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RETENTION OF ALKALIS BY CALC-ALKALIC RHYOLITES DURING CRYSTALLIZATION AND HYDRATION[1]

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ABSTRACT

Normal calc-alkalic rhyolitic lavas that crystallized at the time of emplacement and initial cooling have alkali contents nearly identical to those of comagmatic obsidians (nonhydrated glasses) in four analyzed suites of samples. Except for loss of volatile constituents and oxidation of iron, the crystallized rocks approximate magmatic compositions closely.

INTRODUCTION

In recent years petrologists have become increasingly concerned about post-emplacement chemical modifications of volcanic rocks that are not obviously altered or weathered. Obsidians (nonhydrated glasses), most nearly represent the composition of a magmatic liquid, but are unfortunately rare in most Tertiary volcanic fields. It is now clear that rhyolitic glasses containing more than a few tenths of a percent water have been subjected to secondary hydration at surface temperatures and pressures (Ross and Smith, 1955; Friedman and Smith, 1958). Hydrated glasses (perlites) have been shown to be very susceptible to additional modification, most conspicuously variations in alkali contents resulting from leaching and ion exchange by ground water (Lipman, 1965; Aramaki and Lipman, 1965; Truesdell, 1966; Noble, 1967). It has been suggested previously that volcanic rocks that have devitrified or crystallized at the time of their consolidation commonly provide good approximations of magmatic compositions (Lipman, 1965, p. D21), but Noble (1965b) has concluded that ground-water leaching and ion exchange may affect such rocks. Significant loss of sodium during primary devitrification has been demonstrated for certain peralkaline volcanic rocks, in which molecular alkalis exceed alumina (Noble, 1965a, p. B88).

This paper seeks to evaluate further the possibility of alkali modifications in typical calc-alkalic rhyolites by comparing glasses with cogenetic primary felsites (devitrified rhyolites) from the same lava flow. The analyzed materials consist of suites of obsidians, hydrated glasses (where present), and devitrified rhyolites from four lava flows (Table 1), all from the Rocky Mountain region and all containing 74–77 percent SiO_2. For two of the suites, those from Race Creek and Nathrop, the

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devitrified and glassy rocks were collected a few feet apart, from the same outcrop. Each of the other suites consists of collections from separate localities within a single lava flow.

The lava flows range in age from late Oligocene to Pleistocene. The older, mid-Tertiary obsidians are especially interesting for the present study because of the substantial time available for postconsolidation modification of alkali contents, but unfortunately such obsidians are scarce. For example, recent remapping by the U.S. Geological Survey of much of the San Juan volcanic field of Colorado, where the rhyolites are late Oligocene to Mid-Miocene (Steven, Mehnert, and Obradovich, 1967), has revealed only one obsidian locality, Race Creek.

ANALYTICAL METHOD

Fourteen of the sixteen samples were analyzed concurrently by the same analyst using atomic-absorption techniques; the other two samples are duplicates of two samples of the main group but were collected at separate outcrops and were analyzed by flame-photometer and gravimetric methods. Several samples of the main group were also analyzed in replicate by flame-photometer or gravimetric methods, affording an estimate of analytical precision, and in the analyses for this report only one of the eight replicate alkali determinations by different methods shows a variation of more than about 1 percent (Na_2O of sample No. 11 varies 2.5 percent). Most variations greater than 1 percent between different samples, especially those analyzed concurrently by atomic absorption, are thought to be significant.

RESULTS

Four of the five obsidian samples are nonhydrated cores ("marekanite," "apache tears") collected from a matrix of secondarily hydrated perlitic glass; for these samples the perlitic glass also has been analyzed. In comparison with the obsidians from the same specimens, the secondarily hydrated perlites contain less Na_2O and three of the four perlites contain significantly more K_2O (Table 1; Fig. 1). Loss of Na_2O and gain of K_2O have also been observed in previous studies of similar rocks (Lipman, 1965; Aramaki and Lipman, 1965; Noble, 1967).

Despite the textural and structural variety of the analyzed felsite suites, including devitrified flow breccia, flow-laminated lava, and porous lava with vapor-phase crystallization, each suite is very similar to its associated obsidian in alkali contents. The largest variations between felsite and obsidian are within the suite from Race Creek; possibly this spread reflects a sampling problem, as this suite was not collected specifically for the present study and the amount of the material available for analysis was small. The alkali variations, especially Na_2O, within the other three suites are near the limits of analytical precision. The variations in K_2O are distinctly greater than those of Na_2O, but both sets of variations are random.

TABLE 1. ALKALI AND VOLATILE CONTENTS OF SOME RHYOLITIC OBSIDIANS, PERLITES, AND FELSITES FROM THE ROCKY MOUNTAIN REGION[a]

	Rhyolite of Race Creek, Colorado (Miocene, 22 m.y.)[c]				Rhyolite of No Agua, New Mexico (Pliocene?)					Rhyolite of Nathrop, Colorado (Oligocene, 28–29 m.y.)[c]					Obsidian Cliff flow Yellowstone Park, Wyoming (Pleistocene)	
	1 Obsidian 65L-161-A	2 Felsite 65L-161-B	3 Felsite 65L-161-D	4 Perlite 65L-161-C	5 Obsidian 66L-234-A	6 Felsite 66L-234-C	7 Felsite 66L-234-D	8 Felsite 66L-234-E	9 Perlite 66L-234-B	10 Obsidian 66L-230-A	11 Obsidian 100414	12 Felsite 66L-230-C	13 Perlite 66L-230-D	14 Perlite 100415	15 Obsidian 6YC-64	16 Felsite 6YC-153
Na_2O	4.09 4.09[d] 4.14[d]	4.30	4.05	3.57 (3.68)[b]	4.59	4.58	4.65	4.57	4.32 (4.44)[b]	4.30	4.31 4.42[d]	4.27	3.47 (3.58)[b]	3.97 (4.10)[b]	3.85 3.87[e]	3.89
K_2O	4.80 4.81[d] 4.85[d]	4.51	4.60	5.09 (5.25)[b]	4.35	4.17	4.30	4.31	4.24 (4.36)[b]	4.41	4.54 4.56[d]	4.58	5.10 (5.26)[b]	4.72 (4.87)[b]	4.85 4.91[e]	4.92
H_2O^+	.16	.15	.29	2.79	.28	.07	.05	.04	2.67	.10	.22	.12	2.93	2.83	.13	.06
H_2O^-	.03	.04	.09	.11	.02	.03	.04	.04	.02	.05	.05	.05	.22	.13	.06	.04
Cl	.09	.07	.04	.08	.04	.00	.01	.00	.03	.07	.07	.01	.05	.05	.10	.01
F	.13	.07	.03	.12	.22	.23	.12	.04	.29	.19	.18	.06	.19	.23	.19	.13

[a] Analyses 11 and 14 by gravimetric methods by E. L. Munson. For other analyses Na_2O and K_2O determined by atomic absorption by I. C. Frost; volatiles determined gravimetrically by Vertie C. Smith.

[b] Recalculated volatile-free to assumed summation of 100.00 percent.

[c] Unpublished K-Ar determinations by H. H. Mehnert and R. F. Marvin, U.S. Geological Survey.

[d] Determination on separate split of same sample by flame photometer by Violet Merritt.

[e] Determination on separate split of same sample by gravimetric methods by George Riddle.

Values for chlorine and fluorine are consistently lower in the felsites than in associated glasses. No significant difference in halogen content was found between the hydrated and nonhydrated glasses, indicating that the halogens were lost from the felsites during devitrification rather than by secondary alteration. These relations are similar to those observed by Noble, Smith, and Peck (1967).

In addition to loss of halogens, volcanic rocks commonly undergo oxidation of iron during devitrification. These appear to be the only significant chemical changes resulting from primary devitrification or crystallization of calc-alkalic rhyolites not having large excesses of molecular alkalies over alumina.

The data presented here also suggest that initially devitrified calc-alkalic rhyolites do not tend to undergo measurable postemplacement modification of alkali contents by ground-water leaching or ion exchange

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Sample descriptions:

Rhyolite of Race Creek, Colorado. Location: Creede 4 SW 7 1/2′ quad. Lat. 37° 31′ N., long. 106° 38′ N. Contains less than 1 percent microphenocrysts of plagioclase (avg. diam. about 0.1 mm).

1. Obsidian cores from glassy flow breccia. Collected at elevation about 11,400 feet, on north side of hill of elevation 11,529. Cores average about 2 cm in diameter and were cleaned for analysis by etching in hydrofluoric acid.

2. Devitrified flow breccia. Same locality as No. 1. Dense aphanitic purplish-gray fragments as much as 2–3 cm across in a pinkish brown aphanitic matrix.

3. Devitrified flow-layered lava. Same locality as No. 1. Light gray aphanitic rock, with flow layering defined by variations in groundmass grain size and by alignment of numerous 1-mm diam. spherulites.

4. Gray perlitic flow breccia. Same locality as No. 1. Matrix of the obsidian cores.

Rhyolite of No Agua, New Mexico. Location: Tres Piedras 7 1/2′ quad. Lat. 36° 45′ N., long. 105° 58′ W. Contains about 1 percent small phenocrysts of plagioclase and sparse quartz (avg. diam. about 0.5 mm).

5. Obsidian cores. Collected along mining road at elevation about 8,400 feet. Nodules average about 5 cm in diameter and were cleaned for analysis by etching in hydrofluoric acid.

6. Porous devitrified lava. Collected just west of hill crest, at elevation about 9,100 feet. Pale-gray aphanitic rock with vapor-phase crystallization in numerous very small vesicles (avg. diam. about 0.3 mm).

7. Dense flow-layered devitrified lava. Same locality as No. 6. Purplish gray with faint flow layering defined by variations in groundmass devitrification texture.

8. Dense structureless devitrified lava. Same locality as No. 6. Light-gray aphanitic rock.

9. Gray-brown perlite. Same locality as No. 5. Matrix of the obsidian cores.

Rhyolite of Nathrop, Colorado. Location: Buena Vista 15′ quad. Lat. 38° 45′ N., long. 106° 04′ W. Contains about 1 percent small phenocrysts of plagioclase (avg. diam. about 1 mm).

10. Obsidian cores. Collected south of Bald Mountain Gulch at elevation about 7,750 feet. Nodules average about 1 cm in diameter and were cleaned for analysis by etching in hydrofluoric acid.

11. Obsidian cores. Collected several hundred feet south of No. 10.

12. Dense faintly flow-layered devitrified lava. Collected about 100 feet upslope from locality No. 10. Light gray, aphanitic, with flow layering defined by lenticular zones of light-colored, more coarsely microcrystalline material interlayered with darker finer-grained material.

13. Dark-gray dense perlite. Same locality as No. 10. Matrix of the obsidian nodules.

14. Dark-grey dense perlite. Same locality as No. 11. Matrix of the obsidian nodules.

Obsidian Cliff flow, Wyoming. Location: Mammoth 15′ quad. Lat. 44° 48′ N., long. 110° 43′ W. Virtually devoid of phenocrysts.

15. Black obsidian with sparse light-gray spherulites about 1 mm in diameter. Collected near mouth of dry gully about 500 feet northeast of Lake of the Woods.

16. Flow-layered rhyolite with alternating medium-gray microspherulitic laminae and light-gray vesicular laminae with vapor-phase tridymite, alkali feldspar, and opaque oxide minerals. Collected about 200 feet east of Crystal Spring patrol cabin.

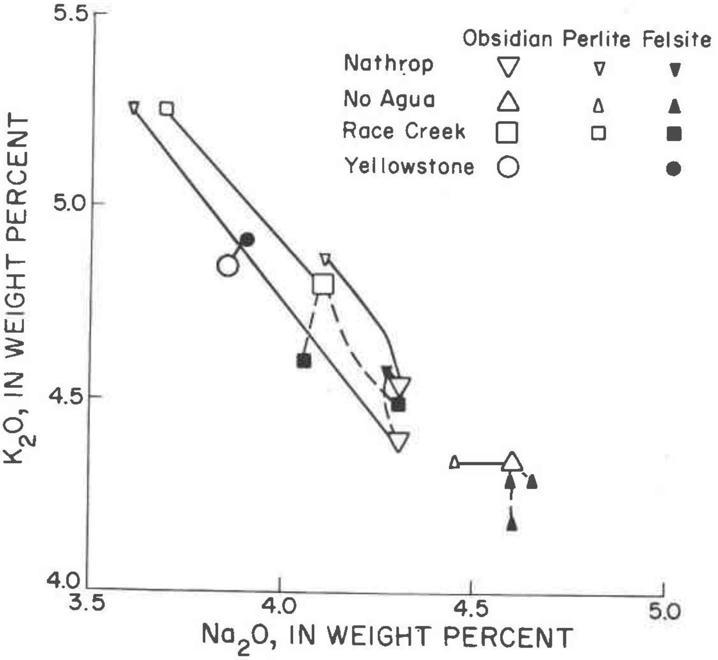

FIG. 1. Na_2O and K_2O contents of cogenetic felsites and glasses. Analytical data are from Table 1 (replicate analyses on different splits of same sample not plotted). Dashed tie-lines connect obsidians and felsites from same lava flow; solid tie-lines connect obsidian cores and perlitic matrix from same sample.

as hydrated rhyolitic glasses do. This conclusion is contrary to that of Noble (1965b), but he probably was working entirely with peralkaline rocks.

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