

Chemical Comparison of Glassy and Crystalline Volcanic Rocks

GEOLOGICAL SURVEY BULLETIN 1201-D

*Prepared on behalf of the
U.S. Atomic Energy Commission*



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By P. W. LIPMAN

CONTRIBUTIONS TO GENERAL GEOLOGY

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UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOLOGICAL SURVEY

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CONTRIBUTIONS TO GENERAL GEOLOGY

CHEMICAL COMPARISON OF GLASSY AND CRYSTALLINE VOLCANIC ROCKS

By P. W. LIPMAN

ABSTRACT

Groundmass crystallization of volcanic rocks is considered in terms of primary crystallization, which occurs during original emplacement and cooling of the body, and secondary devitrification, which occurs subsequent to original cooling. Analyses of glassy and crystallized parts of 13 volcanic bodies, mostly rhyolitic lavas and ash-flow tuffs from southern Nevada and all examples of primary crystallization, show similar trends. The glasses show less oxidation of iron, higher water content ($+105^{\circ}\text{C}$) from secondary hydration, higher aluminum, and lower silicon and sodium contents. These last variations are thought to represent ground-water leaching of silicon and sodium—constituents which are abundant in local ground-water analyses—and resultant residual concentration of relatively insoluble aluminum. Leaching is most advanced in porous glassy tuffs having large surface areas, but is also significant in many dense vitrophyres from lavas and welded tuffs. Those parts of initially homogeneous ash-flow tuffs that have undergone primary crystallization seem to be relatively uniform in present composition and are probably closer compositional approximations of the original magma than are the variably leached glassy margins of the ash-flow sheets. Secondary devitrification of volcanic rock is apparently accompanied by major alkali transfer in many cases.

INTRODUCTION

Consideration of the numerous volcanic rock analyses that have been made for U.S. Geological Survey investigations at the Nevada Test Site has revealed greater compositional scatter within genetically related suites of rocks than expected from magmatic processes. The present study, an investigation of chemical variations between glassy and crystalline parts of volcanic bodies, attempts to determine which parts of a volcanic body are most likely to approximate the original magma in composition. A previous investigation of zonal compositional variations in a welded ash-flow sheet (Lipman and Christiansen, 1964) showed no analytically detectable compositional variations among such differently crystallized zones as vapor phase, lithophysal, or densely devitrified—as defined by Smith (1960, p. 151–153). The glassy parts showed an anomalous composition, however, and apparently have been

leached by ground water to such an extent that they provide less reliable samples of primary magmatic compositions than do the crystallized parts. This tentative conclusion conflicted with the common assumption of petrologists that glasses "are the only rocks of which we can say with complete confidence that they correspond in composition with a liquid" (Bowen, 1928, p. 125), and indicated the need for a more detailed investigation. The following discussion is concerned mainly with chemical evidence but also draws on the author's experience in petrographic and field investigations of upper Tertiary rocks in southern Nevada, including more than 30 ash-flow tuff sheets and 20 rhyolitic lava flows.

Most of the data used in this report were gathered for purposes other than those of the present investigation; accordingly, interpretation presents problems not encountered when data are collected for a specific study. The data are considered from two approaches. First, glassy and crystalline paired analyses from individual localities are compared. Then, separate consideration is given to randomly collected glassy and crystalline rocks from those individual volcanic units for which abundant analytical data are available. Although each batch of data points to the same general conclusions, none permits completely unambiguous interpretation in itself; most conclusions are dependent on a multiple approach to the available data.

For permission to use unpublished chemical data I am grateful to many colleagues on the U.S. Geological Survey, particularly J. T. O'Connor, H. A. Powers, D. L. Hoover, and F. A. McKeown, who contributed glass-crystalline paired analyses for tables 1 and 2. I also wish to thank Irving Friedman, Frank Simons, R. E. Wilcox, and especially H. A. Powers for many stimulating suggestions.

ALTERATION OF VOLCANIC GLASSES

The types of alteration that may affect glassy parts of extrusive volcanic bodies are discussed in terms of four processes: primary crystallization, hydration, secondary devitrification, and leaching. The term "primary crystallization" is used in preference to "primary devitrification" because it is applicable both to ash-flow tuffs and to lava flows. In ash flows primary crystallization of glassy constituents is commonly ascribed to devitrification, as in the zone of devitrification of Smith (1960), but in lava flows crystallization can occur directly from a liquid without an intervening vitreous stage.

Primary crystallization occurs in the interiors of volcanic bodies at temperatures only slightly below melting during and immediately following emplacement. With dropping temperature the rate of crystallization decreases rapidly, and experimental determinations of

crystallization rates indicate that lavas cease crystallizing at a few hundred degrees below melting temperature (Irving Friedman, oral commun., 1963). Primary crystallization results in the zonation of volcanic bodies: the slowly cooled interior crystallizes and is surrounded by a quenched glassy envelope, as described for welded ash-flow tuffs by R. L. Smith (1960). Similar crystallization zonations characterize unaltered rhyolitic lava flows (Christiansen and Lipman, 1964).

Several recent studies have shown that most Tertiary volcanic glasses have undergone secondary hydration (Ross and Smith, 1955, p. 1086-1088; Boyd, 1961, p. 415). Such rocks contained only a few tenths of a percent magmatic water upon cooling; the remainder of the observed water, typically several percent H_2O +, is secondary. The amount of hydration is dependent on time and surface area (Friedman and Smith, 1960); few Recent glasses are hydrated, but only the least fractured Tertiary vitrophyres have escaped hydration. Obviously, chemical analyses of extensively hydrated volcanic glasses must be recalculated on a water-free basis for precise petrologic studies.

Secondary devitrification occurs after cooling of the volcanic body. As glasses are thermodynamically metastable below their melting temperatures (Morey, 1954, p. 29), devitrification may be expected whenever the kinetics of crystallization become significant for geologic time. The occasional preservation of glass as old as Precambrian (Simons, 1962, p. 882; Philpotts and Miller, 1963) indicates that glasses do not devitrify solely from aging, but the rarity of glasses older than Tertiary indicates that the quenched primary glassy borders of most older volcanic bodies have crystallized secondarily. Recent studies by Marshall (1961) and Friedman and Smith (1964) emphasize the importance of water in catalyzing devitrification, and indicate that secondary devitrification of hydrated glasses occurs readily over a few million years at temperatures of no more than 200° C. Although the products of primary crystallization and secondary devitrification may in places be indistinguishable, products of secondary devitrification are suggested by structural relations between glassy and crystalline rocks that differ from the primary-crystallization zonations due to quenching. Crosscutting "devitrification dikes" that follow fractures (Simons, 1962; Terzaghi, 1948, p. 24) and certain glassy sills enveloped by crystalline material along joints and intrusive margins (Judd, 1893; Anderson and Radley, 1915) are thought by the writer to represent secondary devitrification, although they are not necessarily so interpreted in the original reports. In the upper Tertiary volcanic rocks of southern Nevada studied by the author, such features are sparse and are confined to structurally complex rocks that have been sub-

jected to hydrothermal alteration. In the following pages, rocks suspected of secondary devitrification on the basis of field relations will be shown to have undergone chemical changes that differ markedly from those of more obvious cases of primary crystallization.

The effect of leaching in aqueous solution, apparently not much considered by petrologists studying volcanic glasses, has been of considerable concern to the commercial glassware industry. Extensive cation leaching of artificial alkali silicate glasses has been demonstrated by much laboratory experimentation—for instance, by Sen and Tooley (1955), and by study of historically ancient glass (Brill, 1963). Such glasses show compositional affinity to rhyolitic volcanic rocks, and a major purpose of this paper is to evaluate the effects of ground-water leaching on natural volcanic glasses over geologically significant spans of time.

COMPOSITIONAL CHANGES IN EXAMPLES OF PRIMARY CRYSTALLIZATION

ANALYTICAL DATA

Table 1 lists paired analyses of glassy and crystalline rocks from 13 separate volcanic bodies including seven welded rhyolitic ash-flow tuffs, four rhyolitic lava flows, a rhyolitic dike, and a basaltic lava flow.¹ In each the field relations indicate that the crystallized part of the body formed by primary crystallization. The glasses are from the outer parts of the bodies, and the crystallized equivalents were collected toward the interiors, a few feet across the glass-crystalline interface. All sample localities except Nos. 1, 11, 12, and 13 have been examined by the author; relations at these localities have been described to the author by the original collectors—D. L. Hoover, F. M. Byers, H. A. Powers, and F. A. McKeown, oral communications, 1963. All sample pairs except Nos. 10, 11, and 12 have been studied in thin section, and identical phenocryst ratios verify that they represent glassy and crystallized equivalents of single volcanic bodies. Sample 5A is nonwelded glassy tuff; all other glassy samples are dense vitrophyres. Except for pair 11, both samples of any pair were analyzed simultaneously by the same chemist; therefore, few of the differences in the paired analyses should be ascribed to analytical error.

The glasses of sample pairs 11 (Pleistocene) and 12 (within historic times) show little secondary hydration; the glasses of all other sample pairs, which are Tertiary—mostly Miocene and Pliocene—are extensively hydrated. Accordingly, to facilitate comparisons, all analy-

¹ An additional glass-crystalline pair is given by Longwell (1963, table 2, analyses 421, 424), but it has not been used for the present study because the crystalline sample (No. 424) is probably silicified. This sample shows more than 80 percent SiO_2 when recalculated free of water.

ses have been recalculated to 100 percent on an anhydrous basis (table 2). As the appreciable CO_2 in several samples (especially 6B, 10B, 13A, and 13B of table 1) clearly correlates with excessive CaO, all CO_2 was calculated out as CaCO_3 . Net changes in the weight-percent of oxides, obtained by subtracting the recalculated analyses of glasses (table 2, A columns) from the recalculated analyses of crystalline rocks (table 2, B columns), are shown graphically in figure 1. The changes in $\text{H}_2\text{O}+$ were obtained from table 1.

Despite considerable scatter, many changes are consistent. As already noted, $\text{H}_2\text{O}+$ is much lower in all crystalline samples except the two youngest lavas (pairs 11 and 12); their glasses have not had sufficient time to hydrate. The generally higher $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio in the crystalline rocks reflects a widespread conversion of magnetite crystallites in the generally black vitrophyres to hematite in the typically reddish crystallized samples. Total iron is nearly constant; the scatter is of small amplitude, shows no trend, and is probably within the expectable range of analytical error. MnO and TiO_2 are minor constituents of all samples and show no detectable significant variations. Na_2O is generally slightly to considerably higher in the crystalline samples, and K_2O is generally slightly lower; interpretation of these apparently significant variations will be deferred until later in the paper.

MgO and CaO are nearly constant in most pairs; however, in a few crystalline samples—especially 1B, 4B, 5B, and 7B—these constituents are both considerably lower. In thin section the glassy equivalents of these samples, all welded tuffs, showed minor fine dust at shard boundaries, and montmorillonitic clay was detected in samples 4A and 5A by X-ray examination. Such minor argillic alteration probably explains the excess MgO and CaO in these glasses; it may also account for the slight excesses in samples 1A and 7A, even though no clay was revealed by X-ray studies because less than about 5 percent clay probably would not be detected. In addition to this minor argillic alteration of some samples, interpretation of the CaO variations is complicated by the presence of appreciable carbonate— CO_2 in the analyses—in a few samples and by possible base exchange with ground waters enriched in calcium from nearby Paleozoic carbonate rocks.

SiO_2 and Al_2O_3 show sizable and meaningful variations; SiO_2 is generally higher and Al_2O_3 lower in the crystalline rocks. Although the determination of these two oxides by different analysts is known to be subject to sizable variation (Fairbairn and others, 1951; Stevens and others, 1960), relative differences within the pairs under consideration are likely to be significant because, with one exception, both samples of each pair were analyzed simultaneously by a single

TABLE 1.—*Paired chemical analyses, in weight percent, of glassy and crystalline rocks that have undergone primary crystallization*

Symbols in column heads:

A. Glassy rocks

B. Crystalline rocks

[Analyses: 4A, B by Dorothy F. Powers; 7A, B by Christel L. Parker; 1A, B, 2A, B, 3A, B, 8A, B, 9A, B, and 13A, B, rapid methods, by Paul Elmore, Sam Botts, Gillison Choe, Lowell Artis, and H. Smith]

		Paired analyses—											
1—		2—		3—		4—		5—		6—		7—	
A	B	A	B	A	B	A	B	A	B	A	B	A	B
DLH-62-19	DLH-62-23	62L-178-B	62L-178-A	63L-17-I	63L-17-H	AGE-2B	AGE-2A	62L-50-O	62L-50-Q	MC-274-B	MC-274-A	To-193-A	To-193-B
SiO ₂	71.8	69.2	70.8	74.1	76.9	65.73	69.02	71.5	76.0	73.27	75.02	70.09	73.29
Al ₂ O ₃	12.7	15.0	14.8	12.5	12.2	15.46	15.60	12.6	13.0	12.16	12.56	13.76	13.72
FeO.....	2.3	1.2	1.6	.64	.84	1.43	1.93	.80	.13	.74	.15	.25	.26
Fe ₂ O ₃	3.9	.57	1.6	.64	.84	1.43	1.93	.80	.13	.74	.15	.25	.26
MnO.....	1.2	.12	.12	.06	.07	.06	.08	.10	.17	.23	.00	.31	.18
MgO.....	.15	.44	.12	.06	.07	.06	.08	.10	.17	.23	.00	.31	.18
CaO.....	.22	.44	.12	.06	.07	.06	.08	.10	.17	.23	.00	.31	.18
Na ₂ O.....	.53	1.0	1.0	.34	.40	1.39	1.64	2.8	4.3	3.60	4.78	1.33	.97
K ₂ O.....	5.3	4.2	4.2	3.4	3.6	3.88	4.36	4.8	4.7	3.60	4.34	3.44	3.77
H ₂ O ⁺	4.5	5.0	5.0	4.5	4.8	5.70	5.93	4.8	4.7	4.77	4.74	5.2	5.41
H ₂ O ⁻	1.2	2.9	.92	2.9	.51	3.61	3.31	5.6	.68	2.95	3.36	2.58	.33
P ₂ O ₅22	.28	.22	.38	.22	.07	.07	.02	.02	1.07	.18	.88	.11
CO ₂	<.05	<.05	<.05	<.05	<.05	.01	.01	.10	<.05	.01	.43	.01	.00
Total.....	100	100	100	100	100	99.49	99.29	100	100	99.66	99.80	99.64	99.84

Sample	8—		9—		10—		11—		12—		13—	
	A	B	A	B	A	B	A	B	A	B	A	B
63L-15-A	63L-15-B	63L-14-A	63L-14-B	MC-170-B	MC-170-C	#19	#20	C-810	53-2382	E-24A	E-24B	
SiO ₂	75.4	77.3	75.7	77.9	74.68	76.18	72.36	72.77	52.16	52.04	66.8	71.0
Al ₂ O ₃	12.2	12.6	11.7	11.9	12.20	12.32	13.75	13.20	14.13	13.94	15.0	14.6
TiO ₂	.18	.14	.14	.14	.09	.09	.21	.21	2.04	2.05	.38	.32
Fe ₂ O ₃	.59	.73	.51	.70	.41	.50	.59	1.48	1.12	1.58	1.1	1.6
FeO	.34	.14	.34	.16	.16	.13	2.33	1.55	9.90	9.69	.15	.06
MnO	.03	.02	.04	.03	.07	.07	.09	.08	7.07	7.14	.10	.10
MgO	.16	.27	.23	.25	.11	.20	.09	.08	10.53	10.63	.56	.33
CaO	.42	.46	.38	.51	.38	.94	1.53	1.27	2.25	2.2	3.6	4.2
Na ₂ O	3.0	3.0	2.8	3.0	3.42	3.65	4.64	4.72	2.40	2.33	5.3	5.0
K ₂ O	5.3	5.0	5.3	5.0	4.86	4.81	4.16	4.06	.02	.01	2.7	.45
H ₂ O+	2.4	.37	3.0	.49	3.13	.16	.27	.10	.00	.02	.17	.15
H ₂ O-	.18	.17	.03	.15	.14	.21	.03	.02	.21	.02	.52	.28
P ₂ O ₅	.02	.02	.02	.02	.01	.02	.06	.06	nd	nd		
CO ₂	<.05	<.05	<.05	<.05	.01	.41	.00	.00	nd	nd		
Total	100	100	100	100	99.67	99.69	100.11	99.71	100.00	100.12	99	100

EXPLANATION OF PAIRED SAMPLES

1. Rhyolitic welded tuff, Grouse Canyon Member of Indian Trail Formation, Quartet Dome quadrangle, Nye County, Nev. Collected by D. L. Hoover.
A. Vitrophyric welded tuff.
B. Crystallized welded tuff from same locality as A.
2. Quartz latite welded tuff of Chocolate Mountain, Topopah Spring NW quadrangle, Nye County, Nev. Collected by P. W. Lipman.
A. Vitrophyric welded tuff.
B. Crystallized welded tuff, 50 ft from A.
3. Rhyolitic welded tuff, Topopah Spring Member of Paintbrush Tuff, Topopah Spring SW quadrangle, Nye County, Nev. Collected by P. W. Lipman.
A. Vitrophyric welded tuff.
B. Crystallized welded tuff, 50 ft from A.
4. Quartz latite welded tuff, Topopah Spring Member of the Paintbrush Tuff, Topopah Spring NE quadrangle, Nye County, Nev. Collected by J. T. O'Connor.
A. Vitrophyric welded tuff.
B. Crystallized welded tuff, from same locality as A.
5. Rhyolitic welded tuff, Yucca Mountain Member of Paintbrush Tuff, Topopah Spring NW quadrangle, Nye County, Nev. (Lipman and Christiansen 1964, table 1).
A. Glassy nonwelded basal ash-flow tuff.
B. Crystallized welded tuff, 25 ft from A.
6. Rhyolitic welded tuff, Tiva Canyon Member of Paintbrush Tuff, Bare Mountain quadrangle, Nye County, Nev. (Cornwall, 1962, table 2, col. 5-6).
A. Vitrophyric welded tuff.
B. Crystallized welded tuff, 75 ft from A.
7. Rhyolitic lava flow of Fortymile Canyon, Topopah Spring NE quadrangle, Nye County, Nev. Collected by J. T. O'Connor.
A. Vitrophyric welded tuff.
B. Crystallized rhyolitic lava from same locality as A.
8. Rhyolitic lava flow of Fortymile Canyon, Topopah Spring NW quadrangle, Nye County, Nev. Collected by P. W. Lipman.
A. Vitrophyric rhyolitic lava.
B. Crystallized rhyolitic lava, 10 ft from A.
9. Rhyolitic dike—probably feeder for lava flow represented by pair 8—Topopah Spring NW quadrangle, Nye County, Nev. Collected by P. W. Lipman.
A. Vitrophyric rhyolite, 5 ft from A.
B. Crystallized rhyolite, Bullfrog quadrangle, Nev.—Calif. (Cornwall, 1962, table 2, col. 11-12.)
10. Rhyolitic lava flow, Bullfrog quadrangle, Nev.—Calif. (Cornwall, 1962, table 2, col. 11-12.)
A. Vitrophyric rhyolitic lava.
B. Crystallized rhyolitic lava.
11. Rhyolitic lava flow, northeastern Umnak Island, Alaska. (Byers, 1961, table 1, col. 19-20.)
A. Rhyolite obsidian.
B. Felsitic (crystallized) rhyolite.
12. Basaltic lava flow, Mauna Loa (1949 eruption), Hawaii. (Macdonald and Eaton, 1964, table 13, col. 4-5.)
A. Dense glassy basaltic lava.
B. Crystallized basaltic lava.
13. Rhyolitic welded tuff, Rainer Mesa Member of Timber Mountain Tuff, Yucca Lake quadrangle, Nye County, Nev. Collected by F. A. McKeown.
A. Vitrophyric welded tuff.
B. Crystallized welded tuff, 10 ft from A.

TABLE 2.—*Chemical analyses of rocks listed in table 1, recalculated*

Symbols in boxheads:

A columns, glassy rocks recalculated without water or calcium carbonate

B columns, crystalline rocks recalculated without water or calcium carbonate

C columns, glassy rocks recalculated to Al_2O_3 content of crystalline rocks

[Values in parentheses are not included in total percent]

	1—			2—			3—			4—			5—			6—			7—		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
SiO_2	73.0	72.6	69.8	71.2	71.6	69.4	73.9	77.4	72.8	69.10	69.87	67.23	76.0	76.4	74.2	76.60	76.34	77.02	72.96	73.70	70.36
Al_2O_3	13.5	12.9	12.9	15.4	15.0	15.0	13.0	12.3	12.3	16.23	15.70	15.70	13.4	13.1	13.1	12.71	12.78	12.78	14.30	13.79	13.79
FeO	2.4	3.9	2.3	2.3	2.2	2.2	0.6	0.6	0.6	1.62	1.50	1.46	0.5	0.5	0.5	0.7	0.7	0.7	1.30	1.36	1.25
$\text{FeO}^{\text{total}}$	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9
FeO^{calc}	1.3	3.0	1.2	1.2	1.2	1.2	0.6	0.6	0.6	1.57	1.46	1.46	0.5	0.5	0.5	0.7	0.7	0.7	1.30	1.36	1.25
FeO^{calc}	(3.5)	(3.6)	(3.3)	(1.71)	(1.80)	(1.57)	(.89)	(.89)	(.85)	(1.94)	(1.93)	(1.88)	(.91)	(.90)	(.89)	(.93)	(.91)	(.93)	(1.40)	(1.40)	(1.44)
MnO	16	16	16	12	12	12	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
MnO	31	31	31	45	45	45	23	23	23	48	48	48	10	10	10	10	10	10	10	10	10
CaO	56	56	56	1.03	1.01	1.00	5.5	5.5	5.5	1.46	1.46	1.43	3.0	3.0	3.0	3.76	3.76	3.76	3.57	3.79	3.45
Na_2O	2.8	4.8	2.7	4.3	4.3	4.2	3.5	3.6	3.3	4.08	4.42	3.97	5.1	4.7	2.9	4.90	4.82	5.02	5.42	5.03	5.23
K_2O	5.6	4.9	5.4	5.2	5.0	5.0	4.7	4.8	4.7	5.98	6.01	5.82	5.1	4.7	5.0	4.90	4.82	5.02	5.42	5.03	5.23
P_2O_504	.07	.04	.10	.11	.10	.02	.02	.02	.07	.07	.07	.02	.02	.02	.01	.01	.01	.06	.07	.06
Total.....	99.99	99.93	95.67	99.96	99.97	97.36	100.01	99.95	94.92	100.00	100.00	97.31	96.99	100.07	97.64	99.95	99.99	100.49	99.96	99.93	96.50

	8—			9—			10—			11—			12—			13—		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
SiO_2	77.1	77.5	77.7	77.9	78.2	77.9	77.48	77.40	76.02	72.50	73.07	70.19	52.16	52.04	51.46	70.5	72.1	66.2
Al_2O_3	12.5	12.6	12.6	12.0	12.0	12.0	12.66	12.66	12.52	13.78	13.34	13.34	14.13	13.94	13.94	16.8	14.8	14.8
FeO60	.73	.90	.62	.70	.52	.43	.51	.42	.21	.21	.20	2.04	2.06	2.01	1.2	1.6	1.1
$\text{FeO}^{\text{total}}$35	.35	.35	.35	.35	.35	.35	.35	.35	.35	.35	.35	9.90	9.90	9.70	1.2	1.6	1.1
FeO^{calc}	(.89)	(.89)	(.89)	(.82)	(.79)	(.82)	(.56)	(.59)	(.55)	(2.87)	(2.90)	(2.76)	(10.91)	(11.11)	(10.75)	(1.2)	(1.6)	(1.1)
MnO03	.02	.03	.04	.03	.04	.07	.07	.07	.09	.09	.09	7.07	7.07	7.07	1.1	1.1	1.1
MnO16	.27	.16	.23	.25	.23	.38	.38	.38	1.53	1.53	1.48	10.63	10.63	10.63	1.6	1.6	1.6
CaO	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57	4.65	4.74	4.40	2.23	2.23	2.23	3.8	4.3	3.6
Na_2O	3.1	3.0	3.1	2.9	3.0	2.9	3.35	3.35	3.35	4.17	4.08	4.13	3.0	3.0	3.0	5.1	5.1	5.1
K_2O	5.4	5.0	5.0	5.4	5.0	5.4	5.04	4.89	4.88	4.17	4.08	4.13	3.0	3.0	3.0	5.1	5.1	5.1
P_2O_502	.02	.02	.03	.02	.02	.01	.02	.01	.06	.06	.06	.21	.21	.21	5.6	5.1	5.1
Total.....	100.01	99.88	100.81	99.94	100.01	99.93	99.99	100.00	98.88	100.00	100.00	97.00	99.98	100.12	98.63	99.94	100.06	93.87

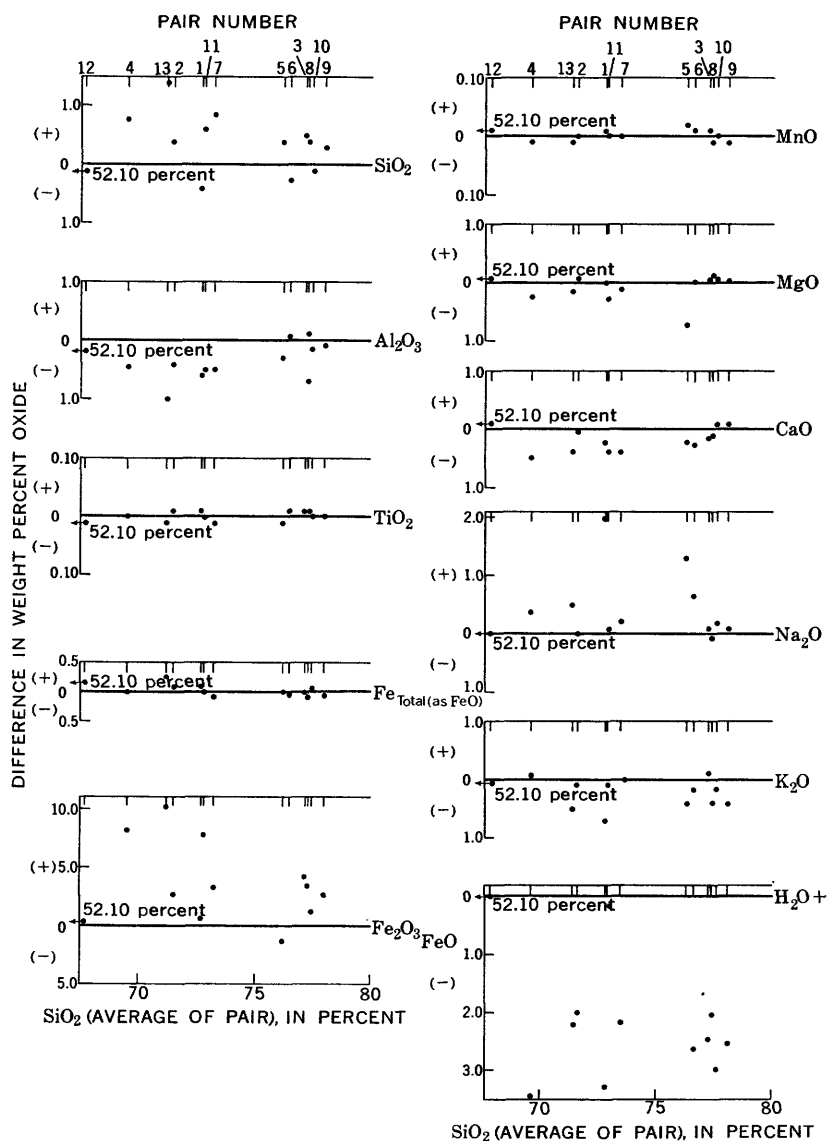


FIGURE 1.—Compositional differences between glassy and crystalline rocks expressed as the percent variation of oxides. Each point represents the change in weight percent of oxide for one pair of analyses. Percent differences obtained from chemical analyses in table 2 by subtracting column A from column B.

analyst. The consistently higher SiO_2 and lower Al_2O_3 in the crystalline samples indicates that the variation is meaningful; determinative error alone would have caused a more random scatter.

CAUSES OF THE MAJOR COMPOSITIONAL VARIATIONS

Although the evidence presented thus far does not indicate whether the variations in SiO_2 , Al_2O_3 , and Na_2O are caused by modification of the glassy rocks, the crystalline rocks, or both, several lines of evidence suggest that the main variation is due to long-continued leaching by ground water. By this interpretation, silicon and sodium are the main constituents removed, and the nearly insoluble aluminum is relatively enriched in the residuum. The main evidence for ground-water leaching is (1) the composition of ground waters from volcanic terranes and (2) positive correlation between the cation deficiencies and surface areas of the glassy rocks.

Although reliable analyses of ground water originating entirely from volcanic rocks appear to be relatively scarce, many have recently been made of waters from the Rainier Mesa area of the Nevada Test Site (Clebsch and Barker, 1960). Rainier Mesa is underlain by glassy, zeolitic, and crystalline rhyolitic ash-flow and ash-fall tuffs, including several of the units sampled for this study (Gibbons and others, 1963). Six analyses of clear waters from this area (many of the reported analyses are cloudy or turbid due to suspended sediment) are listed in table 3, along with additional analyses from other semiarid volcanic terranes. Analysis 10 is also from southern Nevada. These analyses are in general rather consistent; all are very low in Al

TABLE 3.—*Chemical analyses, in parts per million, of ground water from the Rainier Mesa area, southern Nevada, and other semiarid volcanic terranes*

[Only major rock-forming elements listed]

	Samples 1-6							7	8	9	10
	1	2	3	4	5	6	Average				
SiO_2	68	67	47	36	52	54	54	103	60	55	52
Al.....	.4	.5	.1	.1	.0	.2	.2	-----	-----	.1	.0
Fe.....	.00	.40	.20	.10	.06	.00	.13	.1	.01	.08	.22
Mn.....	.00	.00	.00	.00	.00	.00	.00	-----	-----	.0	.0
Mg.....	1.9	1.5	.00	.00	1.0	.00	.8	1.1	7.5	1.4	1.0
Ca.....	13	9.6	2.4	.2	16	2.4	7.2	6.5	14	4.4	8.0
Na.....	18	15	32	24	37	26	25	41	41	11	62
K.....	2.8	2.8	2.2	.6	7.8	3.6	3.3	40	4.2	1.2	2.0

1. Seep in fracture, U12b tunnel, Rainier Mesa (Clebsch and Barker, 1960, table 2, analysis 2589).
2. Seep in fracture system, U12b tunnel, Rainier Mesa (Clebsch and Barker, 1960, table 2, analysis 2893).
3. Seep in fracture, U12e tunnel, Rainier Mesa (Clebsch and Barker, 1960, table 2, analysis 2913).
4. Seep in fracture, U12e tunnel, Rainier Mesa (Clebsch and Barker, 1960, table 2, analysis 3260).
5. Seep in fracture, U12e tunnel, Rainier Mesa (Clebsch and Barker, 1960, table 2, analysis 3354).
6. Seep in fracture, U12e tunnel, Rainier Mesa (Clebsch and Barker, 1960, table 2, analysis 3541).
7. Spring on Rio San Antonio, Sandoval County, N.Mex. Water-bearing formation: rhyolite (Hem, 1959, table 6, analysis 2).
8. Basque Spring, Harney County, Oreg. Water-bearing formation: rhyolite and possibly basalt (Hem, 1959, table 6, analysis 3).
9. Spring, west of Los Alamos, N.Mex. Flows from rhyolite of Tertiary age (White and others, 1963, table 1, analysis 2).
10. Spring, north of Beatty, Nev. Flows from rhyolite of Tertiary age (White and others, 1963, table 1, analysis 5).

and high in SiO_2 , with the Na the next most abundant cation constituent. The analyses show that the main constituents taken into solution by ground water in these volcanic terranes are just those which are relatively the most deficient in the glasses of table 2. The fairly abundant calcium in the water analyses is probably due to widespread Paleozoic carbonate rocks near most of the sample localities.

Independent evidence of ground-water leaching can be inferred from relations between the composition and surface area of various glassy ash-flow tuff units. If the differences within the pairs of analyses in table 2 were due to modification during crystallization, then all glassy parts of any initially homogeneous volcanic body should show similar compositions, and there should be considerable scatter among crystallized samples. In contrast, if the variations were due to leaching of the glasses, then the crystalline samples from any single unit should be uniform, and the glassy samples should show considerable scatter correlative with variable surface area available for leaching. Variations due to leaching should be less extreme in dense vitrophyres (low porosity and surface area) than in nonwelded or partly welded tuffs (higher porosity and surface area).

The main problem with this approach is that most of the compositional variations indicated by table 2 are too small to recognize without the controls afforded by the paired samples. For example, the variations in SiO_2 and Al_2O_3 , which are among the largest in terms of weight-percent differences (fig. 1), are nevertheless relatively small compared to the total amount of these constituents in the rocks. These oxides, moreover, are the dominant constituents of rhyolitic rocks and have a reciprocal relationship to each other that makes recognition of even large variations difficult without some external standard. Fortunately, these difficulties do not seriously affect variations in Na_2O . In table 2 the variations in Na_2O average about 10 percent and some are as high as 40 percent of total Na_2O , a sufficiently large variation to be recognizable in less carefully controlled data. Also, as a relatively minor constituent, Na_2O is not appreciably modified by the reciprocal effects of changes in SiO_2 and Al_2O_3 . Accordingly, Na_2O variations provide a sound basis for examining some additional analyses from southern Nevada.

Considerable chemical data in addition to that already given in tables 1 and 2 is available for the Miocene(?) and Pliocene Paintbrush Tuff (Paul Orkild, written commun., 1964), an extensive ash-flow sequence in the vicinity of the Nevada Test Site. Figure 2 shows Na_2O and K_2O compositions of all available analyses of the Topopah Spring Member of the Paintbrush Tuff, and ash-flow cooling unit that is compositionally zoned from silicic rhyolite at its base to

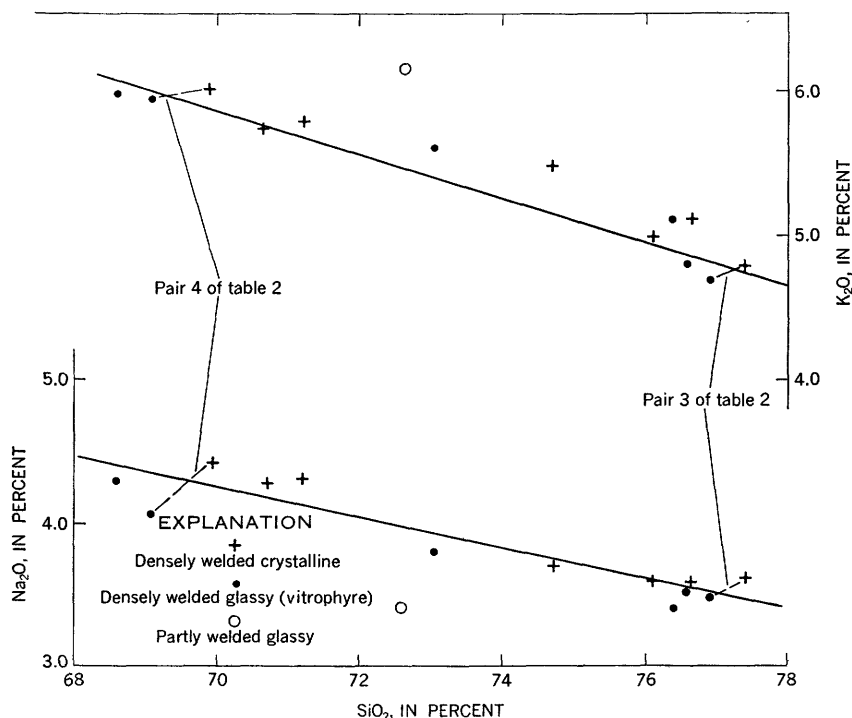


FIGURE 2.—Alkali variations in Topopah Spring Member of Paintbrush Tuff. Generalized variation trends drawn by inspection through all analyses of densely welded rocks. Tielines connect multiple analyses from individual localities. Unpublished analyses provided by P. W. Lipman, J. T. O'Connor, and E. N. Hinrichs, U.S. Geological Survey.

quartz latite at its top. The crystallized tuffs, all of which are densely welded, plot on a linear variation trend and have very little scatter. Both alkalis increase systematically as SiO_2 decreases. The vitrophyres, especially those of rhyolitic composition, plot fairly close to this trend, but for any given SiO_2 content the vitrophyres are slightly lower in Na_2O than are the crystallized welded tuffs. The glass that is lowest in Na_2O (and highest in K_2O) is only partly welded and accordingly has greater porosity and surface area than the other samples.

Na_2O contents of available analyses of Yucca Mountain and Tiva Canyon Members of the Paintbrush Tuff, all rhyolitic ash-flow tuffs, show a pattern similar to that of the Topopah Spring Member (fig. 3). The analyses of Yucca Mountain and Tiva Canyon Members show very limited SiO_2 variation, and all devitrified samples have similar Na_2O contents. The Na_2O content is somewhat lower in a vitrophyre from the Tiva Canyon Member and decidedly lower in a nonwelded glassy basal ash-flow tuff from the Yucca Mountain Member. K_2O tends to be higher in the glassy samples than in the crystalline ones.

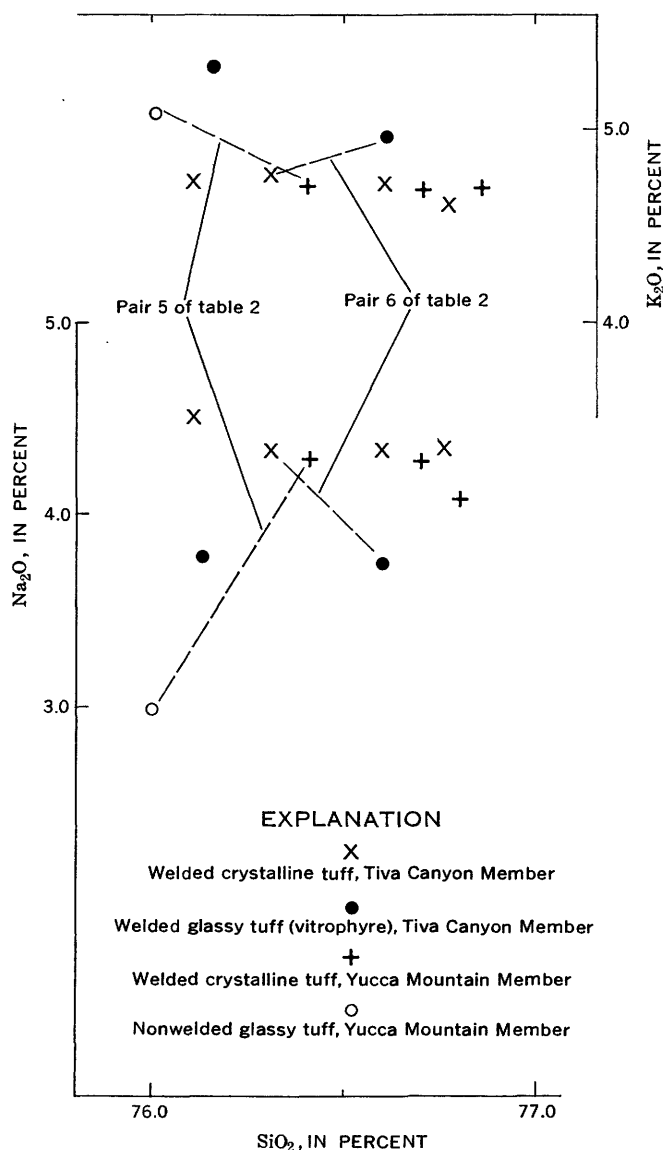


FIGURE 3.—Alkali variations in Yucca Mountain and Tiva Canyon Members of Paintbrush Tuff. Tielines connect multiple analyses from individual localities. Analyses of Yucca Mountain Member from Lipman and Christiansen (1964); analyses of Tiva Canyon Member connected by tieline are from Cornwall (1962, table 2, col. 5-6); the other analyses of Tiva Canyon Member are unpublished and were provided by J. T. O'Connor, U.S. Geological Survey.

Many analyses are available for the Pliocene Timber Mountain Tuff, a somewhat more complex ash-flow sequence that includes several compositionally zoned cooling units. The considerable scatter of Na_2O in figure 4 is probably due in part to this complexity and in part to the fact that many of the analyses were made primarily for purposes other than petrochemical study. Nevertheless, the analyses show that nonwelded porous glasses are strikingly lower in Na_2O than are the dense vitrophyres and the approximately similar crystallized tuffs of comparable SiO_2 content, a relation which suggests that sodium has been removed from the glasses in proportion to their surface area. The vitrophyres may average slightly lower in Na_2O content than the crystallized welded tuffs, especially for less silicic compositions. The porous glasses are higher in K_2O than are the vitrophyres and crystalline rocks.

Similar alkali variations between glassy and crystalline tuffs can be demonstrated for the Grouse Canyon and Tub Spring Members of

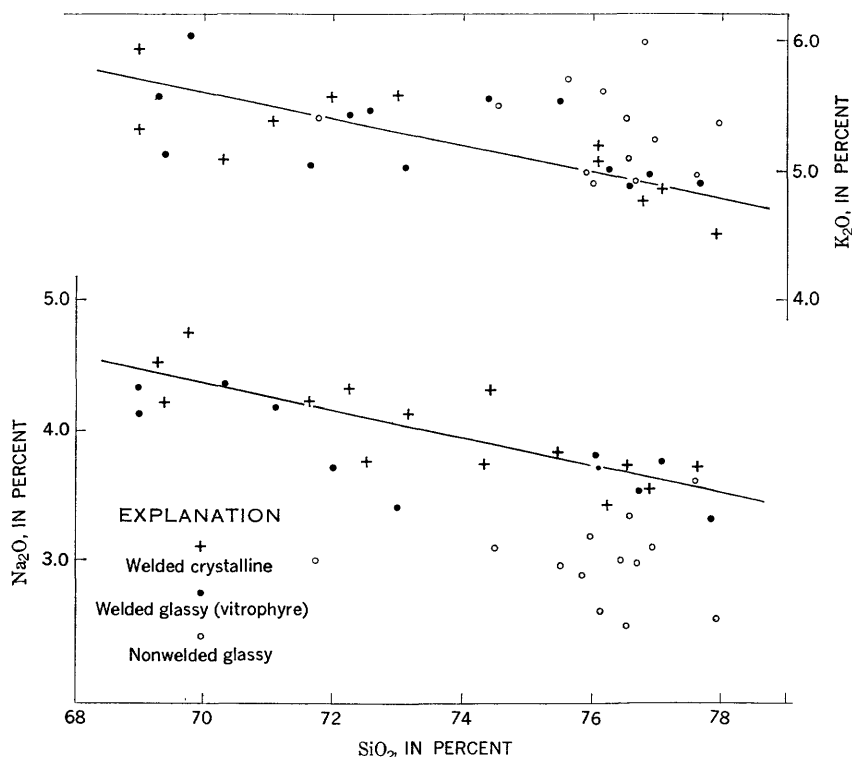
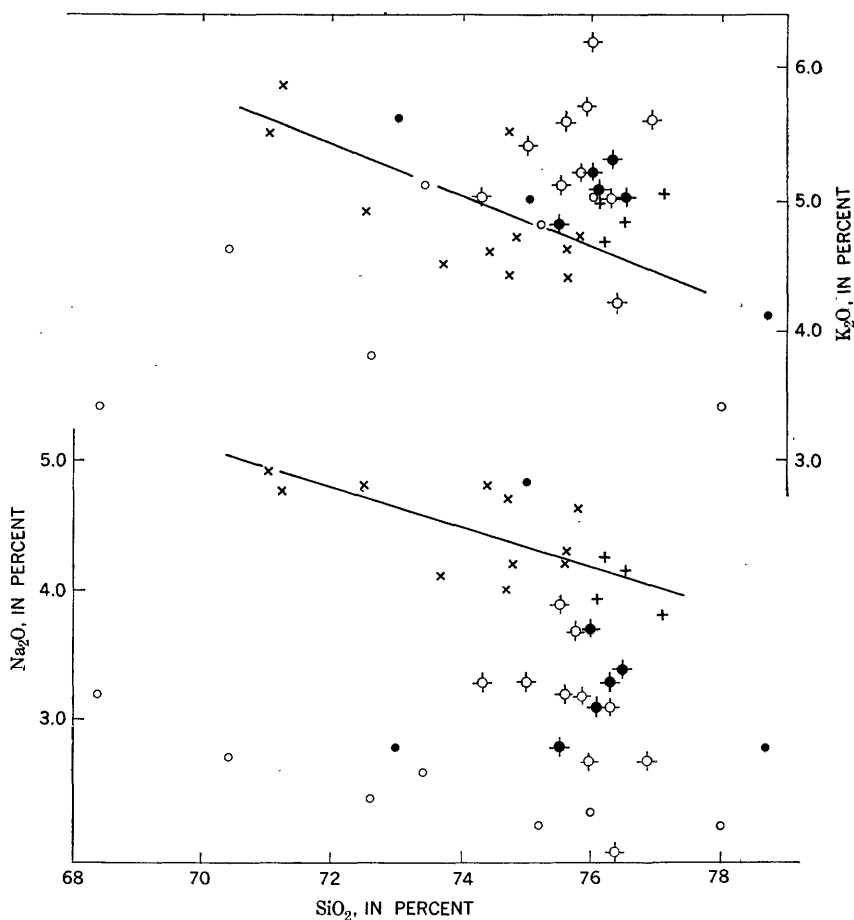


FIGURE 4.—Alkali variations in Timber Mountain Tuff. Generalized variation trends drawn by inspection through all analyses of welded rocks. Unpublished analyses provided by W. J. Carr, F. M. Byers, Jr., E. N. Hinrichs, J. T. O'Connor, P. Orkild, and others, of the U.S. Geological Survey.

the Miocene and Pliocene(?) Indian Trail Formation (fig. 5), another major volcanic sequence in the Nevada Test Site area for which abundant analytical data are available. The scatter in overall Na_2O values is so great that no trend can be seen; however, the devitrified samples make a well-defined trend, and most of the glassy samples



EXPLANATION

Grouse Canyon Member

Tub Spring Member

x Densely welded crystalline

+

● Densely welded glassy (vitrophyre)

◆

○ Nonwelded and partly welded glassy

◇

FIGURE 5.—Alkali variations in Grouse Canyon and Tub Spring Members of Indian Trail Formation. Generalized variation trends drawn by inspection through analyses of densely welded crystalline rocks. Unpublished analyses provided by F. M. Byers, Jr., E. N. Hinrichs, R. D. Krushensky, K. A. Sargent, and others, of the U.S. Geological Survey.

show significantly lower Na_2O contents. Although there is considerable overlap, the nonwelded and partly welded glassy samples are generally lower in Na_2O than are the less porous vitrophyres. Samples from the Grouse Canyon Member show an apparently unsystematic variation in K_2O content, but the Tub Spring samples define an interesting series. The vitrophyres are slightly higher in K_2O than are the devitrified samples, and the nonwelded and partly welded samples are higher than the vitrophyres. These K_2O variations are similar to those in the Timber Mountain Tuff and, like the Na_2O variations, appear to be related to surface areas of the glassy rocks.

Additional evidence of a correspondence between loss of Na_2O and surface area of glassy rocks is available from an unpublished study by H. A. Powers, of the U.S. Geological Survey, on some samples of the glassy Pearlette Ash Member of the Sappa Formation of Pleistocene age. Powers separated shard tufts from several localities into three size fractions and then had each fraction analyzed for alkalis. In each sample the finest fraction showed lower Na_2O and higher K_2O than the coarsest fraction (fig. 6); one intermediate fraction was anomalous. In conjunction with the previously presented data, these analyses suggest that sodium has been removed and potassium added to the tufts in proportion to their surface area.

ESTIMATION OF ABSOLUTE COMPOSITIONAL CHANGES

Thus far in this study only the relative compositional differences between glassy and crystalline samples have been considered, but it is also desirable that the absolute compositional changes be estimated. Unfortunately, estimation of the absolute change requires several additional assumptions and, accordingly, is less precise than determination of the relative compositional changes. If the compositional differences between glasses and rocks that have crystallized by primary crystallization result mainly from ground-water leaching, the material removed from the glasses of table 2 can be approximated by assuming negligible leaching of silicon and sodium from the crystalline rocks and of aluminum from the glassy rocks. The very low aluminum in the ground-water analyses (table 3) suggests that this assumption is reasonable, at least with respect to aluminum.

Accordingly, each glass analysis in table 2 has been recalculated to the Al_2O_3 content of its crystallized equivalent (table 2, C columns) and the differences between C and B columns of table 2 have been plotted graphically in figure 7. These differences are analogous to the relative compositional changes of figure 1, and should provide an approximation of the absolute compositional changes. The most pronounced difference in comparison with figure 1, the increased positive

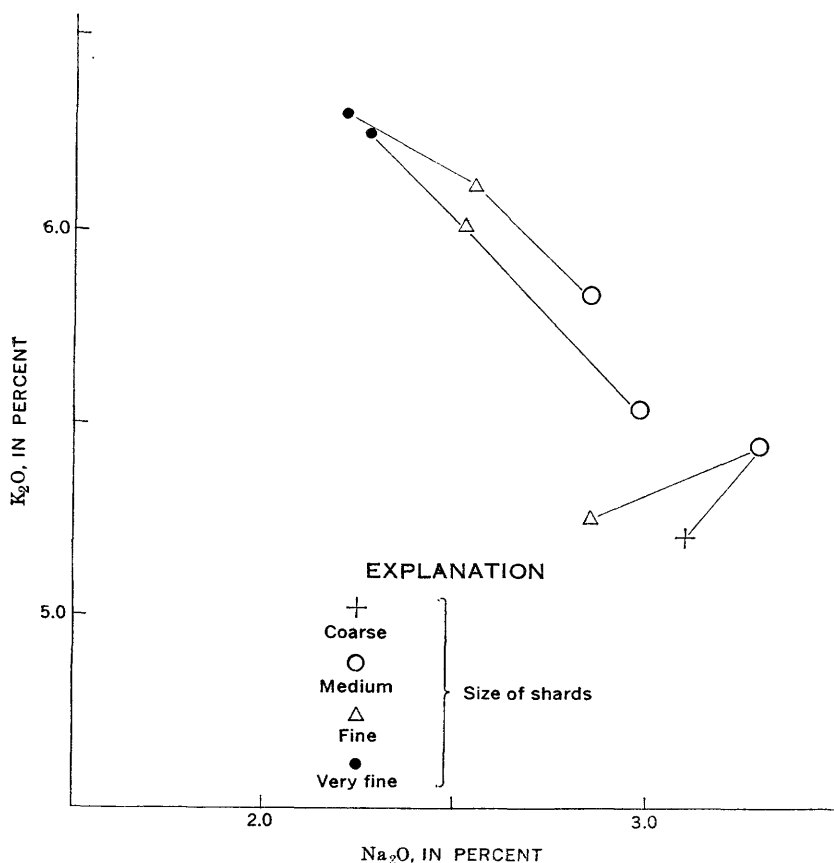


FIGURE 6.—Relations between alkali compositions and shard size in samples of the glassy Pearllette Ash Member of the Sappa Formation from three localities. Each sample collected from a single homogeneous bed and separated into three size fractions. Definition of size classification: Coarse shards, +150 mesh; medium shards, -150 mesh to +200 mesh; fine shards, -200 mesh, sink in water in 2 minutes; very fine shards, -200 mesh, float in water for 2 minutes but sink in 2 hours. Unpublished analyses provided by H. A. Powers, U.S. Geological Survey.

values for SiO_2 , should approximate the amount of SiO_2 actually leached from the glasses, but the large scatter of these values appears to reflect an inherent difficulty in the recalculation. Although analytical error in Al_2O_3 determinations is probably not seriously large for the original data, as discussed previously, any determinative error would be multiplied approximately five times in the recalculated SiO_2 values in column C of table 2 and is undoubtedly responsible for some of the SiO_2 scatter in figure 7. In spite of such weaknesses, assumption of constant aluminum appears to be the best base from which to estimate the absolute compositional changes. Certainly, constant-volume calculations would be inaccurate because of volume

changes during leaching and secondary hydration of the glasses. More precise determination of the absolute compositional changes will probably require experimental leaching of glassy and crystalline rocks under controlled laboratory conditions.

As an approximation, the values of figure 6 suggest that about 0.5 percent Na_2O and several percent SiO_2 have been removed from many vitrophyres. Accordingly, the analyzed glasses have been leached of perhaps four times as much SiO_2 as Na_2O , while the analyses of ground

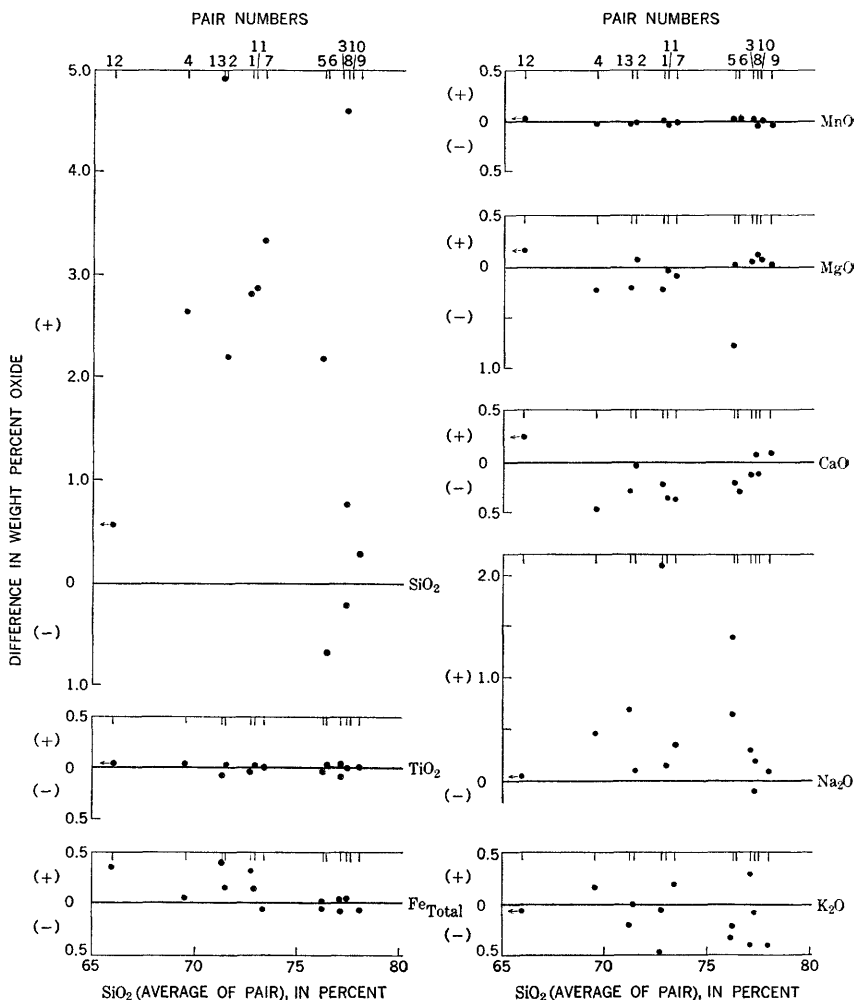


FIGURE 7.—Compositional differences between glassy and crystalline rocks with glassy rocks recalculated to Al_2O_3 content of crystalline rocks. Each point represents the net change in weight percent of oxide for one pair of analyses. Percent differences obtained from chemical analyses in table 2 by subtracting column C from column B.

water average approximately twice as much SiO_2 as Na_2O (table 3). Because of the scatter in the present data, the significance of the variation between these ratios cannot be assured, but the data suggest that the ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ leached from glasses may be higher than that leached from crystalline rocks.

Consideration of K_2O variations has been left until this point because the behavior of this oxide presents the most perplexing feature of the present data. Higher K_2O in most glasses than in associated crystallized samples is indicated on both figure 1 and figure 7, although the recalculation to constant Al_2O_3 reduces the amount somewhat. Generally similar behavior of K_2O is clearly shown by many tuffs from the Nevada Test Site (figs. 3-5), although two units, the Topopah Spring Member (fig. 2) and the Grouse Canyon Member (fig. 5), do not show a consistent trend. The variations are particularly striking for the Timber Mountain Tuff and the Tub Spring Member. Although any systematic variations between crystallized and densely welded glassy parts of the Timber Mountain Tuff are obscured by considerable scatter in the data, the porous nonwelded glasses are significantly higher in K_2O than are welded rocks of comparable SiO_2 content, probably because of greater surface area. The Tub Spring Member (fig. 5) and the Pearlette Ash Member (fig. 6) also show a correlation between surface area (shard size) and increasing K_2O in glassy tuffs. The reason for these K_2O variations is not clear. Perhaps some excess K_2O is related to the argillic alteration described previously that accounts for high MgO and CaO in a few glasses, especially sample 5A (table 2). However, sample 4A (table 2) contains clay in amounts detectable by X-ray, but is deficient in K_2O . Most of the volcanic glasses containing high K_2O also have low Na_2O (figs. 3 through 5), and some excess K_2O is possibly due to base exchange, K_2O substituting for some of the leached Na_2O . Examples of base exchange of K_2O (and CaO) in industrial glasses are cited by Stanworth (1950, p. 117, 151).

COMPOSITIONAL CHANGES IN EXAMPLES OF SECONDARY DEVITRIFICATION

Compositional variations between glasses and crystallized rocks that have undergone secondary devitrification, although not the principal topic of this paper, are considered briefly because most previously described glass-crystalline pairs fall into this category, and because the typical compositional changes seem to differ from those observed for examples of primary crystallization.

Six analyzed pairs of crystalline and glassy rocks that probably exemplify secondary devitrification are listed in table 4; they have been recalculated free of water and calcium carbonate in table 5. According

TABLE 4.—*Paired chemical analyses, in weight percent, of glassy and crystalline rocks that have undergone secondary devitrification*

[A, glassy rocks; B, crystalline rocks]

	1		2		3		4		5		6	
	A	B	A	B	A	B	A	B	A	B	A	B
SiO ₂	71.46	73.52	61.69	59.21	72.37	75.31	74.11	77.30	72.20	76.40	71.46	75.94
Al ₂ O ₃	12.72	12.17	14.43	14.06	11.64	13.62	11.20	12.39	10.75	10.60	12.29	12.40
TiO ₂21	.19	1.00	1.06	-----	-----	.11	.12	.06	.06	.17	.17
Fe ₂ O ₃94	1.08	1.23	2.66	1.42	2.31	.52	.57	.89	1.40	.65	.97
FeO.....	.31	.14	5.86	4.87	1.08	.00	.28	.19	.80	-----	.45	.17
MnO.....	.07	.05	.30	.24	-----	-----	-----	-----	-----	-----	.06	.06
MgO.....	.22	.20	2.81	3.71	.52	.20	.23	.10	.65	.38	.32	.19
CaO.....	.86	.74	4.97	5.95	1.30	.97	1.88	.68	.45	-----	1.20	.50
Na ₂ O.....	3.40	1.03	3.20	2.06	4.15	3.02	3.17	3.14	3.95	2.57	3.63	3.41
K ₂ O.....	4.72	7.97	1.72	2.83	3.98	4.07	1.04	4.36	3.17	7.45	3.60	5.62
H ₂ O+.....	3.67	1.42	2.36	1.54	4.86	1.48	{ 5.14	{ .60	7.32	1.60	{ 5.31	.28
H ₂ O-.....	.98	1.12	.25	2.05								
P ₂ O ₅03	.02	.24	.20	-----	-----	.02	.02	-----	-----	.58	.09
CO ₂02	.01	-----	-----	-----	-----	-----	-----	-----	-----	.04	.01
Total.....	99.61	99.66	100.06	100.44	101.32	100.98	99.90	99.78	100.24	100.46	99.80	99.85

1. Rhyolitic welded tuff, Klondyke quadrangle, Arizona.

A. Vitrophyric tuff. (Simons, 1962, table 2, col. 1.)

B. Same rock as A, devitrified. (Simons, 1962, table 2, col. 2.)

2. Leidlette (dacite) sill, Mull, Scotland.

A. Glassy part. (Anderson and Radley, 1915, p. 212, col. 1a.)

B. Stony (devitrified) part, same locality as A. (Anderson and Radley, 1915, p. 212, col. 1b.)

3. Porphyry dike, Arran, Scotland.

A. Pitchstone. (Judd, 1893, p. 545, col. 3.)

B. "Quartz-felsite" derived from A. (Judd, 1893, p. 545, col. 2.)

4. Extrusive rhyolite dome, Wenatchee, Wash.

A. Perlite. (Coombs, 1952, table p. 202, col. 2.)

B. Spherulitic breccia, presumably derived from A. (Coombs, 1952, table p. 202, col. 3.)

5. Rhyolitic lava flow, Colle de la Motte, Esterel, France.

A. Black obsidian. (Terzaghi, 1948, table 1, col. 11.)

B. Devitrified obsidian a few hundred feet from A. (Terzaghi, 1948, table 1, col. 7.)

6. Rhyolitic lava flow, Bullfrog Hills, Nev.

A. Basal vitrophyre zone. (Cornwall, 1962, table 2, col. 8.)

B. Felsite zone, same flow as A. (Cornwall, 1962, col. 9.)

TABLE 5.—*Paired chemical analyses of rocks listed in table 4 recalculated without water or calcium carbonate*

Symbols:

A, Glassy rocks

B, Crystalline rocks

[Values in parentheses are not included in total percent]

	1		2		3		4		5		6	
	A	B	A	B	A	B	A	B	A	B	A	B
SiO ₂	75.29	75.71	63.30	61.14	75.02	75.69	80.06	78.18	77.70	77.28	76.14	76.31
Al ₂ O ₃	13.41	12.53	14.81	14.52	12.07	13.69	12.10	12.53	11.57	10.72	13.10	12.46
TiO ₂22	.20	1.03	1.09	-----	-----	.12	.12	.06	.06	.18	.17
Fe ₂ O ₃99	1.11	1.26	2.74	1.47	2.32	.66	.58	.96	1.42	.69	.97
FeO.....	.32	.14	6.01	5.03	1.12	.00	.30	.19	.86	.00	.48	.17
Fe ₂ O ₃	(1.21)	(1.14)	(7.14)	(7.50)	(2.44)	(2.09)	(.80)	(.71)	(1.72)	(1.28)	(1.10)	(1.04)
MnO.....	.07	.05	.31	.25	-----	-----	-----	-----	-----	-----	.06	.06
MgO.....	.23	.21	2.88	3.83	.54	.20	.25	.10	.70	.38	.34	.19
CaO.....	.88	.75	5.10	6.14	1.33	.97	2.03	.69	.43	-----	1.22	.49
Na ₂ O.....	3.58	1.06	3.28	2.13	4.30	3.03	3.42	3.18	4.25	2.60	3.87	3.43
K ₂ O.....	4.97	8.21	1.76	2.92	4.14	4.09	1.12	4.41	3.41	7.54	3.84	5.65
P ₂ O ₅03	.02	.25	.21	-----	-----	.02	.02	-----	-----	.04	.04
Total.....	99.99	99.99	99.99	100.00	99.99	99.99	99.98	100.00	99.99	100.00	99.96	99.94

to descriptions by the collecting geologists, the field relations of pairs 1 to 5 are indicative of secondary devitrification, as defined at the beginning of this paper. The field relations of pair 6 from the Bullfrog Hills, Nevada, are not described, but it is tentatively included in the examples of secondary devitrification because it shows similar compositional variations. All the pairs are characterized chemically by higher K_2O and lower Na_2O in the crystallized samples than in the glassy samples, essentially the reverse of the relation obtained for examples of primary crystallization in table 2. The K_2O/Na_2O ratios of several crystallized samples, especially 1B and 5B, are much higher than normal siliceous igneous rocks, a relation that suggests potassium metasomatism during devitrification (Simons, 1962, p. 881-882; Terzaghi, 1948, p. 21-26). The glass of pair 2 seems to be a normal dacite, but its crystallized counterpart shows a high K_2O/Na_2O ratio for rocks of its SiO_2 content, and perhaps was also subjected to potassium metasomatism. The compositional variations in pair 4 have been attributed to metasomatic addition of potassium during devitrification (Coombs, 1952, p. 202-203). However, the K_2O/Na_2O ratio of the glass is atypically low, and the compositional changes in this pair possibly were due to modification of the glassy phase.

IMPLICATIONS FOR PETROCHEMICAL STUDIES

The data presented in this paper indicate the difficulty of determination of the composition of a volcanic magma. Most porous Tertiary glasses from the Nevada Test Site area have undergone secondary hydration and are so chemically modified by ground-water leaching that they are useless for petrochemical studies (figs. 2-5). The paired analyses of tables 1 and 2 show the same trends for vitrophyres, although in a less extreme fashion. This evident leaching of glassy rocks suggests that the most likely compositional approximations of original magma, at least for nonvolatile constituents, may be rocks that have undergone primary crystallization. This inference is supported by examples of consistent compositions among carefully sampled suites, such as the crystalline rocks of the Yucca Mountain and Tiva Canyon Members (fig. 3), and by linear variation trends such as that characterizing the crystalline rocks of the Topopah Spring Member (fig. 2). For some geologic purposes the compositional differences between vitrophyre and crystalline samples would be unimportant, but consideration of figures 2 through 5 indicates that variation trends utilizing only the crystallized samples would differ considerably from trends using the glasses or mixed samples.

Perhaps obsidians that have not undergone secondary hydration may provide as close an approximation of original magma as samples

of primary devitrification. Some interesting analyses of welded vitrophyres of the Walcott Tuff, provided by H. A. Powers, show a striking correlation between alkali changes and degree of secondary hydration (fig. 8). The least hydrated glasses appear to be least modified, suggesting that much of the modification in alkali composition takes place in conjunction with secondary hydration. Similar variations are shown by analyses of an obsidian core (Apache tear) having a low H_2O content and its extensively hydrated glassy rind (Longwell, 1963, table 2, analyses 307 and 311). The hydrated rind contains 1.06 percent more K_2O and 0.77 percent less Na_2O (analyses recalculated on H_2O -free basis); it also contains more Al_2O_3 and less SiO_2 than the obsidian—variations characteristic of the leached glasses described previously. Probably only inconsequential leaching can take place without secondary hydration. Certainly the nonhydrated glassy basalt

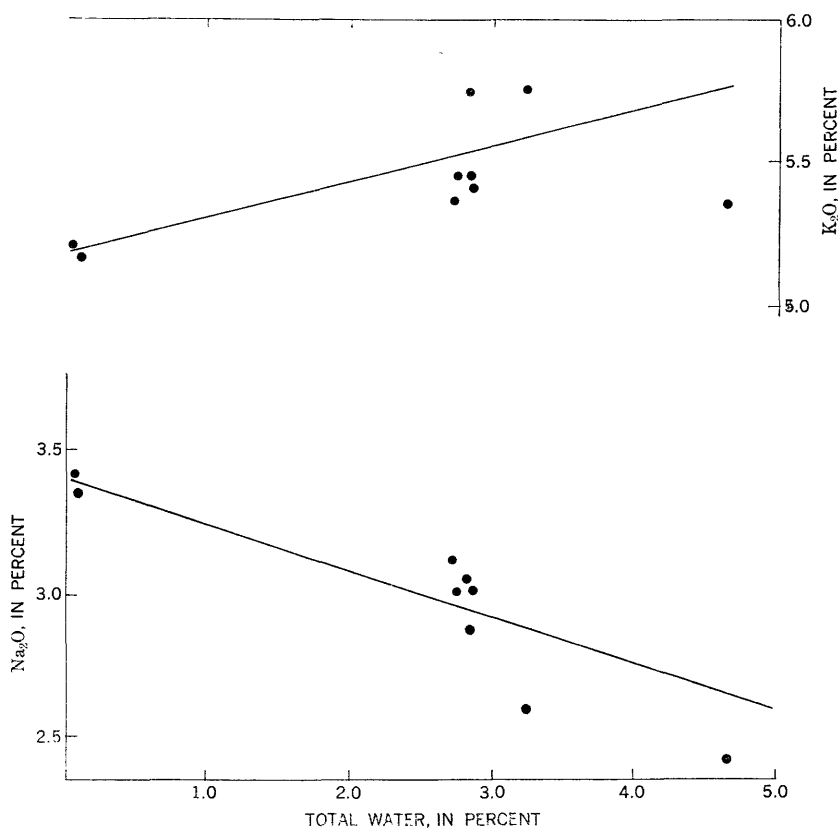


FIGURE 8.—Alkali variations in vitrophyres of Walcott Tuff, south-central Idaho. Unpublished analyses provided by H. A. Powers, W. J. Carr, and D. E. Trimble, U.S. Geological Survey.

and its crystalline equivalent (table 2, pair 12), erupted in 1949, are strikingly similar in composition. However, the only slightly hydrated glass of Pleistocene age (table 2, pair 11) shows in less extreme fashion the same trends of compositional modification that characterize the extensively hydrated pairs. Hydrated glasses cannot be used for precise petrochemical calculations without careful evaluation of their reliability.

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