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SODIUM, POTASSIUM, AND FERROUS IRON CONTENTS OF SOME
SECONDARILY HYDRATED NATURAL SILICIC GLASSES¹

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INTRODUCTION

A few workers (e.g., Bowen, 1938, p. 26-27) recognized many years ago that certain natural silicic glasses have unusual sodium and potassium contents. Robert L. Smith of the U. S. Geological Survey strongly suspected that natural glasses which have undergone secondary hydration (Ross and Smith, 1955; Friedman and Smith, 1958), although fresh appearing, may have lost or gained significant amounts of certain constituents in addition to water, and warned colleagues against basing petrogenetic interpretations on chemical analyses of rocks containing hydrated glass. Lipman (1965), using data from the literature and unpublished data from the files of the U. S. Geological Survey, showed that many rocks containing large amounts of secondarily hydrated glass contained significantly lower amounts of sodium and silica than did primarily crystallized (Lipman, 1965, p. D2) rocks from the same units. As discussed by Lipman, these changes are almost certainly the result of leaching of the glass and by ion exchange with ground water.

MATERIAL STUDIED

During the study of several volcanic centers in southern Nevada over the past several years, the writer has collected nonhydrated glasses for chemical analysis wherever possible. Nonhydrated glasses are completely unaltered and exactly represent the composition of the magmatic liquids on solidification. Such glasses are preferable to crystallized material for

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determining the original composition of a magmatic liquid, as devitrified or granophyrically crystallized material in most cases has undergone small but significant changes in alkali and alkaline earth contents (Noble, 1965; 1966) and much larger changes in halogen (Noble, *et al*, 1966) and ferrous iron contents.

Most of the nonhydrated glasses collected occurred as marekanite (obsidian nodules) (Ross and Smith, 1955) enclosed in a matrix of secondarily hydrated glass. Marekanite is not common in glassy late Tertiary volcanic rocks, and its occurrence suggests that the rate of hydration had been unusually slow. Consequently, compositional changes effected by ground water in the associated hydrated glasses may have been relatively slight, allowing a crude lower limit to be set on the magnitude of secondary chemical changes to be expected in hydrated natural silicic glasses.

Hydrated and nonhydrated glass from eight hydrated glass-marekanite pairs have been partially or completely analyzed for major constituents using the methods of Peck (1964). The hydrated glasses are perlitically fractured but fresh-appearing, and show no incipient secondary crystallization or alteration other than hydration. The hydrated glasses were separated from the marekanite by hand picking, and were crushed and ultrasonically cleaned prior to analysis.

The pertinent analytical results are given in Table 1. The analyses of hydrated glass were recast volatile-free (values given in parentheses). The need for this correction is substantiated by the alumina values available for three of the dense hydrated glasses; when corrected for water of hydration these values are identical to the alumina contents of the nonhydrated equivalents within the limits of analytical error.

SODIUM AND POTASSIUM CONTENTS

In all but one sample pair the hydrated glasses have lower Na:K ratios than do the associated nonhydrated glasses. When corrected for the added water of hydration, all the hydrated glasses show an absolute decrease in Na_2O . The changes range from less than -0.1 to greater than -0.5 weight percent Na_2O , with the median compositional change being approximately -0.4 weight percent Na_2O .

All but two of the dense hydrated glasses show an absolute increase in potassium content, which would appear to result from ion exchange between the glass and ground water. The absolute changes show approximately the same range as for sodium, with the median change being approximately $+0.3$ weight percent K_2O . Data presented by Lipman (1965, Figs. 3,4,5,6, 7) also suggest an absolute increase in the potassium contents of some hydrated glasses. In other specimens K_2O appears to have been lost.

TABLE 1. ANALYTICAL DATA ON HYDRATED-NONHYDRATED GLASS PAIRS, NEVADA

Specimen No.	Lab No.	Type ¹	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Na ₂ O ²	K ₂ O ²	H ₂ O ⁺	H ₂ O ⁻
Gold Flat Member of the Thirsty Canyon Tuff (pantellerite) 7 m.y. lat. 37°20'20" N.; long. 116°39'40" E.										
1A	D100126	N	—	—	—	—	7.05	4.38	0.14	0.01
	D100126	N	—	—	—	—	7.07	4.41	—	—
1B	D100872	N	—	—	—	—	6.94	4.35	0.12	0.03
1C	D100578	D	—	—	—	—	6.53 (6.64)	4.40 (4.47)	1.82	³
Spearhead Member of the Thirsty Canyon Tuff (comendite) 7 m.y. lat. 37°42'10" N.; long. 117°5'50" E.										
2A	D100320	N	75.37	11.95	0.84	0.99	4.43	4.82	0.45	0.04
2B	D100437	N	75.29	12.12	0.88	0.99	4.42	4.88	0.36	0.04
	D100437	N	—	—	—	—	4.42	4.88	—	—
	D100442	N	—	—	—	—	4.48	4.88	—	—
2C	D100394	D	73.32 (75.23)	11.76 (12.07)	0.95 (0.98)	0.81 (0.83)	4.29 (4.40)	4.66 (4.78)	2.77	0.17
2D	100454	P	71.94 (74.74)	11.89 (12.38)	1.28 (1.33)	0.60 (0.63)	4.02 (4.19)	4.52 (4.71)	3.32	0.82
2E	100459	P	—	—	—	—	3.90 (4.05)	4.50 (4.67)	3.10	1.04
Rhyolite of Shoshone Mountain (rhyolite) 7 to 11 m.y. lat. 36°54' N.; long. 116°16' E.										
3A	D100425	N	74.23	13.49	0.33	0.97	3.93	5.33	0.23	0.04
3B	D100426	D	72.04 (74.15)	13.14 (13.53)	0.64 (0.66)	0.61 (0.63)	3.36 (3.46)	5.62 (5.78)	2.94	0.18
Rhyolite of Obsidian Butte (rhyolite) 7 to 11 m.y. lat 37°18'40" N.; long. 116°50'40" E.										
4A	D100319	N	—	—	—	—	3.82	5.16	0.15	0.03
4B	D100443	D	—	—	—	—	3.28 (3.37)	5.55 (5.70)	2.74	0.14
Rhyolite of Saucer Mesa (comendite) 13 m.y. lat 37°22'20" N.; long. 116°17'10" E.										
5A	D100318	N	—	—	—	1.27	4.84	4.81	0.21	0.03
5B	D100444	D	—	—	—	—	4.58 (4.73)	4.69 (4.84)	3.13	0.19
5C	D101017	D	—	—	—	1.12 (1.16)	4.58 (4.73)	4.62 (4.78)	3.22	0.15
6A	D101019	N	—	—	—	1.25	4.93	4.65	0.30	0.03
6B	D101018	D	—	—	—	1.08 (1.11)	4.51 (4.64)	4.79 (4.92)	2.86	0.08
Grouse Canyon Member of the Belted Range Tuff (comendite) 14 m.y. lat. 37°20'30" N.; long. 116°1'00" E.										
7A	D100317	N	73.98	11.28	1.71	1.80	5.33	4.55	0.16	0.02
7B	D100393	D	71.70 (73.70)	10.94 (11.25)	2.00 (2.06)	1.48 (1.52)	4.63 (4.76)	4.85 (4.99)	2.90	0.10

TABLE 1—(Continued)

Specimen No.	Lab No.	Type ¹	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Na ₂ O ²	K ₂ O ²	H ₂ O ⁺	H ₂ O ⁻
Rhyolite of Split Ridge (comendite) 14 m.y. lat 37°10'20" N.; long. 116°20'40" E.										
8A	D100641	N	—	—	—	1.51	5.24	4.38	0.16	0.03
8B	D100642	D	—	—	—	1.17	4.53	4.58	2.16	0.09
						(1.21)	(4.67)	(4.72)		

Analyses performed in the standard rock analysis laboratory of the U.S. Geological Survey by E. S. Daniels, C. L. Parker, D. F. Powers, G. O. Riddle, and V. C. Smith. Values in parentheses are recalculated minus water of hydration. Silica, alumina, and iron contents are included only when data are available for both hydrated and nonhydrated glasses. Ages of rock units, in millions of years before present, based on unpublished K-Ar determinations.

¹ N=nonhydrated glass; D=dense hydrated glass; P=porous hydrated glass.

² Alkali analyses not corrected for rare alkalis.

³ Sample dried at 105°C prior to analysis.

Loss of potassium is shown by analyses of pumice-rich ash-fall tuff underlying the Grouse Canyon Member of the Belted Range Tuff. Fragments of dense glass as much as 15 mm in diameter make-up as much as 5 percent of the tuff. Locally some of these fragments have escaped hydration, thus allowing the original composition of the tuff to be determined. If one makes what appears to be a valid assumption that the hydrated glasses have neither lost nor gained aluminum, Figure 1 shows that, although some specimens have gained potassium, most have lost 5–10 percent of their original potassium in addition to over half their original sodium. Significant loss of potassium is also shown by porous tuffs 2D and 2E in Table 1. The higher degree of alteration of these tuffs, as indicated by their greater sodium loss, probably reflects both the greater surface area and greater permeability of porous rocks.

The data suggest that in most cases the earlier stages of ground-water alteration of hydrated glass will consist of loss of sodium and gain of potassium. With continued alteration sodium will be progressively removed and potassium also may be leached. No matter how fresh a hydrated glass may appear, it will almost always contain less sodium than the parent nonhydrated glass. Potassium content of secondarily hydrated glasses may be greater or smaller than the original contents: at present there appears to be no way to predict which¹. These changes are consistent with the very low sodium and high potassium contents of many hydrated glasses and glassy rocks described in the literature (e.g., Bowen,

¹ It should be noted that such gains or losses of potassium will cause potassium-argon ages obtained on hydrated glass to be more or less in error even if radiogenic argon is quantitatively retained.

1928, figs. 38, 39) and with the experimental data obtained by Truesdell (1963, 1966).

SILICA CONTENT

The recalculated silica contents of specimens 2C, 3B, and 7B (Table 1) are slightly, but probably not significantly, less than that of their non-hydrated equivalents. The recalculated silica content of porous glass 2D appears to be significantly less than that of 2A and 2B (Table 1). This,

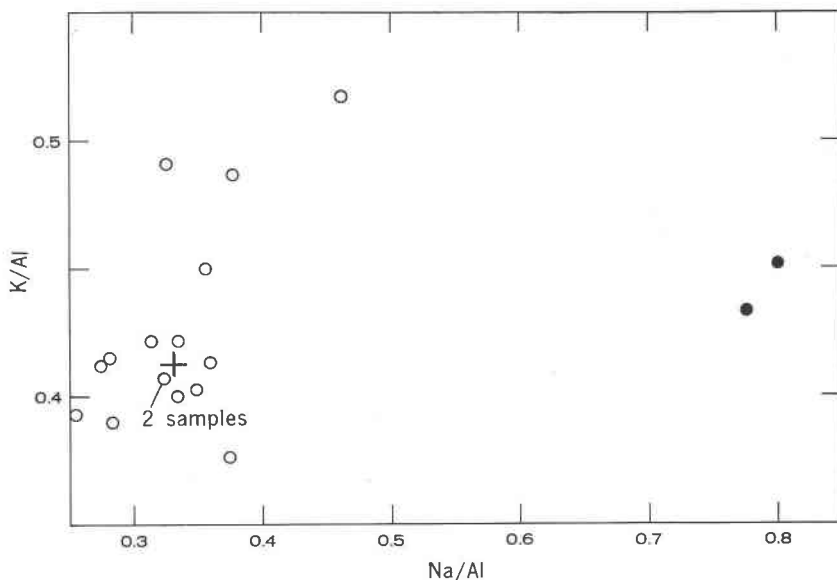


FIG. 1. Plot of Na:Al and K:Al ratios for specimens of ash-fall tuffs occurring beneath the Grouse Canyon Member of the Belted Range Tuff. Solid circles, nonhydrated glass; open circles, hydrated porous tuff. Nonhydrated glass analyses are on samples each comprising many glass fragments from an individual outcrop. Cross gives median value for hydrated tuffs. Hydrated tuffs analyzed by rapid methods (Shapiro and Brannock, 1962).

along with the higher alumina content of 2D, suggests leaching of silica from the porous glass.

FERROUS IRON CONTENT

Total iron was determined on hydrated glasses from three of the pairs. No leaching or gain of iron is apparent. Ferrous iron determinations on hydrated glasses from six of the eight pairs show very significant oxidation of the hydrated glasses. Several nonpaired analyses of both nonhydrated and hydrated glasses from the lower ash-flow sheet of the Grouse Canyon Member are available in addition to analyses 7A and 7B (Table

TABLE 2. FERRIC AND FERROUS IRON CONTENTS OF NONHYDRATED AND HYDRATED GLASSES FROM THE GROUSE CANYON MEMBER OF THE BELTED RANGE TUFF
[Analyses of hydrated glasses corrected for water of hydration]

Specimen No.	Lab. No.	Type	Fe ₂ O ₃	FeO
1	D101090	N	1.83	1.74
2	D100209	N	1.01	2.07
3A	D100317	N	1.71	1.80
3B	D100393	D	2.06	1.52
4	D111302W	D	2.4	1.3
5	D110341W	D	2.4	1.3
6	D100258	D	3.14	0.62

N=nonhydrated glass; D=dense hydrated glass.

1). As shown in Table 2, all the hydrated glasses have lower FeO:Fe₂O₃ ratios than any of the nonhydrated glasses.

Most of the original ferrous iron in the specimens of porous hydrated ash-fall tuff plotted in Figure 1 has been oxidized. The two nonhydrated glass analyses have FeO:Fe₂O₃ ratios of 1.24 and 1.28 whereas the hydrated tuffs have ratios of between 0.1 and 0.5 with a median value of 0.35. Porous glass 2D (Table 1) also has a significantly lower FeO:Fe₂O₃ ratio than associated dense hydrated glass 2C.

It seems likely that the ferrous iron content of a natural glass represents fairly closely the ferrous iron content of the parent melt prior to eruption. Some oxidation may occur if hydrogen produced by the thermal dissociation of water in the melt can escape, or it possibly may be caused by atmospheric oxygen, particularly in ash-flow tuffs, but such changes are probably very small. However, as shown by the data presented above, this statement applies only to nonhydrated glasses: hydrated glass can only provide a lower limit on the original FeO content.

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A PROCEDURE FOR THE IDENTIFICATION OF SMALL
CRYSTALS BY X-RAY DIFFRACTION ANALYSIS¹

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INTRODUCTION

In the analysis of rock and mineral fragments, especially from soils and sediments, it is often necessary to identify small single grains. Normally, mineralogical analysis of single grains is done with the petrographic microscope, but in many instances a much more satisfactory analysis would result if both X-ray and petrographic information were available. The objective of this investigation was to create a general procedure whereby X-ray diffraction data could be obtained on the same grain used for petrography. The techniques described herein were developed for use with Norelco Debye-Scherrer type powder cameras.

MOUNTING THE GRAIN

The grain should be mounted as securely as possible, since very small grains, when accidentally detached, are usually irretrievably lost. Several cements were tried,² but by far the best found for this purpose is Shell

¹ Scientific Paper No. 2815, College of Agriculture, Washington State University, Pullman, Project 3489.

² General Cement Mfg. Co. label, vinyl, general, and service cements; Dupont Duco cement; U. S. Plywood Corp. Weldwood white glue; Vaseline petroleum jelly; gelatin.