Minor-element abundances in obsidian, perlite, and felsite of calc-alkalic rhyolites

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Abstract

Evaluation of differences in minor-element composition between coexisting obsidian, perlite, and felsite from four Cenozoic rhyolite lava flows in the Rocky Mountain region indicates that significant errors can be made in estimating the original composition of rhyolitic obsidian simply by relying on abundances of elements in associated perlite and/or felsite.

Perlites have low Li, high Sr and Ba, and variable F relative to obsidian. Variations of Li, Sr, and Ba in perlites are controlled by low-temperature ion exchange with groundwater. Felsites have low Li, Cs, U, Mo, and F, and high Sr, Ba, and Eu relative to obsidian. Variations of elemental abundances in felsites result from a combination of high-temperature (crystal-melt fractionation and volatile transport) and low-temperature processes (ion exchange, differential solution, and absorption by secondary phases). For rhyolitic rocks that evolve by major feldspar fractionation, the rare-earth elements (REE), and particularly Eu, are useful for evaluating abundance variations produced by magmatic heterogeneity of feldspar. The component of Sr and Ba variations caused by magmatic heterogeneity of feldspar may be estimated using the Eu data. Young felsites have significantly different abundances of F, REE, Cs, and Li than coexisting obsidian, and this indicates that variations are produced by either crystal-melt fractionation or processes active during or shortly after eruption. Compared to obsidian, felsites exhibit relative depletions of U and Mo that increase with age, which indicates that losses are caused by weathering.

Introduction

This study evaluates minor-element variations within different parts of individual rhyolitic lava flows. The reported elements represent a variety of chemical groups of different geochemical affinities. The purpose of such a study is to provide additional data on (1) the extent to which hydrated or crystallized glass represents chemical equivalents of original non-hydrated glass, (2) the mechanisms and rates of elemental mobility related to hydration and crystallization of rhyolitic glass.

The four flows studied are from the Rocky Mountain region and range in age from Pleistocene to Oligocene. An obsidian, one or more felsites, and, generally, a secondarily-hydrated perlite were analyzed from each flow. Obsidian and perlite were in intimate contact, and felsites were collected within a few meters of glassy samples. The same samples were earlier utilized for a study of the retention of alkalis and halogens (Lipman et al., 1969).

During eruption and emplacement, silicic lava flows are typically quenched at their margins to a glassy envelope of obsidian, while the more slowly cooled interiors undergo primary crystallization to dense felsite. Rhyolitic felsite is typically composed of alkali feldspar and cristobalite with minor iron oxides. Subsequent to emplacement, the quenched glass gradually hydrates to grey perlite (Ross and Smith, 1955; Friedman and Smith, 1958; Noble, 1968), containing up to 5 weight percent water.

Previous studies have documented several changes accompanying hydration and crystallization of acidic volcanic glass. Hydration causes oxidation of iron, loss of Na, and increase of K (Lipman, 1965; Aramaki and Lipman, 1965; Truesdell, 1966; Noble, 1967). Alkali contents of crystallized cale-alkalic rhyolites are very similar to those of coexisting obsidian (Lipman et al., 1969), but peralkaline volcanic rocks in which molar alkalis exceed alumina tend to lose Na during crystallization (Noble, 1965; Noble,

1970). Ewart (1971) reported small-scale migration of Na and K within spherulites contained in rhyolite glass. Other elements reported depleted in crystallized rhyolites relative to glassy portions include halogens (Noble et al., 1967; Lipman et al., 1969), Mo (Haffty and Noble, 1972), U (Rosholt and Noble, 1969; Rosholt et al., 1971; Shatkov et al., 1970), Cs (Shatkov, 1971), and Be (Shatkov et al., 1970; Steven et al., 1973, p. 92–98). Sr has been reported to be enriched in crystallized rhyolites relative to glassy portions (Noble and Hedge, 1969).

Analytical techniques

Approximately 100 g aliquots of hand-size samples were ground in ceramic plates to -100 mesh. Splits were distributed for analysis of 38 elements by a variety of analytical techniques chosen to optimize accuracy and precision for each element.

Twenty-four elements (Na, K, Cs, Cr, Mn, Fe, Co, Sc, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Lu, Zr, Hf, Ta, Sb, and Th) were determined by instrumental neutron activation analysis (Gordon et al., 1969; Gijbels and Hertogen, 1971). Splits of 1.5 g were irradiated with standards for 30 minutes in the USGS TRIGA reactor in a neutron flux of 3 × 1010 n/cm²/sec. The standards were USGS standard rock G-2 and synthetic standards (CQS-1 and -2) prepared by adding the elements of interest to highpurity quartz powder. Following this short irradiation, the samples and standards were counted over an interval of decay of 4 hours using coaxial Ge(Li) detectors (resolution 2.0 keV FWHM at 1333 keV, efficiency ~ 10 percent). The samples and standards were then irradiated for 8 hours in a neutron flux of 3 \times 10¹²n/cm²/sec and counted on the coaxial Ge(Li) detectors as well as planar Ge(Li) detectors (resolution ~500eV FWHM at 122 keV) after decay times of 7, 14, and 60 days. The spectra of induced γ -ray activites were stored on magnetic tape and areas under the photopeaks calculated and compared by com-

Uranium abundances were determined by a delayed-neutron counting technique (Millard, 1976). Splits of 8 grams of samples and standards (U-doped dunite) were irradiated for 1 minute in the USGS TRIGA reactor in a neutron flux of $6 \times 10^{11} \text{n/cm}^2/\text{sec}$ and transferred by pneumatic tube to an array of BF₃ neutron detectors. After a 20-second period of decay the samples and standards were counted for 1 minute. This procedure was repeated but with irradiation in a Cd-lined terminus to determine thorium. Corrections for detector dead-time,

thorium, and oxygen were applied. Sample transfers and data collection and reduction were computer-controlled.

The remaining analyses were performed by a number of standard procedures including atomic absorption, X-ray fluorescence, emission spectrometric and isotope dilution (analysis performed by C. E. Hedge) mass spectrometic techniques.

Results and discussion

Elemental concentrations are expressed as parts per million (ppm) by weight (Table 1) along with estimated analytical precision. Of note are the extremely low concentrations of Ba and Sr compared to average acidic crustal rocks and the low concentrations of elements normally concentrated in mafic phases (Co, Cu, Cr, Sc). These abundances, as well as those of the rare earth elements (Fig. 1), indicate origin of the rhyolitic magmas by large degrees of fractional crystallization and/or small degrees of partial melting involving equilibration of melt and a feldspar residuum (Noble et al., 1969; Zielinski and Frey, 1970).

Concentrations of 29 selected minor elements in perlite and felsite are normalized to concentrations in closely coexisting obsidians (Fig. 2). Elements omitted from Figure 2 include major elements obtained by neutron activation (Na, K, Fe) but discussed elsewhere (Lipman et al., 1969), and minor elements with consistently large analytical errors (Tm, Gd, Sb, Cu, As, Se). No correction was made for density differences between samples. This could introduce small systematic errors in some of the normalized ratios, but inspection of Figure 2 indicates that such effects are not a major problem. Perlites of this study contain up to 3 weight percent H₂O (Lipman et al., 1969), resulting in a density decrease of less than 5 percent. Density corrections should be more important for glasses undergoing extensive dissolution and secondary alteration to zeolite and clay (Hoover, 1968).

Conclusions regarding elemental variability are drawn only when measured differences are large relative to analytical uncertainties and when consistent trends appear in more than one sample suite. The general validity of the observed trends can only be documented through additional studies of this nature.

Minor-element differences between obsidian and perlite

All three perlites show large relative depletion of Li, and two show enrichment in Sr compared to

Table 1. Compositions of some rhyolite obsidians, perlites, and felsites from the Rocky Mountain region

66L- Na 3300 K 397(Rb 30 Cs Be 5r Ba	95. 000.	47. 25100. 43000. 310. 7.2 9. 4.7 2. 731. 3790. 0.05	51. 32900. 39800. 295. 6.1 8. 3.1 28. 11. 700. 4190. 0.09		30. 25300. 41300. 212. 7.4 6. 8.3 12.		Pelsite 2 65L-161D 21. 30900. 40100. 230. 6.3 7. 8.7 24.		88. 32500. 36700. 278. 6.4		75. 35800. 37800. 273. 6.2	Felsite 3 66L-234E 133. 33900. 37300. 294. 5.1	63. 27800. 39400. 222. 5.3	6YC-153	Anal. Technique A.A. INAA INAA XRF INAA	
Na 3300 K 397(R 5 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	700. 700. 304. 7.7 10. 1.3 <1. 11. 155. 170. 0.1 <.3	25100. 43000. 310. 7.2 9. 4.7 2. 731. 3790. 0.05	32900. 39800. 295. 6.1 8. 3.1 28. 11. 700. 4190. 0.09	30000. 38500. 225. 7.8 6. 8.7 18.	25300. 41300. 212. 7.4 6. 8.3 12.	30900. 39500. 227. 7.4 5. 8.5 4.	30900. 40100. 230. 6.3 7. 8.7	34800. 35200. 280. 6.8 9. 2.5	32500. 36700. 278. 6.4 11. 3.0	34400. 35000. 252. 5.5	35800. 37800. 273. 6.2	33900. 37300. 294. 5.1	27800. 39400. 222. 5.3	63. 28800. 41500. 238.	A.A. INAA INAA XRF	10 1-2 1-7 10
Na 3300 K 397(R 5 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	700. 700. 304. 7.7 10. 1.3 <1. 11. 155. 170. 0.1 <.3	25100. 43000. 310. 7.2 9. 4.7 2. 731. 3790. 0.05	32900. 39800. 295. 6.1 8. 3.1 28. 11. 700. 4190. 0.09	30000. 38500. 225. 7.8 6. 8.7 18.	25300. 41300. 212. 7.4 6. 8.3 12.	30900. 39500. 227. 7.4 5. 8.5 4.	30900. 40100. 230. 6.3 7. 8.7	34800. 35200. 280. 6.8 9. 2.5	32500. 36700. 278. 6.4 11. 3.0	34400. 35000. 252. 5.5	35800. 37800. 273. 6.2	33900. 37300. 294. 5.1	27800. 39400. 222. 5.3	28800. 41500. 238.	INAA INAA XRF	1-2 1-7 10
Be : Sr Ba Cr	10. 1.3 <1. 11. 255. 270. 0.1 <.3	9. 4.7 2. 7. 731. 3790. 0.05	8. 3.1 28. 11. 700. 4190. 0.09	6. 8.7 18.	6. 8.3 12.	5. 8.5 4.	7. 8.7	9. 2.5	11. 3.0	10.	13.			3.4	INAA	4-7
Ba Cr Mn 75 Fe 422 Co Cu Sc La Ce Nd Sm Eu Gd Tb	<1. 11. 255. 270. 0.1 <.3	7. 731. 3790. 0.05	28. 11. 700. 4190. 0.09	18. 12. 407.	12.	4.					3.2	4.4	2.5	7.	E.S.	15 5
Mn 7: Fe 42: Co Cu Sc La 2: Ce Nd 3: Sm Eu Gd Tb	755. 270. 0.1 <.3	731. 3790. 0.05	700. 4190. 0.09	407.		12			12.	9.	13.	85.	34.	37.	XRF	10-30
Cu Sc La 2 Ce 3 Sm Eu Gd Tb	<.3				5080.	353. 5380.	8. 267. 5440.	9. 1220. 4490.	4. 1150. 4070.	11. 1180. 3950.	10. 1210. 4790.	8. 1610. 4180.	13. 190. 8660.	13. 147. 8830.	INAA INAA INAA	2-45 1-3 1-5
Ce S Nd S Sm Eu Gd Tb		3.67	<.3 4.01	0.2 0.3 1.52	0.2 0.3 1.53	0.2 0.4 1.38	0.7 0.9 1.41	0.09 <.3 7.69	0.1 0.4 7.52	0.4 0.3 7.24	0.3 0.4 7.89	0.4 1. 7.28	0.3 3. 1.13	0.3 2. 1.14	INAA E.S. INAA	1-41 50 1-2
Sm Eu Gd Tb	20.0	18.8 46.3	16.3 46.3	33.5 52.5	32.7 51.4	32.4 52.7	32.8 49.1	10.6 27.6	10.7	10.6 27.3	10.8 28.6	13.5 33.7	56.8 118.0	58.7 127.0	INAA INAA	1-4 2-8
Tb	26.3 5.9 0.18 2.9	22.2 4.9 0.17 6.3	13.7 3.3 0.18	19.3 2.7 0.20 2.2	19.5 2.5 0.22	11.7 2.3 0.20	16.9 2.1 0.29	18.9 5.9 0.14	15.9 5.3 0.14	14.9 5.2 0.19 6.1	17.9 5.8 0.18 9.4	21.9 6.3 0.26 6.0	56.9 12.3 0.18 9.3	61.2 13.6 0.15 12.1	INAA INAA INAA INAA	1-36 1-9 1-8 14-92
Tm	0.9 3.6 0.7	0.7 3.6 0.5	0.6 2.4 0.2	0.3 1.2 1.2	2.6 0.3 1.4 0.5	6.1 0.3 1.3	3.8 0.2 1.2	4.6 1.2 7.5 0.7	8.1 1.3 6.6 0.9	1.2 5.2 0.9	1.2 6.7 0.6	1.3 7.0 0.7	1.8 10.5 0.9	1.7 10.1 0.9	INAA INAA INAA	1-14 1-27 2-46
Yb Lu	3.0 0.34	2.5 0.30	2.6 0.35	1.1	1.1 0.17	0.2 1.0 0.13	0.8 1.0 0.15	6.0	5.8 0.68	3.6 0.54	5.8	5.8	7.1 0.91	6.5 0.75	INAA	4-10 2-31
	216. 83.	187. 74.	119. 76.	207. 50.	182. 55.	173. 28.	178. 49.	190. 110.	200. 120.	193. 130.	232. 130.	185. 99.	272. 58.	271. 63.	INAA E.S.	1-6 15
Mo Hf	5.	3. 3.8	2. 4.2	9. 4.8	8. 4.8	3. 4.9	5. 4.9	3. 5.9	2.	2.	2.	2. 5.4	4. 7.6	5. 7.8	E.S. INAA	20 1-13
Ta B	5.1 30.	4.3 30.	4.5 30.	3.4 30.	3.1 30.	3.5 30.	3.3 30.	8.1 30.	7.9 30.	7.2 70.	8.3 50.	7.7 30.	3.7 20.	3.9 <20.	INAA E.S.	1-5 15
Sb	43. 0.5 <1.	48. 0.3 <1.	38. 0.5 1.	19. 1.1 <1.	31. 1.1 1.	33. 0.8 <1.	29. 1.1 1.	50. 1.1 <1.	46. 1.1 <1.	46. 1.0 1.	43. 2.0 1.	40. 0.9 5.	42. 0.6 <1.	41. 0.6 2.	E.S. INAA Spectr	15 5-92 . 10
Se	0.3	<0.1 1700. 30.2	<0.1 700. 33.8	<0.1 1200. 22.8	<0.1 1500. 26.1	<0.1 600. 25.6	<0.1 <400. 27.5	<0.1 1900. 24.3	<0.1 2500. 23.4	<0.1 2100. 24.3	<0.1 1100. 24.1	1.2 400. 22.4	<0.1 1600. 26.4 7.3	<0.1 1200. 27.0 6.6	XRF Electrod INAA D.N.	50

A.A. - atomic absorption, INAA - instrumental neutron activation, XRF - x-ray fluorescense, I.D. - isotope dilution mass spectometry, E.S. - quantitative emission spectrometry, Spectr. - spectrophotometric, Electrode - specific ion electrode, D.N. - delayed neutron technique. * Estimated coefficient of variation (percent)

obsidian. Ba abundances are variable, showing relative enrichment and depletion. If Na and K abundances in perlite are controlled by low-temperature ion-exchange processes with groundwater (Lipman, 1965; Lipman et al., 1969), the chemically similar alkali and alkaline-earth elements probably are susceptible to the same exchange mechanisms. The rate of such exchange is probably controlled by the speed at which ions can diffuse through glass. Truesdell (1966) measured ion-exchange constants in 12 natural glasses at 25°C and documented increases in K₂O/Na₂O ratios during glass hydration. He also reported increased selectivity of alkaline-earth-rich glasses for alkaline-earth ions. Measured diffusion coefficients for alkalis in glass decrease in the order Li > Na > K (Sipple, 1963; Yuskeshira and Antoney, 1967; Ryback and Laves, 1967). Reported results and the data of this paper suggest exchanges of the type

hydration.

Two of three perlites have higher fluorine abundances than coexisting obsidians. Based on analyses of natural glasses, fluorine concentrations are also reported to show no change (Friedman and Harris, 1961) or depletion (Noble et al., 1967) during hydration. Documentation of fluorine homogenity in obsidian must precede interpretation of relative changes during hydration. Obsidians from the same flow are reported to be remarkably homogeneous in major elements and most trace elements of this study, with respective coefficients of variation of \pm 5 percent and ± 15 percent (Borchardt et al., 1971; Condie and Hayslip, 1975; Laidley and McKay, 1971; Gordus et al., 1968), but halogens have not been examined. Ellis and Mahon (1963, 1967) state that much fluorine in rhyolite glass occurs as surficial coatings.

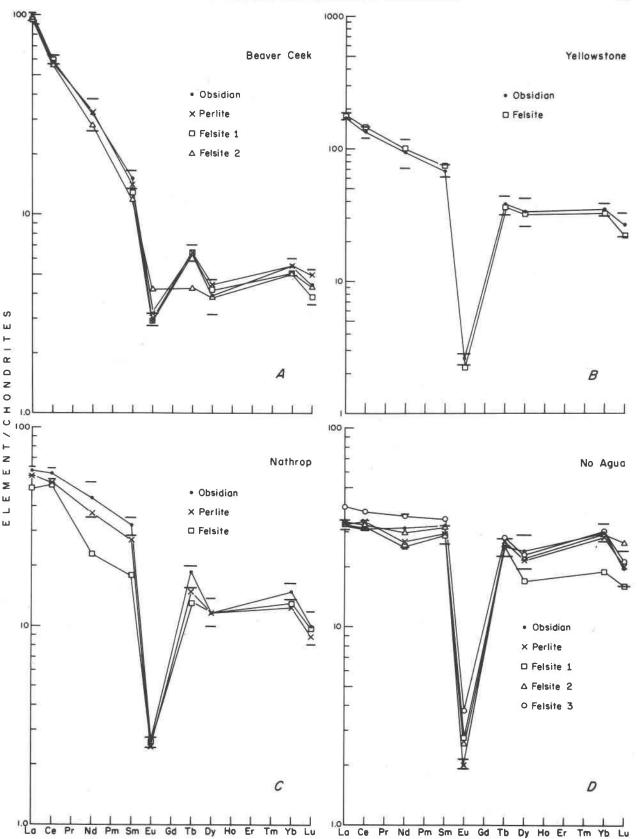


Fig. 1. Chondrite-normalized rare-earth concentrations of calc-alkalic obsidians, perlites, and felsites of this study. Bars represent typical estimated analytical precision for obsidian values ($\pm 1\sigma$).

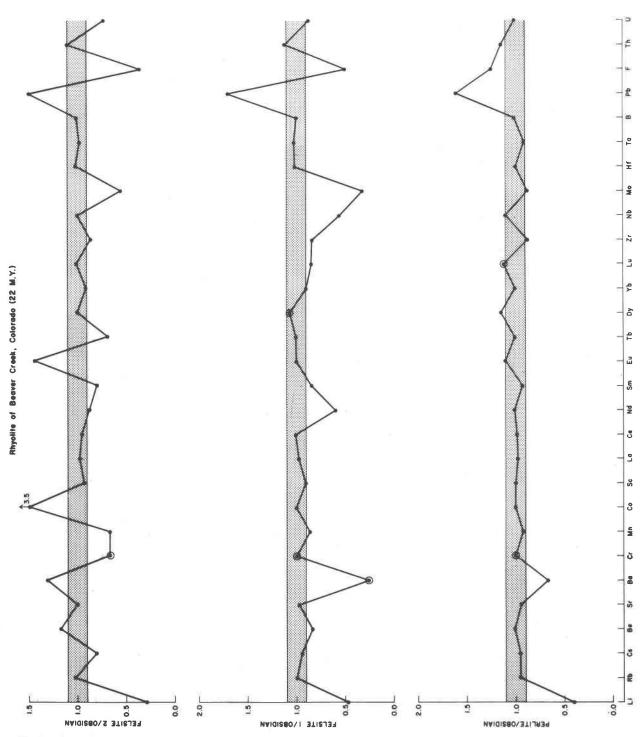


Fig. 2. Minor-element compositions of perlites and felsites normalized to coexisting obsidian. Shaded areas equal to typical analytical precision of \pm 10%. Circled points have estimated errors >30%.

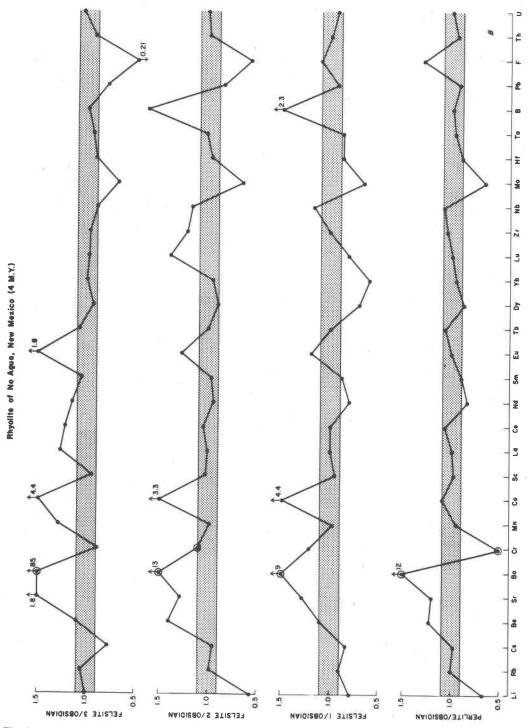
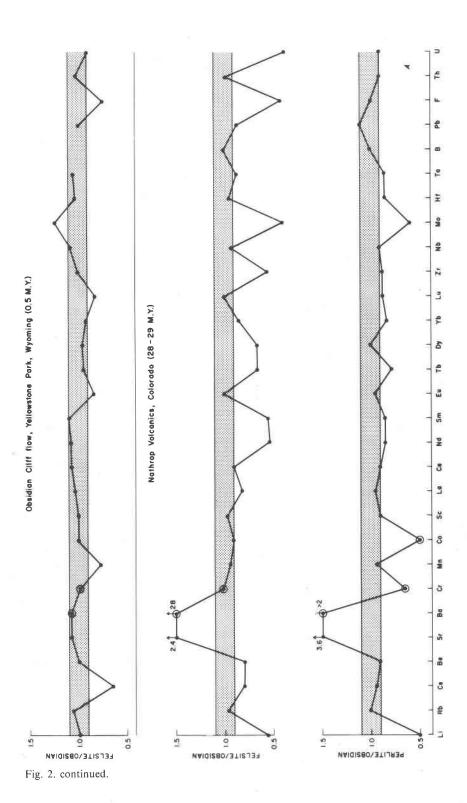


Fig. 2. continued.



Although analytically marginally significant, Mo shows relative depletions in all three perlites. Interpretation is subject to the same restrictions as fluorine.

The variable content of Cu, Co, and Cr in perlites and felsites relative to obsidian cannot be interpreted because of (1) increased analytical uncertainty due to extremely low concentrations in the rhyolites, (2) possible inhomogeneity in the analyzed splits for elements highly concentrated in minor phases, (3) possible contamination during crushing in steel jaws (the samples were originally prepared for other work, without minor-element studies in mind).

Minor-element differences between obsidian and felsite

The felsites show consistent enrichments of Ba and Sr, depletion of Li and Mo, and increased variability of Cu, Co, and Cr concentrations relative to obsidians. In contrast to perlites, six of seven felsites have lower F contents than the corresponding obsidians. Properties peculiar to felsites are higher concentrations of Eu and consistently lower concentrations of Cs and U.

The minor-element variations in felsites are more complex than in glasses, because of the combined effects on a multiphase assemblage of high-temperature processes (crystal-melt fractionation, volatile transport) and low-temperature processes (ion exchange, differential solubility, absorption on secondary phases).

Elemental variability caused by crystal-melt fractionation can be reflected in crystalline samples from the same flow collected over distances as small as a few meters (Watkins et al., 1970). The rare earth elements (REE) provide a sensitive measurement of the elemental variability caused by magmatic processes. The immobility of REE during weathering and metamorphism has been documented by numerous studies of natural suites (Frey, 1969; Cullers et al., 1974; Philpotts et al., 1969). Inspection of Figure 1 shows that some felsites have analytically significant differences in REE, and especially in Eu, compared to obsidian. Eu variations can be explained by attributing some felsite to different eruptive episodes whose compositions reflect evolution of the magma via addition or subtraction of feldspar, a major phase that shows high preference for Eu. Crystallization of 20 percent of a rhyolitic magma as alkali feldspar, or

assimilation of 20 percent feldspar can change Eu abundances by 30 percent (feldspar/melt distribution coefficient = 2.5). The sample area at No Aqua, New Mexico, shows the greatest variability in Eu and contains the most widely-spaced sampling localities. If eruption is in the sequence obsidian-felsite, the rare earth abundances indicate that the most evolved (Eu depleted) liquid erupted first. The obsidian-felsite suite at No Aqua may reflect the compositional heterogeneity of a stratified magma chamber.

One may use the variations of Eu to predict complementary magmatic variability of Sr and Ba caused by feldspar fractionation. Both Sr and Ba are also strongly incorporated in feldspar, with typical reported feldspar/rhyolitic-melt distribution coefficients (D.C.) ranging from 3 to 6 (Arth and Hanson, 1975). Minor-element abundances in coexisting solid and liquid phases relative to original melt are calculated for variable values of crystallization and distribution coefficients (Fig. 3). One may consider vertical tie lines connecting two curves of similar D.C. to give relative abundances in solid and liquid for a given percent crystallization. For D.C. ≤5, magmatic processes leading to efficient separation of crystals and melt at a given percent crystallization cannot produce new assemblages differing from the original bulk concentration C_0 by greater than a factor of 5. Such a mechanism can explain observed Eu abundance variations, but values of percent crystallization required for Eu (D.C. = 2.5) are often marginal or insufficient to explain observed relative Sr and Ba abundance (D.C. = 3-6) within the same sample. Other possible mechanisms affecting Ba and Sr mobility include ion exchange of the type observed in perlites or selective uptake by alteration products such as clays, zeolites, or Ba-rich manganese oxides (observed).

In spite of the unresolved problem of fluorine homogeneity in obsidian, fluorine is strongly depleted in most felsites, in agreement with previous studies of crystallized rhyolites (Noble et al., 1967; Rosholt et al., 1971; Lipman et al., 1969). Loss of fluorine as a gas phase during eruption is well-known from studies of volcanic emanations and F metasomatism near fumaroles. Loss of halogens during interaction of rhyolite and hot water was demonstrated by Ellis and Mahon (1963, 1967), who removed 3.5 percent of the F and 13 percent of the Cl from a partly crystallized flow rhyolite after exposure to aqueous vapor at 300°C for 24 hours. Percentages of halogens removed from rhyolitic pumice were even greater. The relative F concentrations in coexisting felsites and obsidians of variable age (Fig. 4a) show little correlation with

¹ Variability of composition caused by partitioning of elements between silicate melt and growing crystals and crystal-melt redistribution prior to and during eruption.

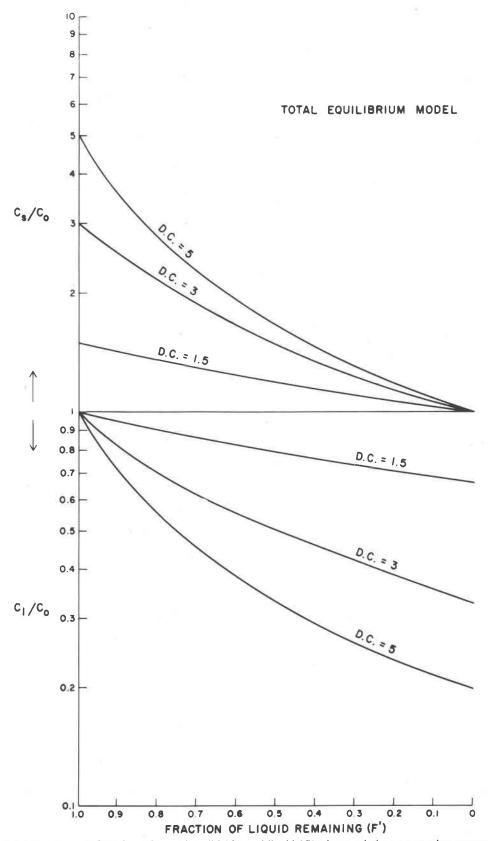


Fig. 3. Calculated abundances of a minor element in solid (C_s) and liquid (C_t) phases relative to a starting composition (C_0) , as a function of degree of crystallization (F), for various large distribution coefficients (D.C.). One may consider vertical tie lines connecting C_s/C_0 and C_t/C_0 curves for a constant D.C. to give relative abundances in solid and liquid phases for a given percent crystallization.

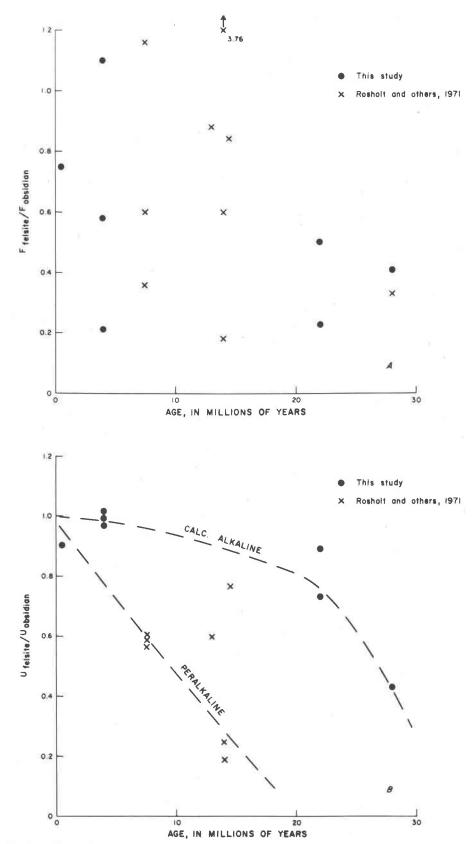


Fig. 4. Relative fluorine and uranium concentrations in coexisting pairs of felsite and obsidian of various ages and compositional types, (a) Fluorine (b) Uranium.

age. There are large variations in F concentration among different samples of the same suite, and young felsites show F depletions similar to much older rocks. Inclusion of data for peralkaline rocks (Rosholt et al., 1971) substantiates the above observation. Evidently, much F loss occurs during or shortly after crystallization.

In contrast, relative uranium depletion in felsites appears uniformly small in the younger suites and generally increases in older suites (4b). Inclusion of the data of Rosholt et al. (1971) indicates a similar, possibly accelerated, trend for peralkaline compositions. Additional data from a separate study by R. A. Zielinski (oral communication, 1976) support the above conclusions. Enhanced uranium loss from felsites appears to be caused by slow weathering processes; the speed of the processes are determined by local climate, rock permeability, and bulk composition. Uranium and fluorine mobilites do not generally correlate in time, at least for the processes active during crystallization and weathering of rhyolite flows.

Data are insufficient to generate comparable age-dependance plots for the other trace elements of this study. Molybdenum is the only other element analyzed that appears to show age-related depletions in felsite relative to obsidians. The high mobility of Mo under oxidizing alkaline conditions as the molybdate anion (MoO₄²⁻) is well-known (Pokalov and Orlov, 1974; Kim and Zeitlin, 1969). If Mo is mobilized dominantly during low-temperature processes, rhyolitic compositions should contribute U and Mo (Table 1) to groundwaters at an approximately similar rate. The common association of these two elements in sedimentary uranium deposits argues for a similar source.

Less is known about the high-temperature behavior of Li and Cs during crystallization, but both are concentrated in rhyolitic magmas, indicating general exclusion from major rock-forming minerals. Cesium may be mobilized as a volatile halide (Shatkov, 1971), and both elements are leached from rhyolites by hot water (Ellis and Mahon, 1963, 1967). Lithium appears expecially mobile, showing large depletions relative to obsidians in all suites, regardless of age.

Conclusions

Trace element analyses of coexisting suites of rhyolitic obsidian-perlite-felsite of various ages indicated:

(1) Hydration of rhyolite glass causes little mobilization of most trace elements other than alkalis or alkaline-earths. Variations are dominantly explained by low-temperature ion exchange with groundwater.

- (2) Felsites are more variable in trace element abundances compared to coexisting obsidian or perlites, reflecting the more complex crystallization and alteration history of a multiphase assemblage.
- (3) Young felsites exhibit significantly different abundances of F, REE, Cs, and Li compared to coexisting obsidian, indicating variations are produced by crystal-melt fractionation or other processes active during or shortly after crystallization. In felsites, relative depletions of U and Mo increase with age and are caused by slow weathering processes. Strontium and barium abundance variations in felsites are complex, with variability caused by both rapid and slow processes.
- (4) Rare earth elements, and particularly Eu, are very useful for evaluating elemental variations within rhyolitic flows caused by magmatic processes involving crystallization of feldspar.
- (5) Considerable errors in estimating the original trace element abundances of a rhyolitic obsidian can be made by relying on perlite or felsite values. Obsidians, while generally homogeneous, represent the quenched record of a magmatic composition which may differ from that parental to closely associated felsites.

References

Aramaki, S. and P. W. Lipman (1965) Possible leaching of Na₂O during hydration of volcanic glasses. *Proc. Japan Acad.*, 41, 467-470.

Arth, J. G. and G. N. Hanson (1975) Geochemistry and origin of early Precambrian crust of northeastern Minnesota. Geochim. Cosmochim. Acta, 39, 325-362.

Borchardt, G. A., M. E. Harward and R. A. Schmitt (1971) Correlation of volcanic ash deposits by activation analysis of glass separates. *Quaternary Res.*, 1, 247-260.

Condie, K. D. and D. L. Hayslip (1975) Young bimodal volcanism at Medicine Lake volcanic center, northern California. Geochim. Cosmochim. Acta, 39, 1165-1178.

Cullers, R. L., L. T. Yeh and S. Chaudhuri (1974) Rare earth elements in Silurian pelitic schists from N.W. Maine. *Geochim. Cosmochim Acta*, 38, 389-400.

Ellis, A. J. and W. A. J. Mahon (1963) Natural hydrothermal systems and experimental hot water-rock interactions. *Geochim. Cosmochim. Acta*, 28, 1323-1357.

and ——— (1967) Natural hydrothermal systems and experimental hot water/rock interactions (Part II). *Geochim. Cosmochim. Acta*, 31, 519-538.

Ewart, A. (1971) Chemical changes accompanying spherulitic crystallization in rhyolitic lavas, central volcanic region, New Zealand. *Mineral. Mag.*, 38, 424-434.

Frey, F. A. (1969) Rare earth abundances in a high temperature peridotite intrusion. *Geochim. Cosmochim. Acta*, 33, 1429-1447.

- Friedman, I. and R. L. Smith (1958) The deuterium content of water in some volcanic glasses. Geochim. Cosmochim. Acta, 15, 218-228.
- and J. Harris (1961) Fluorine during hydration of rhyolitic glass. U.S. Geol. Surv. Prof. Pap., 424C, C304-305.
- Gijbels, R. and J. Hertogen (1971) Instrumental neutron activation analysis of rocks with low energy photon detector. *Anal. Chim. Acta*, 56, 61-82.
- Gordon, G. E., K. Randel, G. G. Goles, J. B. Corliss, M. H. Benson and S. Oxley (1969) Instrumental activation analysis of standard rocks with high resolution γ-ray detectors. Geochim. Cosmochim. Acta, 32, 369-396.
- Gordus, A. A., G. A. Wright and J. B. Griffin (1968) Obsidian sources characterized by neutron activation analysis. Science, 161, 382-384.
- Haffty, J. and D. C. Noble (1972) Release and migration of Mo during the primary crystallization of peralkaline silicic volcanic rocks. Econ. Geol., 67, 768-775.
- Hoover, D. L. (1968) Genesis of zeolites, Nevada test site. Geol. Soc. Am. Mem., 110, 275-283.
- Kim, Y. S. and H. Zeitlin (1969) The role of iron (III) hydroxide as a collector of molybdenum from sea water. *Anal. Chim. Acta*, 46, 1-8.
- Laidley, R. A. and D. S. McKay (1971) Geochemical examination of obsidians from Newberry Caldera, Oregon. Contrib. Mineral. Petrol., 30, 336-342.
- Lipman, P. W. (1965) Chemical comparison of glassy and crystalline volcanic rocks. U.S. Geol. Surv. Bull. 1201-D, 24 p.
- ——, R. L. Christiansen and R. E. Van Alstine (1969) Retention of alkalis by calc-alkalic rhyolites during crystallization and hydration. Am. Mineral., 54, 286-291.
- Millard, H. T. (1976) Determinations of uranium and thorium in the U.S. Geological Survey standard rocks by the delayed neutron technique. U.S. Geol. Surv. Prof. Pap., 840, in press.
- Noble, D. C. (1965) Ground-water leaching of sodium from quickly cooled volcanic rocks (abstr.). Am. Mineral., 50, 289.
- —— (1967) Sodium, potassium and ferrous iron contents of some secondarily hydrated natural silicic glasses. Am. Mineral., 52, 280-286.
- ——— (1968) Stress-corrosion failure and the hydration of glassy silicic volcanic rocks. Am. Mineral., 53, 1756–1759.
- ——— (1970) Loss of sodium from crystallized comendite welded tuffs of the Miocene Grouse Canyon member of the Belted Range tuff, Nevada, Geol. Soc. Am. Bull., 81, 2677-2688.
- —— and C. E. Hedge (1969) Sr⁸⁷/Sr⁸⁶ variations within individual ash flow sheets. *U.S. Geol. Surv. Prof. Pap.*, 650-C, 133–139.
- —, V. C. Smith and L. C. Peck (1967) Loss of halogens from crystallized and glassy silicic volcanic rocks. *Geochim. Cosmochim. Acta*, 31, 215–223.

- —, J. Haffty and C. E. Hedge (1969) Strontium and magnesium contents of some natural peralkaline silicic glasses and their petrogenetic significance. *Am. J. Sci.*, 267, 598–608.
- Philpotts, J. A., C. C. Schnetzler and S. R. Hart (1969) Submarine basalts: Some K, Rb, Sr, Ba, rare-earth, H₂O and CO₂ data bearing on their alteration, modification by plagioclase, and possible source materials. *Earth Planet. Sci. Lett.*, 7, 293-299.
- Pokalov, V. T. and B. G. Orlov (1974) Behavior of molybdenum in the oxidation zone. *Geochim. Int.*, 11, 447-452.
- Rosholt, J. N., and D. C. Noble (1969) Loss of uranium from crystallized silicic volcanic rocks. *Earth Planet, Sci. Lett.*, 6, 268-270.
- —, Prijana and D. C. Noble (1971) Mobility of uranium and thorium in glassy and crystallized silicic volcanic rocks. *Econ. Geol.*, 66, 1061–1069.
- Ross, C. S. and R. L. Smith (1955) Water and other volatiles in volcanic glasses. *Am. Mineral.*, 40, 1071-1089.
- Rybach, L. and F. Laves (1967) Sodium diffusion experiments in quartz crystals. *Geochim. Cosmochim. Acta*, 31, 539-546.
- Shatkov, G. A., L. N. Shatkova and E. N. Guschin (1970) The distribution of uranium, thorium, fluorine, chlorine, molybdenum, and niobium in liparites and volcanic glasses. *Geochem. Int.*, 7, 1051-1063.
- Shatkov, G. A. (1971) The mode of occurrance of cesium in felsic volcanic glasses. *Geochem. Int.*, 8, 553–556.
- Sippel, R. F. (1963) Sodium self diffusion of natural minerals. *Geochim. Cosmochim. Acta*, 27, 107-120.
- Steven, T. A., P. W. Lipman, F. S. Fisher, C. L. Bienieuski and H. C. Meeves (1973) Mineral resources of study areas contiguous to the Umcompahgre primitive area, San Juan Mountains, Southwestern Colorado. U.S. Geol. Surv. Open File Report, 205 p.
- Truesdell, A. H. (1966) Ion exchange constants of natural glasses by the electrode method. *Am. Mineral.*, 51, 110-121.
- Watkins, N. D., B. M. Gunn and R. Coy-yll (1970) Major and trace element variations during the initial cooling of an Icelandic lava, Am. J. Sci., 268, 24-29.
- Yuskeshira, L. G. and A. S. Antonev (1967) An electrophoto graphic method for determination of the diffusion coefficient of Li in P type silicon, *Soviet Phys. Solid State*, 8, 2025–2028.
- Zielinski, R. A. and F. A. Frey (1970) Gough Island: evaluation of a fractional crystallization model. *Contrib. Mineral. Petrol.*, 29, 242-254.

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