0.0168	4.33	0.0039
2	Pitchstone	1.4950	1.4805	0.0145	3.22	.0045
3	Pitchstone	1.4966	1.4810	0.0156	3.86	.0040
4	Perlite	1.4982	1.4811	0.0171	4.20	.0041
5	Perlite	1.4950	1.4802	0.0148	4.00	.0037
6	Pumice	1.503	1.485	0.018	3.80	.0047
7	Welded tuff	1.500	1.487	0.013	2.85	.0045
8	Pumice	1.520	1.496	0.024	5.3	.0045
9	Pumice	1.520	1.505	0.015	4.0	.0037
10	Perlite	1.498	1.483	0.015	3.7	.0040
11	Pitchstone	1.499	1.483	0.016	4.5	.0035
12	Perlite	1.496	1.482	0.014	4.45	.0032
13	Perlite	1.495	1.420	0.013	2.96	.0044
14	Perlite	1.500	1.485	0.015	3.85	.0039

## LOCALITIES OF HYDRATED GLASSES

1. Perlite, Bear Jump, Peralta Canyon, Valles Mountains region, New Mexico.
2. Perlite  $1\frac{1}{2}$  mi. NW of Bland, Valles Mountains region, New Mexico.
3. Brown glass, Bears Head, Valles Mountains region, New Mexico.
4. Perlite,  $1\frac{1}{4}$  mi. SSE of Bears Head, Valles Mountains region, New Mexico.
5. Perlite, mouth of Colle Canyon, Valles Mountains region, New Mexico.
6. Pumice, El Cajete, Valles Mountains region, New Mexico.
7. Obsidian-like welded tuff, Ammon Quad., southeastern Idaho. Specimens 1 to 7 collected by Ross and Smith.
8. Pumice, from 2 kilometers west of Mexico-Michoacan boundary, on Mexico-Guadalajara Highway, collected by Carl Fries.
9. Pumice, from 3 kilometers west of Tenango Highway, State of Mexico, Mexico. Collected by Carl Fries.
10. Perlite, Black Canyon, NW 1/4 Opal Mt. Quadrangle, Calif. Collected by Robert G. Schmidt.
11. Pitchstone, Saipan, Pacific Ocean. Collected by Robert G. Schmidt.
12. Perlite from Sarashene-gou, of Shinano, Japan. Received from U. S. National Museum, Museum No. 11857.
13. Perlite from Nagngiho,  $3\frac{1}{2}$  mi. NNW of Wairakei on Waihruru stream, New Zealand.
14. Perlite, Earthquake Flat, 12 mi. south of Rotorua, New Zealand. Nos. 13 and 14 were received from Dr. J. J. Reed, New Zealand Geological Survey.

vary a little more from the mean, but present the same relationships.

We have observed only one glass with the character of an obsidian in which there may be a question about its origin. A glass from Xalapazguillo, Puebla, Mexico, submitted by Carl Fries of the Geological Survey,

had an H<sub>2</sub>O content of 0.89 and an index of refraction of 1.4864 before, and 1.4825 after dehydration, giving a ratio of 0.0044. By the criteria outlined, therefore, it should be a hydrated glass notwithstanding its obsidian character. Its most conspicuous difference is strongly contrasting bands of dark- and light-gray glass. The relations lead to a tentative suggestion that this obsidian represents a magma which was erupted into a moist environment where it became hydrated at a temperature, possibly of 600° C. or less, that is below a temperature at which the water assumes combinations giving the higher effect on the index of refraction.

Additional information about H<sub>2</sub>O-index of refraction relationships is presented by the curves shown in Fig. 1. Here indices of refraction have

TABLE 4. OBSIDIAN AND PERLITE FROM ARROYO HONDO, WATER-INDEX OF REFRACTION RELATIONS

Perlite		Obsidian	
H <sub>2</sub> O (Per cent)	Index of refraction	H <sub>2</sub> O (Per cent)	Index of refraction
3.35	1.4960	0.345	1.4862
3.00	1.4950	0.245	1.4855
2.60	1.4940	0.155	1.4842
1.71	1.4910	0.110	1.4836
1.25	1.4890	0.049	1.4830
0.64	1.4870	0	1.4822
0.30	1.4855		
0.19	1.4840		
0.10	1.4830		
0	1.4819		

been plotted against the amount of H<sub>2</sub>O held in the obsidian and perlite from Arroyo Hondo. On the smaller scale the curve shows two parts (*A* to *B* and *B* to *C*) with a very distinct change in the inclination at the point ( $n=1.4857$ , H<sub>2</sub>O=0.3). The curves plotted on the larger scale show that the curve for obsidian (*E* to *D*) corresponds with that part of the curve (*B* to *C*) for perlite lying between 0 and 0.3 per cent H<sub>2</sub>O. That is, the curves show that the water of hydration in perlite has been added to the original glass represented by obsidian without affecting the original H<sub>2</sub>O.

The foregoing relations mean that the true effect of the water of hydration is exemplified by that portion of the curve lying between points *A* to *B*, where  $n=1.496$  and 1.486. The difference between the two is about 0.010 and the H<sub>2</sub>O loss about 3 per cent. Therefore the figure for

the corrected ratio becomes  $0.0101/3=0.0034$  as compared with 0.0127 for obsidian. If the calculation is based on the relations between the points between *A* and *C* we have  $1.496-1.4819=0.0141$  and  $w=3.35$ , giving  $0.0141/3.55=0.0039$ . In other words, the effect of  $H_2O$  on the index of refraction as corrected is in fact nearly  $3\frac{1}{2}$  times as great for obsidian as for perlite. Thus the ratios expressing the relation between  $H_2O$  and indices of refraction for hydrated glasses in Tables 1 and 3 are in fact the mean effect of two states of water. For purposes of determination, however, the figures given in these tables are adequate, and there should be no doubt as to which group the specimen belonged.

#### THE STATE OF WATER IN GLASS

The cause of the large difference in the effect of water on the indices of refraction of the two types of glass—that in obsidian and that with

TABLE 5. GASES FROM ROCKS IN VACUO (SHEPHERD, 1938, p. 326)

(Volume percentages)

No.	CO <sub>2</sub>	CO	H <sub>2</sub>	N <sub>2</sub>	A	S <sub>2</sub>	Cl <sub>2</sub>	F <sub>2</sub>	H <sub>2</sub> O
Obsidians (Rhyolitic)									
1	1.402	0.705	0.101	2.897	0.000	0.367	2.965	3.163	88.386
2	1.595	0.035	0.174	1.420	0.000	0.014	0.499	0.516	96.299
3	0.179	0.073	0.501	3.897	0.002	0.000	1.820	7.795	89.246
4	0.075	0.008	2.253	1.153	0.000	0.039	1.498	2.205	94.434
5	0.672	0.007	0.377	0.138	tr.	0.000	1.713	4.329	92.761
6	0.077	0.032	0.080	0.053	udt.	0.000	0.069	1.136	98.551

water of hydration—is not clear. We are only sure that there must be some marked difference in the way water is combined. It is commonly believed that in a solution, such as glass, the different ions are present in essentially all possible combinations. The determination of the character of these combinations presents a difficult problem in physical chemistry, and an evaluation of those combinations as they affect indices of refraction poses an even more difficult one.

In studies of gases in artificial glass Harrison (1947, p. 362–366) and also Florence and associates (1950, p. 121–128) report the presence of OH among the volatiles present in glass at fusion temperatures. Keller and Pickett (1954, p. 87–98) also have reported OH among the forms of water present in perlite, especially that proportion (about 1.12 per cent) retained at higher temperatures. Water is evidently present in glass in several forms, but the way these combine with silica and other constituents to control indices of refraction is problematical.

## CHEMICAL COMPOSITION OF VOLATILES

By remarkably good fortune a pair of glasses, which are a part of this study, were investigated by Shepherd (1938) in his classical study of water in glasses. The following Table 5 from that paper (p. 326) gives the volatile content of 3 pairs of glasses, nos. 5 and 6 being those of the Cerro No Agua glasses. Our data on the relation between  $H_2O$  and the indices of refraction of these glasses are given in Table 1, nos. 5*a* and 5*b*.

No. 5 of the foregoing Table 5, called black obsidian by Shepherd, represents the low-water glass, and material called "pitchstone" by Shepherd, is the same glass after hydration. The significant changes here shown are the large losses, particularly of  $CO_2$ ,  $Cl_2$ , and  $F_2$ , and the gain in  $H_2O$  on the change of obsidian into "pitchstone." That is, hydration has had the effect of flushing these volatiles from the system and replacing them by  $H_2O$  in the hydrated glasses.

Our studies of the Cerro No Agua glasses have shown that the perlite (pitchstone of Shepherd) has about 3.35 per cent of  $H_2O$  which agrees closely with Shepherd's determination of 3.10 per cent (Shepherd, 1938, p. 329). On the other hand we have found only about 0.3 per cent of  $H_2O$  in the obsidian as a result of numerous tests. We now know, as Shepherd could not have known, that the obsidian cores have an outer hydrated film. Thus there is a strong probability that the  $H_2O$  determined for the "pitchstone" by Shepherd was in part water of hydration. This in no way detracts from the definite evidence of change in the composition of the water. It merely suggests that the difference in the composition of the two states of water may have been even greater than indicated.

Shepherd made similar determinations on "dense black obsidian" and "pumiceous phase of the same block" from Big Glass Mountain, California (nos. 1 and 2), and on "dense black obsidian" and a "coarsely vesiculated portion of same block" from Coso Mountains (nos. 3 and 4). These tests show the same trend in the removal of  $CO_2$ ,  $Cl_2$ , and  $F_2$  with an increase in  $H_2O$  as in the Cerro No Agua materials.

## SOURCE OF WATER IN GLASS

The probable explanations of water in normal obsidian is that it was inherited directly from the magma, that is, it represents pristine  $H_2O$ . The very large difference in the effect on the indices of refraction shows that the water in perlite and obsidian was fixed under very different conditions. The fact that the  $H_2O$  of obsidian is held tenaciously and released almost explosively at temperatures of  $800^\circ$  to  $1000^\circ$  C. indicates fixation at temperatures characteristic of magmas. The data presented by Shepherd (1938, p. 326) show that obsidian is characterized by im-



portant proportions of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{Cl}_2$ ,  $\text{S}_2$ , and  $\text{F}_2$ —volatiles probably derived directly from a magma.

The water of hydration may have been derived from volatiles escaping at depths from the cooling magma. However, the water of hydration was deficient in other volatiles and so water derived from a magma seems to present a doubtful source. A distinctly post-magmatic episode, probably the result of rain, snow, or ground water seems more probable. This reaction could occur during a late cooling stage or at a still later time.

#### BASALTIC AND ANDESITIC GLASSES

As previously stated, basaltic and andesitic glasses seem to present a somewhat different problem from that of the rhyolitic ones. For this

TABLE 6. INDICES OF REFRACTION OF BASALT-ANDESITE GLASSES

No.	Character	Indices of Refraction			Water loss ( <i>w</i> )
		$n_h$	$n_e$	$n_h - n_e$	
1	Basalt (pumice)	1.597	1.600	+0.003	0
2	Basalt	1.598	1.598	0	1.2
3	Basalt (Pele's hair)	1.603	crystallized on cooling		1.2
4	Basalt (thread pumice)	1.600	1.600	0	3.35
5	Andesite (pumice)	1.536	1.536	-0.006	4.75

#### LOCALITIES OF BASALT AND ANDESITIC GLASSES

1. Pumice formed at the surface of the 1948 summit flow, Mauna Loa.
2. Beach pellets formed where the 1950 flow from Mauna Loa entered the ocean near Hoopuloa. Collected by Jewell J. Glass.
3. Pelee's hair from Mauna Loa.
4. Thread pumice or "reticulite" from near Volcanic Observatory, Kilauea, collected by Chester K. Wentworth.
5. Andesitic pumice from Paso de Cortes between Ixtaccihuatl and Popocatepetl volcanoes.

reason such glasses have not been included in this study. Also the small tendency for basaltic magmas to form glasses and the very ready alteration of such glasses are handicaps to such a study. However, the reader will be interested in data on a few basaltic glasses for purposes of comparison, and the data for 4 such glasses, all from Hawaii, are given in Table 6. The basaltic glasses have indices of refraction not far from 1.600, and the andesitic glass from the pass between Popocatepetl and Ixtaccihuatl, Mexico, has an index of refraction around 1.530. The notable thing about the basaltic glasses is that their indices of refraction show

little response to water content. With actual alteration of basaltic glasses the effect on physical properties, of course, becomes important. The indices of refraction of a group of basaltic glasses are listed by Tilley (1922, p. 279).

The basaltic glasses are so high in ferrous iron that the relations between water content and oxidation of ferrous iron would all be inter-related. A detailed study of all these would be necessary for any definitive study of basaltic glasses.

#### SUMMARY

Three independent methods of study have shown that volcanic glasses are of two types, each with distinctive properties. The relation between water content and indices of refraction indicates that there must be a marked difference in the physical state of the two types of water. An earlier study by Shepherd shows distinct different proportions of certain volatiles ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{F}_2$ ,  $\text{S}_2$ , and  $\text{Cl}_2$ ) in the two types of glass. When interpreted in the light of later geologic studies there is a new significance added to the classic study of Shepherd. We believe that this will lead others, as it has us, to an increased appreciation of his work.

One type of glass (obsidian) is believed to be characterized by pristine water derived from the magma, and the other (hydrated) to be the result of a later episode probably unrelated to magmatic processes. The relations present a seemingly clear-cut method for distinguishing between glasses with pristine water and those which have undergone later hydration. The glasses characterized by pristine water contain under 1 per cent of  $\text{H}_2\text{O}$  in those available for study. The hydrated glasses have an  $\text{H}_2\text{O}$  content ranging most commonly from 3 to 5 per cent. If, as seems evident, the  $\text{H}_2\text{O}$  in the high-water glasses is the result of post magmatic processes, these glasses high in water present no evidence about the amount of  $\text{H}_2\text{O}$  in the magma from which they are derived. On the other hand the glasses with pristine water do not set a limit on the amount of water in the magma from which they were derived. This is because we have no way of determining the amount of water lost by diffusion during the eruption and emplacement of the magma, or during the vesiculation of a pumice.

The very small amount of water necessary for the vesiculation of a glass and the development of a very large proportion of voids, has interesting geologic implications which can not be developed here.

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