DISTRIBUTION OF CALCIUM BETWEEN ALKALI FELDSPAR AND GLASS IN SOME HIGHLY DIFFERENTIATED SILICIC VOLCANIC ROCKS

DONALD C. NOBLE, Department of Geological Sciences, Harvard University, Cambridge, Massachusetts 02138;

MARJORIE K. KORRINGA, Department of Geology, Stanford University, Stanford, California 94305;

AND


Abstract

Sodic sanidine and anorthoclase phenocrysts from three specimens of comendite ash-flow tuff and four lavas of comendite composition contain appreciably less calcium than do the enclosing glassy groundmass materials. Since crystallization of such feldspars from melts having the composition of the associated glasses would tend to raise the calcium contents of the residual liquids, slightly peralkaline silicic magmas will contain significant amounts of calcium regardless of the degree of fractional crystallization that they have undergone. Late-stage intratelluric crystallization of small amounts of calcium-rich mafic minerals probably is responsible for the glasses being poorer in calcium than the low-temperature compositions which would have obtained through feldspar crystallization. Strontium, which is preferentially incorporated in alkali feldspars relative to glass, and which is excluded from pyroxenes and amphiboles, provides a more meaningful parameter by which to infer the degree of crystal fractionation that a silicic melt has undergone.

Introduction

Experimental study of the low-temperature region of the system NaAlSiO₃-KAlSiO₃-CaAl₂Si₂O₈-SiO₂-(H₂O) is difficult because marked changes in phase relations and tie-line orientation take place within very small ranges of temperature and composition. The main purpose of this paper is to present chemical data on the phenocrystic alkali feldspar and associated groundmass material of seven calcium-poor silicic volcanic rocks which strongly suggest that under certain conditions of temperature, pressure, and bulk composition, the compositions of the low-temperature liquids project within the system Ab-Or-An rather than on the Ab-Or join.

Previous Work

The possibility that the minimum melting fraction in the "granite" system may contain significant amounts of calcium is implicit in the theoretical treatment of Stewart and Roseboom (1962). The experimental data of James and Hamilton (1969) are consistent with, but do not prove, the existence of a minimum within the system NaAlSiO₃-
KAlSi₃O₈-CaAl₂Si₂O₈-SiO₂ at 1000 bars water pressure. Pantellerites from several localities contain alkali feldspar phenocrysts with much less calcium than the associated glassy groundmass material (Carmichael, 1962; Chayes and Zies, 1964; Noble, 1968b; Bryan, 1969). Although these relations indicate that the low-temperature melting compositions project off the Ab-Or join, it is not obvious from the above data that similar relations will hold for magmas which are not highly peralkaline and rich in iron.

**Analytical Methods**

Calcium was determined by five methods. Gravimetric determinations (indicated below by G) were made by E. L. Munson, C. L. Parker, G. O. Riddle, and V. C. Smith under the supervision of L. C. Peck using procedures described by Peck (1964). Optical emission spectrographic (ES) determinations were made by Haffty using methods similar to those of Bastron et al. (1960). X-ray fluorescence (XRF) analyses were made by Korringa and Noble on powdered material using as standards a number of rhyolites previously analyzed by gravimetric methods in Peck’s laboratory. Electron microprobe (EMP) analyses were made by Korringa and Noble using an ARL EMX instrument. A variety of feldspars and natural glasses analyzed by other methods were used as standards. An atomic absorption spectrophotometric (AA) determination was made on one sample by Wayne Mountjoy. The other elements were determined by a variety of methods. Magnesium values are based on optical emission spectrographic and atomic absorption spectrophotometric determinations by Haffty, gravimetric determinations by G. O. Riddle, C. L. Parker, and V. C. Smith, and electron microprobe analyses by Korringa. Strontium was determined by the authors and C. E. Hedge using combinations of X-ray fluorescence, optical emission spectrographic, and isotope dilution techniques. Barium was determined by optical emission spectrography by Haffty, Harriet Neiman, and J. C. Hamilton. Sodium, potassium, and iron values were determined either by gravimetric methods, E. L. Munson, C. L. Parker, G. O. Riddle, and V. C. Smith analysts, and/or by Korringa and Noble using X-ray fluorescence or electron microprobe procedures. Rubidium values, in part from Noble and Hedge (1970), were obtained by X-ray fluorescence methods.

**Data**

The rocks reported on here are rather iron-poor and only slightly peralkaline comendites of late Cenozoic age from the Great Basin of the western United States. General geologic, petrologic, and geochronologic information on the rock units from which the specimens were collected are given in Table 1. The alkaline earth, alkali, and iron contents of the sanidines and associated glasses are given in Table 1 and the calcium and atomic Ca/(Na+K) ratios of the sanidines and glasses are compared in Table 2. Modal analyses are given in Table 3. The silica and alumina contents of the glasses are typical of slightly peralkaline natural silicic glasses (Noble, 1968b), ranging from 74 to 76 and 10 to 13 weight percent, respectively.

The low to extremely low Mg, Ca, Ba, and particularly Sr contents of
| Pair | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass | Feldspar | Glass |
|------|----------|-------|----------|-------|----------|-------|----------|-------|----------|-------|----------|-------|----------|-------|----------|-------|----------|-------|----------|-------|----------|-------|
| MgO  | <0.007   | 0.10  |          |       | <0.005   |       |          |       | <0.007   |       |          |       |          |       |          |       |          |       |          |       |          |      |
| CaO  | 0.25     | 0.33  | <0.02    |       | 0.13     |       | <0.02    |       | 0.03     |       | 0.11     |       | 0.25     |       | 0.11     |       | 0.35     |       | 0.04     |       | 0.15     |      |
| Sr   | 0.0006   | 0.0006 | <0.0002  |       | <0.001   |       | 0.00018  |       | <0.001   |       |          |       | 0.0004   |       | 0.0002   |       | 0.0002   |       | 0.0002   |       | 0.0002   |      |
| Ba   | 0.0036   | <0.0005 |          |       | 0.0009   |       |          |       | 0.0003   |       |          |       | 0.0004   |       |          |       | 0.0004   |       |          |       | 0.0004   |      |
| Na2O | 6.86     | 4.44  | 4.86     |       | 7.0      |       | 5.2      |       | 6.04     |       | 4.9      |       | 8.5      |       | 5.73     |       | 7.9      |       | 5.6      |       | 7.5      |       |
| K2O  | 6.59     | 4.88  | 7.45     |       | 4.60     |       | 7.1      |       | ~4.5     |       | 7.87     |       | 4.7      |       | 4.28     |       | 5.3      |       | 4.6      |       | 3.9      |       | 4.43     |      |
| Pb   | 0.0072   | 0.0228 | 0.0127   |       | 0.0151   |       | 0.0100   |       | 0.0004   |       | 0.017    |       | 0.0016   |       | 0.0004   |       |          |       |          |       | 0.039    |       |          |      |
| Fe as Fe2O3 | 0.135 | 0.68 |          |       |          |       | 0.48     |       |          |       |          |       | 0.48     |       |          |       |          |       |          |       |          |       |          |      | 3.21   |       |
| Fe as FeO  | 1.76  | 2.84  |          |       |          |       | 2.4      |       |          |       |          |       | 2.07     |       |          |       |          |       |          |       |          |      | 3.58     |       |

1. Spearhead Member of the Pliocene (7 m.y.) Thirsty Canyon Tuff at lat. 37°49'0"W., long. 115°39'0"E., Nye County, Nevada (Noble et al., 1964; Noble, Bath et al., 1968). Data based on analyses of samples Twa-94, Twb-8346, Twa-986, Twa-7AFL, and Twa-986A.
2. Soldier Meadow Tuff of Miocene (15 m.y.) age at lat. 40°54'0"W., long. 118°59'15"E., Humboldt County, Nevada. (Noble et al., 1970). Data based on analyses of samples N-90 and N-90B.
3. Unit YU-7 (of Cook, 1965) of the Miocene (14 m.y.) laze wash tuff at lat. 37°32'0"N., long. 119°09'15"W., Lincoln County, Nevada. (Cook, 1965; Noble, 1966a). Data based on analyses of samples YU-7, YU-3, and YU-7AFL.
4. Rhyolite of Kavich Valley of Miocene (15 m.y.) age at lat. 37°21'10"N., long. 116°03'00"W., Nye County, Nevada. (Noble, Sargent et al., 1968; Rogers and Noble, 1969). Data based on analyses of samples YPO-100, YPO-500B, YPO-500A, YPO-5, and YPO-501.
5. Comendite obsidian of Quaternary age from a lava flow on San Francisco Mountain, San Francisco volcanic field, Arizona (Robinson, 1915). Sanidine and glass are from the same specimen (1927) analyzed by Robinson. Data based on analyses of samples 1921, 1922, and 1922.
6. Fragment of comendite obsidian of lava-flow origin from air-fall tuff underlying the Trail Ridge Member of the Pliocene (7 m.y.) Thirsty Canyon Tuff at lat. 37°37'17"N., long. 116°22'3"W., Nye County, Nevada (Noble et al., 1964; Orrick et al., 1969). Data based on analyses of samples Twa-8B, Twa-8A, Twa-8B-2, and Twa-8B, and YPO-7AFL.
7. Comendite obsidian from a cove of the Miocene (14 m.y.) rhyolite of Split Ridge at lat. 37°10'15"N., long. 118°19'30"W., Nye County, Nevada (Orrick et al., 1969; Noble, Sargent et al., 1968). Data based on analyses of samples SBR-2, SBR-2-G, and SBR-2-S.
Table 2. Comparison of Calcium Contents and Atomic Ca/(Na+K) Ratios of Feldspars and Glasses

<table>
<thead>
<tr>
<th>Pair</th>
<th>( \frac{\text{Ca}_s}{\text{Ca}_g} )</th>
<th>( \frac{\text{Ca}_s(\text{Na+K})}{\text{Ca}_g(\text{Na+K})} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>(&lt; 0.15)</td>
<td>(&lt; 0.1)</td>
</tr>
<tr>
<td>3</td>
<td>(~ 0.25)</td>
<td>(~ 0.2)</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>6</td>
<td>0.3</td>
<td>0.25</td>
</tr>
<tr>
<td>7</td>
<td>0.25</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\( \frac{1}{s} = \text{sanidine}, \ g = \text{glass} \)

Table 3. Modal Analyses of Rocks Studied

<table>
<thead>
<tr>
<th>Specimen</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sanidine or anorthoclase</td>
<td>5</td>
<td>14</td>
<td>15</td>
<td>4</td>
<td>(~4)</td>
<td>(~1)</td>
<td>(~1)</td>
</tr>
<tr>
<td>Quartz</td>
<td>(&lt;1)</td>
<td>7</td>
<td>8</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sodic plagioclase</td>
<td>tr</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ferrorichterite</td>
<td>tr</td>
<td>(&lt;1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Iron-rich clinopyroxene</td>
<td>tr</td>
<td>tr</td>
<td>(&lt;1)</td>
<td>tr</td>
<td>tr</td>
<td>tr</td>
<td>tr?</td>
</tr>
<tr>
<td>Fayalite</td>
<td>tr</td>
<td>0</td>
<td>(&lt;1)</td>
<td>tr</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Biotite</td>
<td>tr</td>
<td>tr</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Iron Oxides</td>
<td>0</td>
<td>(&lt;1)</td>
<td>(&lt;1)</td>
<td>tr</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Glass</td>
<td>94</td>
<td>78</td>
<td>76</td>
<td>94</td>
<td>(~96)</td>
<td>(~99)</td>
<td>(~99)</td>
</tr>
</tbody>
</table>
the glasses and sanidines testify that the rocks themselves are the products of a high degree of fractional crystallization. The quartz and feldspar phenocrysts in specimens 1, 3, 4 and 5 are euhedral, and there are no textural or other reasons to believe that during intratelluric crystallization the outermost portions of the phenocrysts were not in equilibrium with melt phases now represented by the glasses with which they are now associated. Specimens 1 and 3 are from the lowermost parts of ash-flow sheets, which minimizes the chance that the rocks contain cumulate crystals which had settled from overlying magmas of possibly somewhat different chemical composition. The quartz and sanidine phenocrysts of specimen 2 are somewhat rounded and embayed, probably as a result of resorption attendant on reduction of pressure on the water-undersaturated magma during eruption from considerable depth.

The individual analyses and details of the samples on which the calcium contents of the sanidines and associated glasses are based are given below.

**Pair One.** Pair one is from the densely welded glassy base of an apparently compositionally unzoned ash-flow cooling unit approximately 50 feet in thickness. The CaO content of the groundmass material is based on determinations of 0.33 (G), 0.33 (G), and 0.31 (ES) weight percent on nonhydrated glass from large completely appressed pumice fragments, and a determination of 0.35 (G) weight percent CaO on densely welded hydrated glass from the same hand specimens from which the sanidine was separated. These contents are corroborated by very similar CaO values obtained on nonhydrated and hydrated glasses separated from other specimens of this unit collected at different localities. The sanidine separate was split into heavy and light fractions by centrifuging material of minus 250 mesh. CaO values of 0.25 (ES) and 0.26 (XRF) weight percent were obtained on the heavy portion and values of 0.24 (ES) and 0.25 (EMP) on the light fraction.

**Pair Two.** The specimen studied is densely welded glassy tuff. Groundmass composition is based on determinations of 0.13 (AA), 0.135 (XRF), 0.13 (EMP), and 0.04 (G) weight percent CaO on small cores of nonhydrated glass. CaO contents of <0.02 (XRF) and <0.02 (EMP) were determined for the sanidine. Both the glass and sanidine compositions are corroborated by very similar CaO values obtained on other glass and sanidine separates from the formation.

**Pair Three.** Both glass and sanidine were separated from a densely welded hydrated vitrophyre from the base of a several hundred foot thick cooling unit. The 0.30 weight percent CaO found by X-ray fluorescence analysis of the hydrated glass may well include some calcium added by groundwater, for a value of 0.15 weight percent CaO was obtained on a densely welded granophyrically crystallized whole-rock specimen collected several feet above the top of the vitrophyre. CaO contents of 0.05 (XRF) and 0.05 (EMP) were determined for the sanidine.

**Pair Four.** The specimen studied is a very slightly vesicular hydrated glassy rock from near

---

1 Gravimetric procedures are relatively imprecise at this range of concentrations (Peck, 1964).
the margin of an endogenous dome. CaO contents of 0.04 (XRF) and 0.02 (EMP) were
determined for the sanidine. The CaO content of glass phase was determined by X-ray
fluorescence. Values of 0.06 (G) and 0.11 (XRF) weight percent CaO were obtained on a
granophyrically crystallized whole-rock specimen from another part of the dome. Addi-
tional indirect evidence which suggests that the CaO content of specimen WPN-500 ap-
proximates the original rock composition is provided by gravimetric analyses of nine non-
hydrated glasses from several other units of the volcanic center, which range from 0.15 to
0.29 weight percent CaO (Noble et al., 1968; Noble, 1970; Noble, unpublished data).

The Na2O contents of the glass phases of pairs 3 and 4 are inferred from the total iron
contents of the glasses. In nearly all cases Na has been lost from both hydrated and primarily
crystallized peralkaline silicic glasses (e.g., Noble, 1967; 1970), and the most reliable esti-
mates of original Na contents in such materials are provided by the iron contents which
show a strong positive correlation with Na in the unaltered nonhydrated equivalents
(Noble, 1968b).

**Pair Five.** The specimen studied is a dense nonhydrated rock. The CaO content of the feld-
spar was determined by electron microprobe methods. The CaO content of the glass is
based on determinations of 0.24 (G) and 0.22 (EMP).

**Pair Six.** The specimen studied is dense and nonhydrated. The CaO content of both the
glass and feldspar phases were determined by electron microprobe. The glass composition
is corroborated by gravimetric determinations of 0.37, 0.34 and 0.47 on other very similar
nonhydrated glass fragments from the same unit.

**Pair Seven.** The specimen studied is dense and nonhydrated. The CaO content of the feld-
spar was determined by electron microprobe methods and that of the glass is based on de-
terminations of 0.13 (G) and 0.16 (EMP).

**DISCUSSION**

The alkali feldspars from all seven specimens contain significantly less
calcium than do the associated glasses (Table 2). No evidence of com-
positional zonation was observed, either optically or by microprobe
methods, in any of the feldspars. If such Ca-poor sanidines and anortho-
classes undergo continual intratelluric reequilibration with respect to Ca,
possibly facilitated by the presence of all or part of the calcium com-
ponent as the "Schwantke molecule" (Carman and Tuttle, 1968), the
Ca\textsubscript{f}/Ca\textsubscript{g} ratios given in Table 2 may represent true distribution co-
efficients.

Separation of such relatively calcium-poor alkali feldspar obviously
will increase the calcium content of the residual melt. The orientation of
the feldspar-liquid tie lines thus strongly suggests that slightly peral-
kaline silicic melts will contain significant, although variable, amounts of
CaO, regardless of the degree of fractional crystallization that they have
undergone. The low-temperature liquid having a given degree of per-
alkalinity and mafic-element content could lie at a ternary minimum
(Fig. 1, top), a minimum on the cotectic (Fig. 1, middle), or at ternary
eutectic (Fig. 1, bottom) in projections on the system Ab-Or-An.
Fig. 1. Diagrammatic sketches showing three possible configurations of the low-temperature region in the system Ab-Or-An-(Q-H₂O) in which the low-temperature liquids contain significant amounts of Ca. Heavy lines, cotectic (projected); light lines, isothermal contours on the liquidus surface (projected); and dots, lowest-temperature liquids. Horizontal lines represent the Ab-Or join. Since peralkaline liquids contain an atomic excess of alkalis over aluminum, these diagrams must be considered as projections from alumina-undersaturated compositions onto the plane Ab-Or-An.

The observed relations may, to a greater or lesser degree, reflect the presence of an atomic excess of alkalis over alumina in the melt, a factor which is known to stabilize the presence of a number of elements, such as Fe, Zr, Nb, and the rare earths, within the magmatic liquid. The influence of the degree of peralkalinity of a melt on feldspar-liquid phase relations is suggested by the extremely low Ca₉/Caₑ ratios observed for certain highly peralkaline pantellerites. No data have yet been obtained on subalkaline rhyolites containing a single alkali-feldspar phase. However, the occurrence of very highly differentiated subalkaline rhyolites containing 0.3 to 0.5 weight percent CaO (e.g., Noble et al., 1972) sug-
gests that similar phase relations may hold for some subaluminous and peraluminous rhyolitic magmas.

The comendites undoubtedly were derived by fractional crystallization from appreciably more calcium-rich melts which precipitated feldspar having higher atomic Ca/(Na+K) ratios than those of the melts. If the low calcium contents of the residual glasses are the result solely of feldspar separation, it is difficult to explain why the alkali feldspars are uniformly less calcic than the associated melts. Rather, the melt should approach the minimum melting composition from the calcium-rich side as the result of separation of relatively more calcic feldspar. However, very small amounts of phenocrystic iron- and calcium-rich clinopyroxene are present in most of the rocks, and phenocrysts of calcium-bearing sodic amphibole also are present in rocks 1 and 2. The observed feldspar-melt relations thus can be explained if late-stage separation of calcium-bearing mafic phases played a significant part in reducing the calcium contents of the glasses. Pyroxene and amphibole crystallization appears to have reduced the calcium contents of the melts below that of the low-temperature composition which would obtain by the separation of feldspar. The data indicate that the calcium contents of highly differentiated silicic melts depend not only on feldspar-melt phase relations, but also on the Fe^{2+}, Fe^{3+}, and Mg contents of the melts and on the other physical and chemical factors which influence the relative stability of clinopyroxene, olivine, amphibole, and the ore minerals.

The sanidines contain appreciably more strontium and barium than do the associated groundmass materials (Table 1). The strontium data are corroborated by the very low Sr/Ca ratios typical of peralkaline silicic glasses (Noble et al., 1969), which can only result from the preferential abstraction of strontium relative to calcium through the crystallization of alkali feldspar. Indeed, we know of no evidence that either strontium or barium are ever enriched in a melt relative to coexisting alkali feldspar. Pyroxene and amphibole are depleted in strontium and barium relative to calcium (e.g., Ewart and Taylor, 1969). The concentrations of strontium and barium, particularly strontium, thus provide a much more reliable measure than does calcium content of the degree of low-pressure crystal fractionation that a silicic magma has undergone.

ACKNOWLEDGEMENTS

This work was begun when the senior author was employed by the U. S. Geological Survey. Completion of this work was supported by grants from the National Science Foundation and the National Space and Aeronautics Administration to the senior author. The second author was supported by grants from the Geological Society of America and a National Defense Education Act graduate fellowship. P. C. Bateman, S. C. Creasey, and T. W. Stern, all of the U. S. Geological Survey, kindly permitted the use of laboratory
facilities for certain of the work. The comments of Fred Barker, T. G. Lovering, D. B. Stewart, and T. L. Wright improved the manuscript.

References


*Manuscript received, December 11, 1970; accepted for publication, May 10, 1971.*