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Natural hydration and ion exchange of obsidian: an electron microprobe study

PETER A. JEZEK

Department of Mineral Sciences
Smithsonian Institution
Washington, D. C. 20560

AND DONALD C. NOBLE

Department of Geology and Geological Engineering
Michigan Technological University
Houghton, Michigan 49931

Abstract

The electron microprobe can be successfully used in the analysis of hydrated glass (perlite), and its ability to analyze very small volumes makes it an ideal tool for studying processes of hydration and ion exchange. Water content, although not measured directly, may be estimated quite accurately by difference-of-sum of oxide components between associated nonhydrated glass (obsidian) and its hydrated equivalent (perlite).

Analyses of four obsidian–perlite pairs with a wide electron beam (100μm in diameter) are very similar to wet-chemical analyses of the samples. Analyses of massive perlite using a narrow (5μm) beam detected about 3 weight percent H_2O, but revealed only a very small amount of ion exchange, mainly a slight loss in Na_2O. Analyses made along fine fractures in the perlite, however, show slightly to significantly higher water contents accompanied by appreciably higher K_2O and appreciably lower Na_2O contents.

The amount of water of hydration in a glass is probably governed by the availability of openings in the polymerized glass structure. A higher degree of hydration in a thin layer along fractures is accompanied by more intense ion exchange. This higher degree of hydration and ion exchange, associated with further weakening and disruption of the glass structure, is an early stage in the eventual formation of secondary argillic or zeolitic assemblages. During the time when the material still retains the optical properties of glass the ion-exchange processes appear to be largely governed by the composition of the glass.

Introduction

Ross and Smith (1955) investigated the influence of water content on the physical properties of obsidian–perlite glass pairs. Subsequently, Aramaki and Lipman (1965), Lipman (1965), Noble (1967), and Lipman *et al.* (1969) found by bulk chemical analyses of such pairs that in the perlite Na_2O is depleted and K_2O enriched with respect to the nonhydrated obsidian core. Changes also have been reported for such minor elements as Sr, Ba and the halogens (Zielinski *et al.*, 1977; Noble *et al.*, 1967).

In addition, many crystalline rocks can have somewhat different contents of alkali and alkaline earth elements, halogens, and other elements than their molten precursors (Noble, 1965, 1970; Noble *et al.*, 1967; Noble and Hedge, 1969; Rosholt *et al.*, 1971; Hart *et al.*, 1971; Haffty and Noble, 1972; Zielinski *et al.*, 1977). Only nonhydrated glasses from rocks that have not undergone partial spherulitic devitrification have behaved as completely closed systems and thus are truly representative of melt composition at the time of eruption (Rosholt *et al.*, 1971; Ewart, 1971).

In the present study obsidian (nonhydrated) –perlite (hydrated) glass pairs were analyzed to investigate on a microscopic scale compositional changes related to the process of secondary hydration, thereby identifying possible ion-exchange processes involved. First, however, it was necessary to determine whether or not the electron microprobe can

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accurately analyze "wet" (either with appreciable primary water or secondarily hydrated) glass material (see, for example, Anderson, 1973).

Material studied

The four rocks investigated consist of nonhydrated obsidian cores surrounded by hydrated perlite. Three of the specimens, SHO-OB, WPN-23A, and OBO-12A, from southern Nevada, were studied by Noble (1967), who gives location and other pertinent data. The glasses are all of late Cenozoic (~10 to 14 m.y.) age. Specimen PA-HG is from the Delamar perlite deposit in southeastern Nevada (Tschanz and Pampeyan, 1970). The perlite underlies the Hiko Tuff, which is radiometrically dated at about 18 to 19 m.y. (Noble and McKee, 1972). For three of the samples, SHO-OB, WPN-23A, and OBO-12A, both the obsidian core and the perlite were analyzed by wet-chemical techniques in the U.S. Geological Survey laboratory using the methods of Peck (1964). Sample PA-HG was not previously analyzed. Colorless glass in specimens SHO-OB and OBO-12A contains layers of crystallites and microlites that are continuous through the perlite and the nonhydrated obsidian core. The partial secondary hydration of the originally completely nonhydrated mass, as described by Ross and Smith (1955), Friedman and Smith (1958, 1960), Friedman *et al.* (1966), and Noble (1968), is supported by the continuity of the layering. Numerous crystallites forming indistinct layers are present in sample PA-HG, composed of colorless perlite and one large obsidian core about 6 mm in diameter. This obsidian core is surrounded by a distinct hydrated layer of perlite about 100 μm thick, distinguished from the obsidian by higher index of refraction and by strain birefringence. The boundary between the obsidian and perlite is sharp but is not marked by fracture. On the outside of the perlite layer is an alteration wall about 100 μm thick composed of glass and secondary minerals growing along herringbone pattern with the long axes perpendicular to the fractures separating this wall from the surrounding perlite. The densely-welded tuff of specimen WPN-23A lacks linear features, but outlines of individual shards are made visible by microcrystalline boundaries between the shards. Typical hydration cracks cut across individual shards, indicating complete welding of the tuff prior to hydration.

Analytical techniques

Polished thin sections prepared from the four specimens were analyzed using the nine-spectrometer ARL-SEMQ electron microprobe at the Department of Mineral Sciences, Smithsonian Institution. A 15 kV accelerating voltage and 0.02 μA sample current were used. The obsidian cores and the perlites were first analyzed using an electron beam 5 μm in diameter. Because the samples contain microlites of pyroxene and opaque minerals, some differences, primarily in FeO* (FeO* = total iron as FeO) but also in other oxides, between the wet-chemical analyses and the probe analyses resulted (see Tables 2–4). A 100 μm spot was subsequently used on all samples to approximate the bulk analysis of the samples.

Table 1. Glass standards used in electron microprobe analysis

SiO_2	75.71	TEKT
TiO_2	1.85	VG-2
Al_2O_3	12.42	VG-568
FeO*	4.85	TEKT
MgO	1.59	TEKT
CaO	2.99	TEKT
Na_2O	3.75	VG-568
K_2O	4.90	VG-568

TEKT - Synthetic tektite glass prepared by Corning
VG-568 - Natural rhyolite glass analysed by J. Norberg, (personal communication)
VG-2 - Basaltic glass from Juan de Fuca ridge analysed by Jarosewich (1975)
FeO* - Total iron as FeO
Note: These anhydrous glasses are standards used in electron microprobe analysis at the Department of Mineral Sciences, Smithsonian Institution.

In order to minimize heating of the glass and resulting vapor evolution the sample was continuously moved (at a rate of 10 to 15 μm in 10 sec) during the analysis of glass bordering fine fractures in the perlite. If any water vapor emanated from the fractures the carbon coating was disturbed and sample conductivity lost, thereby significantly altering the count rates, and the analysis was discarded. In order to evaluate the influence of sample movement during analysis, both the perlite and the obsidian away from fractures were also analyzed by the same technique. No differences between these and the stationary analyses were found. The ten-second count times used during the analyses effectively eliminated Na_2O loss. The accumulated counts were processed by on-line computer, and the raw data were corrected by the method of Bence and Albee (1968). Tektite (synthetic

Table 2. Wet-chemical and electron microprobe analyses of obsidian and perlite in specimen SHO-OB

Glass Type*	NG	NG	NG	HG	HG	HG	HG**	NG†
Spot Size	--	5μm	100μm	--	5μm	100μm	5μm	5μm
Type or No. of analyses	A	16	27	B	20	19	16	6
SiO_2	74.24	74.52	74.67	72.04	72.44	72.41	71.02	74.19
TiO_2	0.22	0.20	0.22	0.22	0.21	0.21	0.22	0.21
Al_2O_3	13.46	13.93	13.64	13.13	13.34	13.49	13.25	13.64
Fe_2O_3	0.38	--	--	0.64	--	--	--	--
FeO	0.92	--	--	0.61	--	--	--	--
FeO*	1.26	0.60	1.25	1.19	0.58	0.97	0.72	0.57
MgO	0.17	0.04	0.14	0.16	0.03	0.09	0.08	0.03
CaO	0.67	0.45	0.73	0.61	0.47	0.67	0.52	0.48
Na_2O	3.97	3.98	3.90	3.36	3.69	3.34	2.38	3.91
K_2O	5.33	5.40	5.34	5.62	5.43	5.76	6.52	5.39
H_2O+	0.24	--	--	2.94	--	--	--	--
H_2O-	0.04	--	--	0.18	--	--	--	--
Total	99.99	--	--	99.77	--	--	--	--
$Total_1$	99.32	99.12	99.88	96.41	96.19	96.94	94.71	98.42
H_2O est.					3.8	3.1	5.3	1.6
H_2O diff.					2.9	3.0	4.4	0.7

A. Average of two wet-chemical analyses; V.C. Smith and C.L. Parker, analysts. Also includes MnO, 0.04; P_2O_5, 0.02; CO_2, 0.01; Cl, 0.05; F, 0.08; other, 0.08; and less O, -0.04.

B. Wet-chemical analysis; C.L. Parker, analyst. Also includes MnO, 0.04; P_2O_5, 0.02; CO_2, 0.03; Cl, 0.05; F, 0.08; other 0.08; and less O, -0.04.

* NG = Nonhydrated glass (obsidian); HG = Hydrated glass (perlite)

** Analyses made along fine fractures in hydrated glass

† Analyses made along fine fractures in nonhydrated glass

FeO* = Total iron as FeO

$Total_1$ = Sum of oxides analyzed by electron microprobe, all Fe calculated as FeO.

See text and Table 6 for discussion of parameters "H_2O est." and "H_2O diff.".

Table 3. Wet-chemical and electron microprobe analyses of obsidian and perlite in specimen WPN-23A

Glass Type*	NG	NG	NG	HG	HG	HG	HG**
Spot Size	--	5μm	100μm	--	5μm	100μm	5μm
Type or No. of analyses	A	12	22	B	20	35	12
SiO_2	73.98	74.06	74.38	71.70	71.74	71.87	70.40
TiO_2	0.22	0.22	0.23	0.22	0.23	0.20	0.20
Al_2O_3	11.28	11.31	11.68	10.94	11.06	11.29	11.11
Fe_2O_3	1.71	--	--	2.00	--	--	--
FeO	1.80	--	--	1.48	--	--	--
FeO*	3.34	3.23	3.19	3.28	3.14	3.11	3.12
MgO	0.01	0.01	0.00	0.12	0.01	0.04	0.51
CaO	0.24	0.18	0.29	0.28	0.22	0.29	0.29
Na_2O	5.33	5.38	5.31	4.63	5.05	4.98	3.83
K_2O	4.55	4.59	4.58	4.85	4.48	4.79	5.18
H_2O+	0.16	--	--	2.90	--	--	--
H_2O-	0.02	--	--	0.10	--	--	--
Total	99.95	--	--	99.81	--	--	--
$Total_1$	98.95	98.98	99.61	96.02	95.93	96.57	94.64
H_2O est.					4.1	3.4	5.4
H_2O diff.					3.0	3.0	4.3

A. Wet-chemical analysis; V.C. Smith, analyst. Also includes MnO, 0.17; P_2O_5, 0.01; CO_2, 0.02; Cl, 0.13; F, 0.17; other, 0.25 and less O, -0.10.

B. Wet-chemical analysis; E.S. Daniels, analyst. Also includes MnO, 0.16; P_2O_5, 0.02; Cl, 0.11; F, 0.15; other, 0.24; less O, -0.09.

* NG = nonhydrated glass (obsidian); HG = Hydrated glass (perlite)

** Analyses made along fine fractures in hydrated glass

FeO* = Total iron as FeO

$Total_1$ = Sum of oxides analyzed by electron microprobe, all Fe calculated as FeO.

Corning glass), natural rhyolite glass (VG-568 analyzed by J. Norberg, personal communication), and natural basaltic glass, (VG-2, Jarosewich, 1975) were used as standards in the analysis of the samples (Table 1).

Comparison of electron microprobe and wet-chemical analyses

In general, very good agreement is found between the wet-chemical and microprobe data, (Tables 2–5). In detail, however, the electron microprobe analyses for most elements obtained with a 5 μm beam differ from the wet-chemical values for both obsidian and perlite in specimens SHO-OB and OBO-12A and for perlite in specimen WPN-23A (Tables 2–4). These differences reflect the fact that the 5 μm spot was used to analyze glass only, whereas the wet-chemical analyses represent the bulk sample regardless of its microcrystalline or other heterogeneities. This conclusion was verified by reanalysis using a 100 μm beam to approximate more closely the conditions of the bulk analysis. Compared with the 5 μm beam the 100 μm beam gives values generally closer to the wet-chemical values. It nevertheless must be kept in mind that electron microprobe analysis of heterogeneous material such as glass with microlites presents an analytical problem, resulting from the complexity of the radiation path as well as from the uneven distribution of crystallites in the glass. Therefore microprobe analysis using a defocused beam provides only an approximate bulk analysis.

Individual electron microprobe analyses of obsidian (non-hydrated) and massive perlite (hydrated) are

Table 4. Wet-chemical and electron microprobe analyses of obsidian and perlite in specimen OBO-12A

Glass Type*	NG	NG	NG	HG	HG	HG	HG**
Spot Size	--	5µm	100µm	--	5µm	100µm	5µm
Type or No. of analyses	A	16	27	B	18	27	10
SiO_2	75.53	75.59	75.42	--	73.18	73.33	72.76
TiO_2	0.12	0.13	0.08	--	0.14	0.11	0.12
Al_2O_3	12.98	13.17	13.29	--	12.92	13.17	12.75
Fe_2O_3	0.37	--	--	--	--	--	--
FeO	0.72	--	--	--	--	--	--
FeO*	1.05	0.98	0.97	--	0.88	0.90	0.88
MgO	0.10	0.09	0.09	--	0.10	0.08	0.19
CaO	0.70	0.64	0.76	--	0.57	0.72	0.61
Na_2O	3.82	3.63	3.59	3.28	3.46	3.19	2.53
K_2O	5.16	5.44	5.48	5.55	5.27	5.62	6.11
H_2O+	0.15	--	--	2.74	--	--	--
H_2O-	0.03	--	--	0.16	--	--	--
Total	99.90	--	--	--	--	--	--
$Total_1$	99.46	99.67	99.68	--	96.52	97.12	95.95
H_2O est.					3.5	2.9	4.0
H_2O diff.					3.2	2.6	3.7

A. Wet-chemical analysis; V.C. Smith, analyst. Also includes MnO, 0.05; P_2O_5, 0.02; CO_2, 0.01; Cl, 0.07; F, 0.07; other 0.05; less O, -0.05.

B. Partial wet-chemical analysis; E.S. Daniels, analyst.

* NG = Nonhydrated glass (obsidian); HG = Hydrated glass (perlite)

** Analyses made along fine fractures in hydrated glass

FeO* = Total iron as FeO

$Total_1$ = Sum of oxides analyzed by electron microprobe, all Fe calculated as FeO.

plotted in Figure 1. The plots show random scatter of the obsidian analyses around the average, whereas the perlite analyses define trends of sodium loss and potassium enrichment. These trends, indistinctly outlined by the 5 μm beam analyses, are well defined by the 100 μm beam analyses.

To allow direct comparison among the individual data sets all analyses were recalculated to 100 percent water-free. The 5 μm beam analyses show a smaller increase in K_2O and decrease in Na_2O from obsidian to perlite than do the wet-chemical analyses and the 100 μm spot-size analyses (Figs. 2 and 3). However analyses of glass along fine fractures in perlite and the analyses of glass in the alteration wall in specimen PA-HG reveal very high K_2O and low Na_2O values accompanied by changes in the content of certain other oxides, particularly MgO (Figs. 2 and 3). These differences are not the result of the geometry of the fracture surface, because the control analyses made along artificial fractures in nonhydrated glass showed no differences from analyses made in the same glass away from such fractures. Also equal values of Na_2O and K_2O were found along very fine ($\sim$1 μm) and quite large (2–5 μm) fractures in the same specimen, thus making the presence of K-rich foreign material in the fracture unlikely. These analyses only approximate the amount of chemical change in this thin layer, because unknown amounts of less ion-exchanged hydrated glass were unavoidably analyzed by the electron beam. The average of the analyses obtained with the 100 μm beam, which represent mixture of massive perlite and perlite along fractures, plot between the 5 μm perlite average and the 5 μm average obtained on glass along fractures (Fig. 3).

Water contents of the perlite samples estimated by two different techniques are shown in Tables 2 through 5. The parameter "H_2O est." is obtained by subtracting the sum of oxides determined by the microprobe from 100 percent. As is shown in Table 6, water estimates obtained this way are higher than the gravimetrically-measured water contents. The parameter "H_2O corr." (Table 6) represents a corrected value obtained by correcting "H_2O est." for the

Table 5. Electron microprobe analyses of obsidian and perlite in specimen PA-HG

Glass Type*	NG	NG	HG	HG	HG**	HG††
Spot Size	5µm	100µm	5µm	100µm	5µm	5µm
Type or No. of analyses	30	14	20	13	18	17
SiO_2	75.41	75.42	72.99	73.15	72.58	69.88
TiO_2	.11	.09	.12	.11	.12	.13
Al_2O_3	13.77	13.60	13.33	13.20	13.57	13.34
FeO*	.60	.75	.66	.72	.68	.66
MgO	.12	.10	.14	.11	.27	.32
CaO	.80	.89	.79	.88	.81	.79
Na_2O	3.68	3.75	3.51	3.34	2.66	2.34
K_2O	4.83	4.89	4.76	5.04	5.51	5.52
Total	99.32	99.49	96.30	96.56	96.20	92.98
H_2O est.			3.7	3.4	3.8	7.0
H_2O diff.			3.0	2.9	3.1	6.3

Note: No wet-chemical analysis is available for this sample. Total H_2O in the obsidian assumed to be .2%. Total H_2O in the perlite assumed to be 3.0%.

* NG = Nonhydrated glass (obsidian); HG = Hydrated glass (perlite)

** Analyses made along fine fractures in hydrated glass

†† Analyses made on alteration wall

FeO* = Total iron as FeO

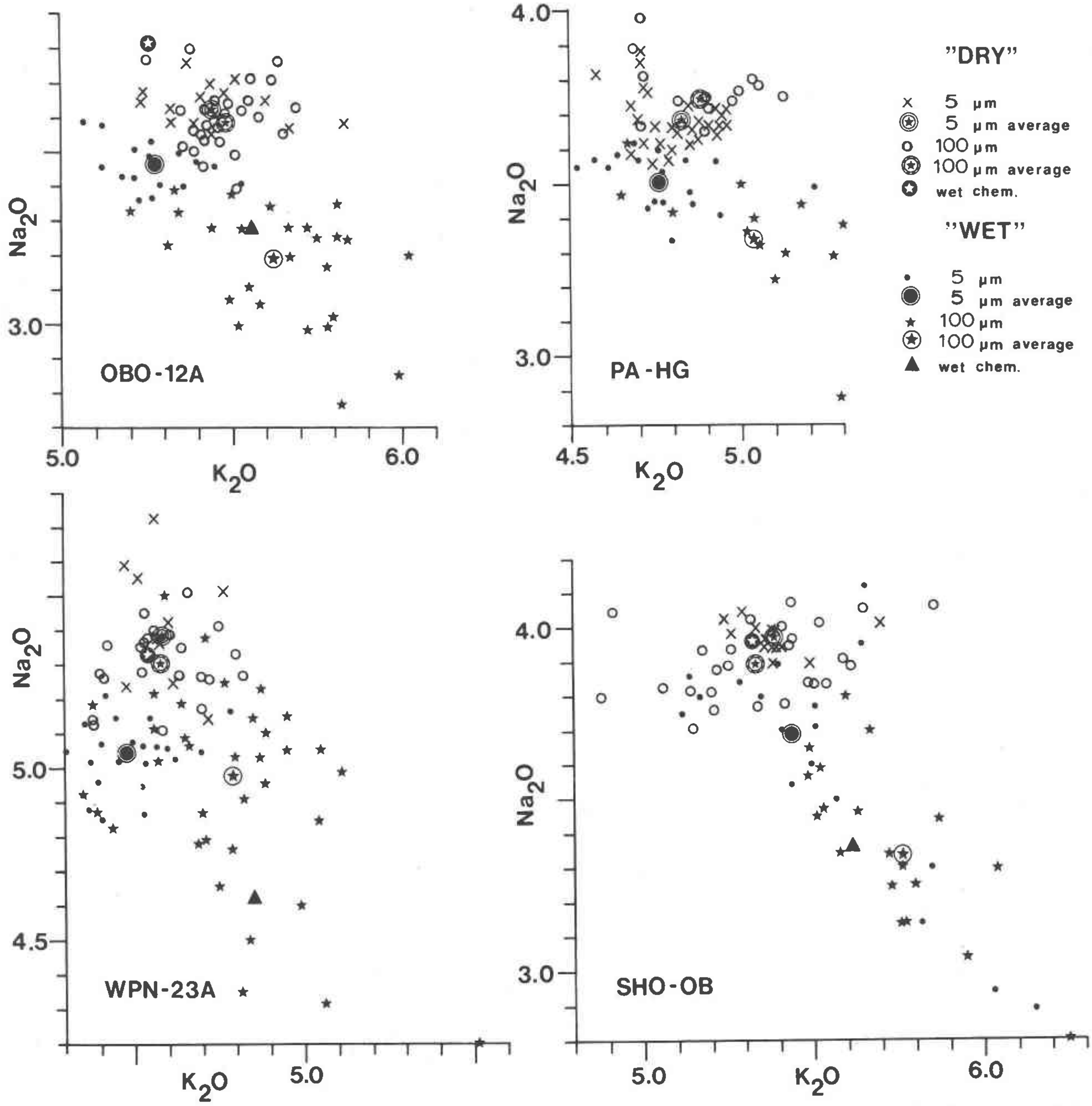

Fig. 1. Analyses of Na_2O and K_2O on obsidian and massive perlite in the four samples investigated show typical random scatter of the obsidian analyses around the average, whereas the analyses on perlite define trends of sodium loss and potassium enrichment. These trends, indistinctly outlined by the 5 µm beam analyses, are well defined by the 100 µm beam analyses. The analyses are not recalculated to 100 percent water-free.

"other" oxides and elements not measured by the microprobe but present in the glass (*e.g.* MnO, ZrO_2, F, Cl, *etc.*). The difference between the "H_2O corr." value and the measured H_2O content is lower than if the "H_2O est." value is used. Generally the error introduced by disregarding the "other" oxides and elements is 0.2 to 0.6 weight percent, and contributes to higher apparent H_2O contents.

Values of "H_2O diff." given in Tables 2 through 5 were derived by subtracting the sum of oxides as measured by the microprobe in the perlite from the sum of oxides measured in the obsidian of the same

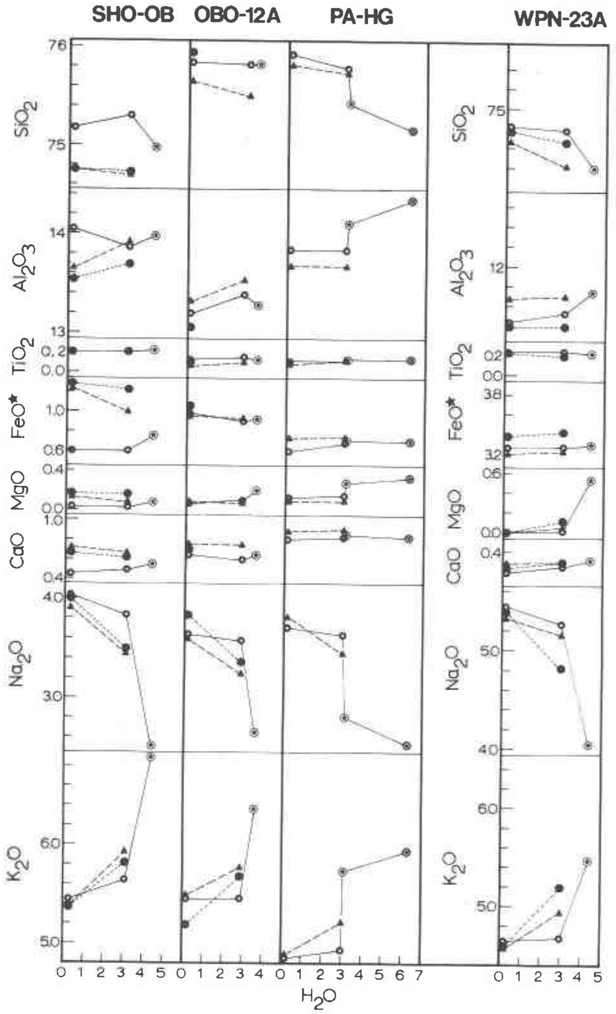

Fig. 2. Plot showing variation in major-element contents of nonhydrated (obsidian) and hydrated (perlite) glasses as a function of water content. All analyses are recalculated to 100 percent water-free. Analyses made with a 100 μm beam size (solid triangles) are, in general, closer to the wet-chemical values (solid circles) than are the analyses made on microlite-free nonhydrated and dense hydrated glass with a 5 μm beam (open stars). The 5 μm-beam analyses made along fractures in the perlite (solid stars) generally show a higher degree of hydration and appreciably more ion exchange. The alteration wall in specimen PA-HG (doubly-circled solid star) is unusually rich in water and has undergone even more intense ion exchange.

pair. Table 6 shows that these values are in a very close agreement with the gravimetrically-measured water values. If this technique is used, it is not necessary to know the concentrations of the "other" oxides in the glass. The values are accurate and can be obtained rapidly, thus adding a value for water of hydration to the oxides measured by the electron microprobe for these sample pairs.

Discussion

This study shows that the oxide concentrations measured by the electron microprobe in nonhydrated as well as hydrated glasses are in good agreement with the values determined by wet-chemical analysis. Water contents determined by the difference of the sum of oxides from 100 percent may be too great by as much as 1 weight percent, whereas water contents determined by the difference of sum of oxides in the related obsidian and perlite are almost identical with gravimetrically-measured water values. The very fine size of the electron microprobe beam permits the analysis of glass, excluding crystals, inclusions, and alteration products. The quantitative nature of the analysis allows the chemical characterization of nonhydrated and associated hydrated glass that have undergone different degree of hydration and ion exchange.

Although the boundary between nonhydrated obsidian and hydrated perlite is very sharp (Ross and Smith, 1955), the process of hydration and ion ex-

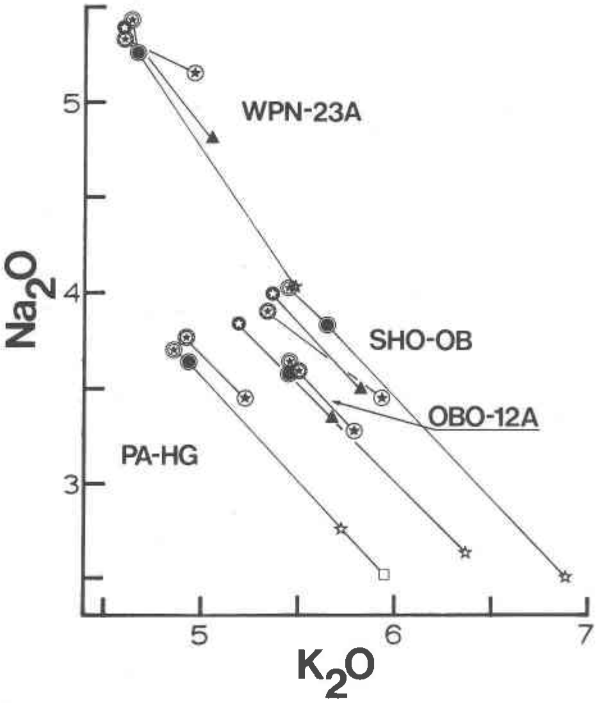

Fig. 3. Plot of Na_2O versus K_2O showing average electron microprobe analyses of obsidian, massive perlite, and perlite along fractures and alteration wall (in sample PA-HG), and wet-chemical analyses of the samples. All analyses are recalculated to 100 percent water-free. Averages of the 5 μm-beam analyses made along fractures in the perlite are shown by white stars. An average of the 5 μm-beam analyses of the alteration wall in PA-HG is shown by the white square. Other symbols are the same as in Fig. 1.

Table 6. Comparison between gravimetrically-measured water contents and water contents inferred from electron microprobe totals

Specimen	SHO-OB	OBO-12A	WPN-23A
H_2O est. 5µm	+0.7	+0.6	+1.1
H_2O corr. 5µm	+0.5	+0.4	+0.5
H_2O est. 100µm	0.0	0.0	+0.4
H_2O corr. 100µm	-0.2	-0.2	-0.2
H_2O diff, 5µm	-0.2	+0.3	0.0
H_2O diff. 100µm	-0.1	-0.3	0.0

H_2O est. = estimate based on the difference between the sum of oxides measured by the microprobe and 100 percent.

H_2O corr. = estimated water content corrected for the oxides and elements not measured by the microprobe, but not including the correction for Fe_2O_3.

H_2O diff. = estimate based on the difference between the sum of oxides obtained for the obsidian and for the associated perlite.

Note: All data are in weight percent. A positive value indicates that the water content inferred from the microprobe data is higher than the gravimetrically measured content whereas a negative value indicates that the microprobe value is lower. Total water ($H_2O^+ + H_2O^-$) was used in these figures but it is more likely that the microprobe data give estimates of H_2O^+ because H_2O^- will be lost rapidly due to beam loading. Because H_2O^- is low in these samples it is difficult to resolve this problem.

change is probably gradual. The massive perlite in the present samples is hydrated, but only a very small amount of ion exchange has taken place. In all of the samples Na_2O decreased slightly and K_2O increased slightly in the massive perlite. Because only very small amounts of Na^+ was removed, and most of this was replaced by K^+, only very small amounts of H^+ and/or H_3O^+ (Truesdell, 1966) may occupy some sites to preserve electroneutrality. We therefore infer that most of the water of hydration in the massive perlite is present as water molecules occupying "sites" between the polymerized silica chains. As pointed out by Friedman and Smith (1958), the introduction of water causes the glass to expand, and formation of perlitic fractures begins.

Glass along the fractures contains slightly to significantly more water of hydration (0.1 to 1.5 weight percent) and has undergone appreciably more ion exchange than the massive perlite. Probably a thin layer of gel-like glass forms on the surface of these fractures. This layer may be a result of reaction with water molecules diffusing through the glass, coupled with a more rapid exchange of even larger ions (Doremus, 1973, p. 244). The significantly lower Na_2O and higher K_2O contents and slightly higher MgO contents of this layer support such a process.

The effectiveness of ion exchange depends on the concentration of ions in the solution in contact with the glass, and on the glass composition. Ion exchange along the fractures will act to approach an equilibrium between the glass and the solution. It is difficult to say exactly how deep the zone of more intense ion exchange will extend from the fracture surface. However, as shown by the microprobe analyses of the specimens studied, this layer is not more than a few microns thick. Because of the thinness of the layer it is not possible to determine if concentration gradients are present.

Friedman and Smith (1958) pointed out that perlites of highly variable age contain approximately 3 weight percent water. Perlites investigated in this study also contain about 3 weight percent water regardless of their age. The rather constant amount of water and its inferred presence as water molecules filling the openings in the glass structure suggest that an approximately constant amount of space is available for occupation by water molecules. The available space is independent of composition, at least in the highly silicic glasses studied.

Figure 3 shows average sodium and potassium values for all four samples recalculated to 100 percent water-free. The trend defined by nonhydrated glass, hydrated glass, and glass along fractures in perlite is almost identical for all four samples. The slope of the line connecting hydrated glass with glass along fractures in perlite in sample WPN-23A has a steeper negative slope. This may be the result of the significantly higher original sodium content of the material or, perhaps more likely, of the peralkaline character of the glass, with the result that a portion of the sodium ions is not closely associated with Al ions in the three-dimensional polymer structure of the glass. The lower Na_2O and higher K_2O values of the hydrated glass and of the glass along the fractures in perlite are the result of ion exchange. Samples PA-HG, OBO-12A, and SHO-OB are very similar in composition but are of different age and come from different areas. Their ion-exchange trends are almost identical, and it is inferred that the glass composition is an important controlling factor in the ion-exchange process. This conclusion was also reached by Friedman and Smith (1960), Truesdell (1966) and Friedman and Long (1976) from different data. Ion concentrations in ground waters in contact with the samples are low and probably do not control the ion-exchange reactions to any large extent.

Glass can undergo hydration and ion exchange of a certain magnitude without decomposing to secondary minerals. These hydrated materials can be distinguished from nonhydrated glass by changes in the index of refraction and by strain birefringence (Friedman and Smith, 1960). The first stage of hydration can proceed until a saturation point of about 3 weight percent of H_2O is reached. During this stage the glass undergoes only a small amount of ion exchange. Additional hydration takes place initially along fracture surfaces and is accompanied by significantly more intense ion exchange. Thereafter, as a result of further weakening and breakage of the bonds of the glass structure, there will be a tendency for the formation of clay and zeolite minerals.

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