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STRONTIUM AND MAGNESIUM CONTENTS OF SOME NATURAL PERALKALINE SILICIC GLASSES AND THEIR PETROGENETIC SIGNIFICANCE†

DONALD C. NOBLE*, JOSEPH HAFFTY**, and CARL E. HEDGE**

ABSTRACT. Nonhydrated comendite and pantellerite glasses from many localities are extremely impoverished in strontium, containing, with very few exceptions, from less than 2 to less than 10 ppm of the element. Most of the glasses also contain less than 0.05 wt percent MgO, and many contain 0.02 wt percent or less. Such pronounced depletion of these elements can only have resulted from protracted fractional crystallization. Calcium, however, is not so markedly depleted, with CaO contents averaging about 0.3 wt percent. Pronounced increase in calcium relative to strontium probably is a characteristic feature of all highly differentiated silicic melts. Glasses from the lowermost parts of several compositionally zoned ash-flow sheets contain 2 ppm or less of strontium and less than 0.03 wt percent MgO. These data support a fractional-crystallization origin for at least part of the elemental and mineralogical zonation of the parent magmas.

INTRODUCTION

Early in the study of volcanic rocks of the Black Mountain and Silent Canyon volcanic centers in southern Nevada (Christiansen and Noble, 1965; Noble, Sargent, and others, 1968) it was recognized that nonhydrated comendite and pantellerite glasses from the two centers contained remarkably small amounts of strontium and magnesium. Almost all analyses showed strontium values of less than 5 ppm and MgO values of less than 0.05 percent by weight. The strontium concentrations in particular were remarkably low, being one to two orders of magnitude less than are usual for silicic igneous rocks (for example, Hurley and others, 1962; Fairbairn, Hurley, and Pinson, 1964; Hurley and others, 1965; Hedge, 1966).

The petrologic significance of these abnormally low concentrations lies in the fact that, so far as we know, strontium and magnesium can be so impoverished in a melt only by protracted fractional crystallization and in particular the separation of feldspar phases. (The literature bearing on the partition of strontium between crystal and between crystal and melt phases is extensive; particularly pertinent references include Heier and Taylor (1959) and Brooks (1968). For this reason, additional information on the strontium and magnesium contents of whole-rock material and of groundmass and phenocryst phases have been obtained during a continuing study of the chemistry of peralkaline silicic rocks. The present note summarizes the data for these elements now available on non-hydrated comendite and pantellerite glasses.

The data provide independent support for a fractional-crystallization origin (for example, Thompson and MacKenzie, 1967, and references cited therein; Noble, 1968b) of the peralkaline character and high

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* Department of Geological Sciences, Harvard University, and the U.S. Geological Survey, Cambridge, Massachusetts 02138.

** U.S. Geological Survey, Denver, Colorado 80225.

iron contents of the comendites and pantellerites. In essence the mechanism involves the separation of large quantities of sodic plagioclase, anorthoclase, sodic sanidine, and quartz and somewhat smaller quantities of mafic silicate minerals from an originally metaluminous to subaluminous melt.

CHEMICAL DATA

To date, 35 nonhydrated comendite and pantellerite glasses, all but one of which are from the western United States, and three glassy pantellerites from Pantelleria have been analyzed for strontium and/or magnesium (tables 1-4). Calcium contents are given for comparison, and total iron as FeO plus MnO contents and atomic Na+K/Al ratios, mutually consistent indices of position within the comendite-pantellerite series (Noble, 1968b) are tabulated if available.

TABLE 1

Strontium, calcium, and magnesium contents of peralkaline glasses of the Black Mountain volcanic center, Nye County, Nevada

Sample no.	Sr (ppm)	CaO (wt percent)	MgO (wt percent)	(Na + K)/Al	Total Fe (as FeO) + MnO (wt percent)
1	2[a]	0.06[e], 0.05[b]	0.010[b], 0.04[e]	1.83	6.13
2	<2[b]	0.12[e], 0.08[b]	0.01[b]	1.81	6.18
3	1.50[d], 1.58[d], <2[c]	—	—	—	—
4	—	0.10[b]	0.011[b]	—	—
5	<2[b]	0.34[e]	0.00[e]	1.19	3.59
6	<2[b]	0.37[e], 0.41[b]	0.020[b], 0.00[e]	1.18	3.63
7	<5[b]	0.47[e]	0.06[e]	1.17	3.66
8	1.6[d], <2[c], 2[b]	0.33[e], 0.33[b]	0.0095[b], 0.00[e]	1.04	1.85
9	<5[b]	0.33[e]	0.00[e]	1.04	1.82
10	—	0.30[e]	0.01[e]	1.01	1.78
11	—	0.36[b]	0.023[b]	—	—
12	2[b]	0.27[e], 0.29[b]	0.010[b], 0.00[e]	1.08	2.14

Explanation

Samples 1 to 4. Nonhydrated glass separates (lab. nos. D100126, D100872, (N-90-3), and D114891, respectively) from basal glassy zone of the Gold Flat Member of the Pliocene Thirsty Canyon Tuff.

Sample 5. Blue nonhydrated glass fragments (aggregate sample) (lab. no. D100775) from bedded tuff at the base of the Trail Ridge Member of the Pliocene Thirsty Canyon Tuff.

Sample 6. Green nonhydrated glass fragments (aggregate sample) (lab. no. D100776) from bedded tuff at the base of the Trail Ridge Member of the Pliocene Thirsty Canyon Tuff.

Sample 7. Green nonhydrated glass fragment (lab. no. D100974) from bedded tuff at the base of the Trail Ridge Member of the Pliocene Thirsty Canyon Tuff.

Samples 8 to 11. Nonhydrated glass separates (lab. nos. D100437, D100320, D101589, and D100740, respectively) from basal glassy zone of the Spearhead Member of the Pliocene Thirsty Canyon Tuff.

Sample 12. Nonhydrated glass fragment (lab. no. D100737) from bedded tuff at the base of the Spearhead Member of the Pliocene Thirsty Canyon Tuff.

[a] Emission spectrographic determination by Paul R. Barnett.

[b] Emission spectrographic determination by Joseph Haffty and/or Harriet Neiman.

[c] X-ray fluorescence determination by C. E. Hedge and Willus Doering.

[d] Isotope dilution determination by C. E. Hedge.

[e] Gravimetric determination by various analysts under the supervision of L. C. Peck.

TABLE 2

Strontium, calcium, and magnesium contents of peralkaline glasses of the Silent Canyon volcanic center, Nye County, Nevada

Sample no.	Sr (ppm)	CaO (wt percent)	MgO (wt percent)	(Na + K)/Al	Total Fe (as FeO) + MnO (wt percent)
13	2^{b}	0.22^{e}	0.01^{e}	1.09	2.28
14	2^{a}	$0.25^{e}, 0.32^{b}$	$0.061^{b}, 0.06^{e}$	1.09	2.31
15	$<2^{c}, <5^{b}$	0.26^{e}	0.00^{e}	1.09	2.31
16	$2.0^{d}, <2^{c}, <5^{b}$	$0.24^{e}, 0.24^{b}$	$0.018^{b}, 0.01^{e}$	1.21	3.51
17	6^{a}	0.29^{e}	0.03^{e}	1.17	3.15
18	$<2^{c}$	0.21^{e}	0.01^{e}	1.21	3.56
19	2.4^{c}	—	—	—	—
20	—	0.28^{b}	0.018^{b}	—	—
21	4^{b}	0.18^{e}	0.03^{e}	1.21	3.55
22	2^{b}	0.15^{e}	—	1.25	3.47
23	9^{b}	$0.22^{e}, 0.28^{b}$	0.027^{b}	1.22	3.53
24	$<5^{b}$	0.15^{e}	—	1.21	3.07
25	—	0.18^{b}	0.012^{b}	—	—
26	$<2^{c}, <2^{b}$	0.13^{e}	0.00^{e}	1.26	3.35

Explanation

Samples 13 to 15. Nonhydrated glasses (lab. nos. D100489, D100259, and D100318, respectively) from basal glassy zones of various lava flows of the rhyolite of Saucer Mesa.

Samples 16 to 20. Nonhydrated glasses (lab. nos. D100317, D100209, D101090, D101362, and D114888, respectively) from basal glassy zone of Grouse Canyon Member of the Miocene Belted Range Tuff.

Samples 21 and 22. Nonhydrated glass fragments (aggregate samples) (lab. nos. D100395 and D100438, respectively) from bedded air-fall tuff at base of the Grouse Canyon Member of the Miocene Belted Range Tuff.

Sample 23. Nonhydrated glass fragment (lab. no. D100338) included in tuff of the upper crystal-rich part of the Grouse Canyon Member of the Miocene Belted Range Tuff.

Samples 24 to 26. Nonhydrated glasses (lab. nos. D100396, D100641, and D100777, respectively) from lava flows (24 and 25) and dike (26) of the rhyolite of Split Ridge.

Symbols ^{a} to ^{e} same as in table 1.

Analytical methods.—Almost all the analytical work was done in the laboratories of the U.S. Geological Survey at Denver, Colorado. Strontium was determined by optical emission spectrography (Bastron, Barnett, and Murata, 1960), by X-ray fluorescence methods (Peterman, Hedge, and Braddock, 1968), and for several specimens, by standard isotope-dilution methods (Peterman, Doe, and Bartel, 1967). Magnesium and calcium were determined by optical emission spectrography using a procedure similar to that described by Bastron, Barnett, and Murata, (1960), but differing in that synthetic perthite was used as the matrix material for the standards. These two elements also were determined by standard gravimetric methods (Peck, 1964), atomic absorption techniques, and X-ray fluorescence methods.

TABLE 3

Strontium, calcium, and magnesium contents of peralkaline glasses from other areas within the western United States

Sample no.	Sr (ppm)	CaO (wt percent)	MgO (wt percent)	(Na + K)/Al	Total Fe (as FeO) + MnO (wt percent)
27	<2[b]	—	—	—	—
28	<2[c], <2[b]	0.48[e]	0.00[e]	1.01	1.66
29	<2[b]	0.47[e]	0.00[e]	1.01	1.66
30	2[c]	0.29[f]	—	—	—
31	<2[c]	—	—	—	—
32	<2[c]	0.17[f]	—	—	—
33	3.8[c], <5[b]	0.24[e]	0.04[e]	1.11	2.13
34	<5[b]	0.11[e]	0.08[e]	1.14	2.27

Samples 27 to 29. Nonhydrated glass (lab. nos. D101241, D101242, and D101245, respectively), from Big Southern Butte, Idaho.

Samples 30 to 32. Nonhydrated glass (lava) (lab. nos. (NN-10), (NN-21B), and (NN-25A), respectively), from basal parts of phenocryst-free lava flows, northern Washoe County, Nevada (Noble, Chipman, and Giles, 1968).

Sample 33. Nonhydrated glass separate (lab. no. D101507) from peralkaline lava (trachytic soda rhyolite) from the San Francisco Mountains, Arizona (Robinson, 1913, p. 109-110).

Sample 34. Nonhydrated glass (lab. no. D123311), from unknown locality, Oregon.

Symbols [b] [c] [e] same as table 1.

Symbol [f] X-ray fluorescence determination (Noble, Chipman, and Giles, 1968).

TABLE 4

Strontium, calcium, and magnesium contents of pantellerites from Pantelleria and New Zealand

Sample no.	Sr (ppm)	CaO (wt percent)	MgO (wt percent)	(Na + K)/Al	Total Fe (as FeO) + MnO (wt percent)
35	7[b]	0.42[h]	0.066[i], 0.10[g]	2.38[h]	8.75[h]
36	3[b]	0.45[h]	0.22[i], 0.23[g]	1.39[h]	6.26[h]
37	9[b]	0.45[h]	0.053[i], 0.05[g]	2.12[h]	8.65[h]
38	<2[c], <2[b]	0.19[e]	0.01[e]	1.36	4.35

Samples 35 to 37. Hyalopantellerites (lab. nos. D101319 (PRC-2000), D101318 (PRC-2007), and D101319 (44B5), respectively) from the Island of Pantelleria, Mediterranean (Zies, 1960; Chayes and Zies, 1964).

Sample 38. Nonhydrated glass (lab. no. D100406), from lava from north shore of Opo Bay, Mayor Island, New Zealand.

Symbols [b], [c], [e] same as table 1.

Symbol [g] Gravimetric determination by E. G. Zies (Zies, 1960; Chayes and Zies, 1964).

Symbol [h] Values for nonhydrated glass calculated from whole-rock data using modal data of Zies (1960) and Chayes and Zies (1964), mineral composition data of Chayes and Zies (1964) and Carmichael (1962), and emission spectrographic data (Noble and Haffty, 1969).

Symbol [i] Atomic absorption determination by Wayne Mountjoy.

Discussion.—With few exceptions the specimens contain less than 5 ppm strontium and 0.04 wt percent MgO. Specimens 35 and 37 (table 4) from Pantelleria contain 7 and 9 ppm strontium, respectively. Both samples, however, are whole-rock material, containing about 10 and 8.8 percent, respectively, of alkali feldspar phenocrysts in addition to smaller amounts of quartz and mafic phenocryst minerals (Zies, 1960; Chayes and Zies, 1964). It thus seems likely that much of the strontium present is contained in the feldspar phenocrysts rather than in the glass. The lower strontium content, 3 ppm, of specimen 36—which contains only 2 percent phenocrysts, mainly alkali feldspar (Zies, 1960)—tends to support this interpretation. The MgO content, 0.06 wt percent, of specimen 14 (table 2) is much greater than that of other glasses from the Silent Canyon volcanic center. We suspect that this relatively high value may reflect contamination during sample preparation. (Contamination definitely occurred during the preparation of specimen 2 (table 1) for gravimetric analysis.)

STRONTIUM AND MAGNESIUM DATA FROM THE LITERATURE

Ewart, Taylor, and Capp 1968) have presented very recently major- and minor-element data on 7 hyalopantellerite specimens from Mayor Island, New Zealand. Certain of their data, which are completely consistent with ours, are reproduced in table 5.

TABLE 5

Strontium, calcium, and magnesium contents of hyalopantellerites and a pantellerite glass separate from Mayor Island, New Zealand

Sample no.	Sr (ppm)	CaO (wt percent)	MgO (wt percent)	(Na + K)/Al	Total Fe (as FeO) + MnO (wt percent)
1	4.7	0.21	0.01	1.64	6.11
2	1.9	0.21	0.01	1.39	4.68
3	1.1	0.26	0.01	1.55	5.83
4	1.8	0.26	0.01	1.33	4.37
5	0.3	0.20	0.01	1.37	4.29
7	—	0.45	0.2	1.71	5.73
8G	—	0.45	0.15	1.73	6.06

Data, by optical emission spectrographic methods, from Ewart, Taylor, and Capp (1968). Sample numbers are the same as in the original paper. Specimens 1, 2, and 7 contain from 8 to 13 percent phenocrysts, and the whole-rock values thus undoubtedly are significantly different from those of the glassy phases of the rocks.

Cann and Renfrew (1965) and Renfrew, Dixon, and Cann (1966) determined strontium by semiquantitative optical emission spectrographic methods on over 70 obsidians, both geologic hand specimens and archeological artifacts, of probably peralkaline chemistry[1] from Armenia,

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[1] Renfrew, Dixon, and Cann do not give major-element data, and the peralkaline nature of certain of their obsidians is inferred from the relatively high Ga, La, Mo, Nb, Y, and Zr contents and low Ba contents and the green color of the glasses as well as from the known petrochemical character of certain of the source areas.

central Anatolia, Abyssinia, Kenya, Tibesti, Pantelleria, and possibly other localities. With the exception of two specimens from Armenia which gave values of 11 ppm, one from Abyssinia which gave 24 ppm, and two hand specimens from Kenya and one artifact of possible Abyssinian provenance which gave values of 13 ppm, all of the probably peralkaline obsidians had strontium contents of less than 10 ppm, the detection limit of the analytical method used. Approximately two-thirds of the probably peralkaline obsidians contain less than 50 ppm magnesium, and, with the exception of two obsidians from Pantelleria containing 460 ppm, one from Abyssinia containing 370 ppm, and two artifacts containing 130 and 170 ppm, all the glasses contain 110 ppm or less of magnesium.

Other published analyses of silicic peralkaline glasses commonly show very low MgO values. Two reliable sets of magnesium data are the four analyses of pantellerite-glass separates made by Carmichael (1962), which show MgO values of 0.03, 0.04, 0.13, and 0.23 wt percent, and the four analyses of phenocryst-free to phenocryst-poor glassy comendities and pantellerites made by Willman and Goldich (Bowen, 1937), which show MgO contents of *none*, and 0.03, 0.04 and 0.06 wt percent. Magnesium oxide values given in the literature for other phenocryst-free and phenocryst-poor nonhydrated glassy comendites and pantellerites are summarized in figure 1. Because of the difficulties inherent in the determination of very small amounts of MgO by gravimetric methods, we consider that most of the values of 0.1 percent or less in the literature provide at best only an upper limit for the actual MgO content.

OTHER MINOR ELEMENTS

Optical emission spectrographic data for a wide variety of other minor elements have been obtained for most of the glasses discussed here as well as for many other comendites and pantellerites from the western United States (Noble, 1965; 1966; 1968a; ms; unpub. data; Noble and Haffty, 1968; Noble, Sargent, and others, 1968). The rocks and

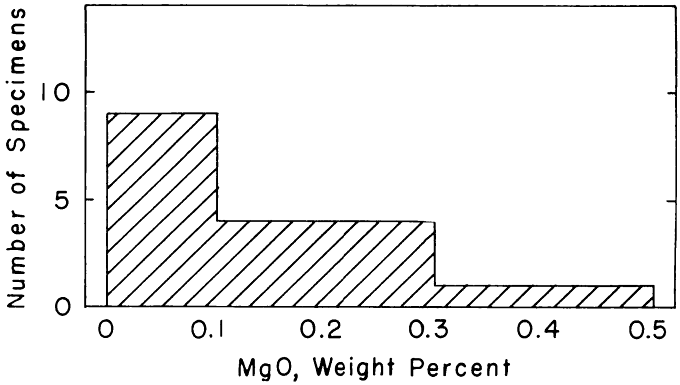

Fig. 1. —MgO values of certain published analyses of phenocryst-free and phenocryst-poor nonhydrated glassy comendites and pantellerites.

glasses have relatively high concentrations of beryllium (0.0004 – >0.001 wt percent), gallium (0.0025 – >0.004 percent), niobium (0.005 – 0.015 percent), yttrium (0.006 – >0.01 percent), ytterbium (0.0006 – >0.001 percent), and zirconium (0.04 – >0.12 percent), and in most cases have higher than average concentrations of boron, lanthanum, molybdinum, and tin than do subalkaline silicic igneous rocks. Barium is depleted but in most rocks not as spectacularly as is strontium, and cobalt, chromium, nickle, scandium, and vanadium contents tend to be low, both absolutely and relative to iron. Similar minor-element patterns have been obtained for other peralkaline silicic rocks (for example, Butler and Smith, 1962; Hamilton, 1964; Bowden, 1964, 1966; Siedner, 1965; Dietrich and Heier, 1967; Ewart and others, 1967; Noble and Haffty, 1969) as well as for highly differentiated silica-undersaturated peralkaline (agpaitic) rocks (for example, Hamilton, 1964). Although we will not further elaborate on these data here, it should be noted that they are consistent with and, in the case of certain elements, strongly support the conclusions drawn from the alkaline-earth data.

DISCUSSION

The extremely low strontium contents of the glasses require, as discussed before, extreme fractional crystallization. Strontium is removed from the melt by sodic plagioclase and especially by later-crystallizing lime anorthoclase, anorthoclase, and sanidine. Most of the glasses also have very low MgO contents, but some show low, but not exceptionally low, MgO values, and others contain appreciable amounts of MgO. Pantelleria specimen 36 is particularly important in this regard, as it contains over 0.2 wt percent MgO but only 3 ppm strontium.

Possible explanation for high MgO values.—The strong sympathetic variation between degree of peralkalinity and total iron content in natural glasses of the comendite-pantellerite series (Noble, 1965; 1968b) strongly suggests that the addition of excess alkalis progressively stabilizes iron within the liquid by suppressing the crystallization of iron-bearing phases. The high concentrations of the rare earths, niobium, zirconium, and related elements in peralkaline rocks and the abnormally low calcium contents of alkali feldspar phenocrysts in certain comendites and pantellerites (Carmichael, 1962; Chayes and Zies, 1964; Noble, unpub. data) also suggest stabilization of these elements within the melt by the presence of excess alkalis. Perhaps the melts from which the relatively high-magnesium pantellerites and comendites were derived became peralkaline at a rather early stage in their evolution. Subsequently, the relatively low rate of separation of ferromagnesian silicate phases compared to that of feldspar phases did not allow Fe/(Fe+Mg) evolution to keep up with the degree of elemental fractionation within the group of elements that enter the feldspar minerals.

Calcium to strontium ratios.—Calcium contents of the glasses analyzed in the present study and of the glasses and glassy rocks analyzed by Carmichael (1962) and Ewart, Taylor, and Capp (1968) (table 5) range from 0.05 to about 0.5 wt percent CaO and average approximately 0.3 wt percent. The specimens analyzed by Cann and Renfrew (1965) and Renfrew, Dixon, and Cann (1966) contain between 0.20 and 0.75 wt percent calcium as CaO, with more than three-fourths of the specimens containing between 0.25 and 0.45 wt percent CaO. These values are not abnormally low for very silicic igneous rocks. The resultant high calcium to strontium ratios of the peralkaline glasses almost certainly reflect the preferential incorporation of strontium relative to calcium into the sanidine-anorthoclase structure. Such strong late-stage enrichment of calcium relative to strontium probably is a general feature of highly differentiated silicic melts.

COMPOSITIONALLY ZONED ASH-FLOW SHEETS

The Spearhead Member of the Thirsty Canyon Tuff (Noble and others, 1964; Noble, Bath, and others, 1968) and the Grouse Canyon Member of the Belted Range Tuff (Sargent, Noble, and Ekren, 1965), both major areally extensive ash-flow sheets, show marked vertical compositional zonation. (Noble, Bath, and others, 1968; Noble and Christiansen, unpub. data; Noble, Sargent, and others, 1968; unpub. data). The less voluminous Gold Flat Member of the Thirsty Canyon Tuff also appears to be significantly zoned (Noble, 1965; unpub. data). In each sheet, zonation involves an increase in magnesium, calcium, strontium, and aluminum and a decrease in silicon from bottom to top: that is to say, an upward change from comendite or pantellerite to chemically more primitive rocks that are transitional to trachyte. The percentage of phenocrysts also increases upward. Such systematic vertical compositional zonation within an ash-flow sheet is generally believed to reflect a preexistent compositional zonation within the parent magma which was inverted by the process of eruption from the magma chamber (for example, Williams, 1942; Ratté and Steven, 1964; Ewart, 1965; Fisher, 1966; Lipman, Christiansen, and O'Connor, 1966; Smith and Bailey, 1966; Noble and Hedge, 1969). Various mechanisms may combine to produce compositional zonation within a magma. As inferred from other lines of evidence, fractional crystallization with attendant settling of phenocrysts would appear to be the most important.

Glasses from the basal parts of the three above-mentioned ash-flow sheets contain 2 ppm or less strontium and less than 0.03 wt percent MgO (tables 1 and 2). Tuffs from the lower part of the Grouse Canyon Member are phenocryst-free. Tuffs from the lower part of the Spearhead Member contain less than 10 percent phenocrysts, which consists almost wholly of sanidine containing less than 10 ppm strontium (Noble and Haffty, unpub. data). Tuffs from the basal part of the Gold Flat Member contain less than 20 percent phenocrysts, mainly sanidine. The average strontium content of the sanidine associated with the Gold Flat glass is not known, but a low-specific-gravity fraction of sanidine separated from a specimen from a different locality contains 60 ppm strontium. Mafic phenocrysts, all iron-rich phases, are very sparse in the basal parts of the Spearhead and Gold Flat Members. The resultant low strontium and magnesium contents of the whole-rock material from the lower parts of these ash-flow sheets are consistent with a crystal-fraction with attendant crystal-settling origin for the overall compositional zonation of the units.

There would appear to be no reason why the strontium-depletion criterion for fractional crystallization should not also be applicable to rocks of subalkaline chemistry. In fact, data currently available on several major compositionally zoned subalkaline (rhyolite to quartz latite) ash-flow sheets show that the rhyolitic tuffs that comprise the lower parts of the sheets are moderately to highly depleted in strontium.

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