

## DISTRIBUTION OF ELEMENTS IN A SPHERULITIC ANDESITE

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### ABSTRACT

Electron microprobe and bulk chemical analyses of a spherulitic andesite indicate that potassium is concentrated in the spherulites, whereas sodium and magnesium are depleted. Calcium, silicon and titanium are concentrated, and aluminum and potassium are depleted in a 10 $\mu$ m-wide band of brittle mica(?) which is peripheral to the spherulites. The spherulites appear to consist of an open aggregate of 10 $\mu$ m-wide, radially-oriented plagioclase fibers with abundant potassium feldspar and minor biotite in the interfibrillar areas. The groundmass contains unoriented plagioclase fibers, some potassium feldspar, hornblende(?) and hematite. Both the groundmass and spherulite plagioclase have a composition of approximately An<sub>40</sub> and have potassium-rich rims. This distribution of elements conforms to that predicted from observations of spherulite formation in polymer melts. The growth rate of the spherulites was approximately 10<sup>-6</sup> cm/sec.

### INTRODUCTION

During a study of the Colombier volcanic sequence in the Terre-Neuve Mountains of Haiti, an unusual distribution of potassium and calcium was discovered in a spherulitic pyroxene andesite when staining for potassium and calcium-bearing feldspars indicated a strong partitioning of potassium into the spherulites and a concentration of calcium at the spherulite borders. This distribution has been verified by bulk and electron microprobe analyses and appears to agree with predictions based on theories of spherulite growth in polymers.

The geology of the Terre-Neuve Mountains has been discussed by Kesler (1966, 1968). The Upper Cretaceous(?) Colombier volcanic sequence from which the spherulitic andesite was collected, is exposed along the axis and periphery of the Terre-Neuve Mountains (Fig. 1). The maximum thickness of the unit is 500 m although the basal unit is not exposed and the upper contact is an erosion surface. The sequence is dominated by terrestrial flows of pyroxene andesite and trachyandesite with some basalt, hornblende andesite, and dacite.

The spherulites are found in a 5 m-thick pyroxene andesite flow from the middle of the exposed volcanic sequence. The flow contains phenocrysts of plagioclase, clinopyroxene (Wo<sub>38</sub>, Fs<sub>20</sub>, En<sub>42</sub>), and orthopyroxene (Wo<sub>4</sub>, Fs<sub>36</sub>, En<sub>60</sub>) in a microcrystalline groundmass which retains a vague perlitic structure. As the modal analyses of Table 1 indicate, the

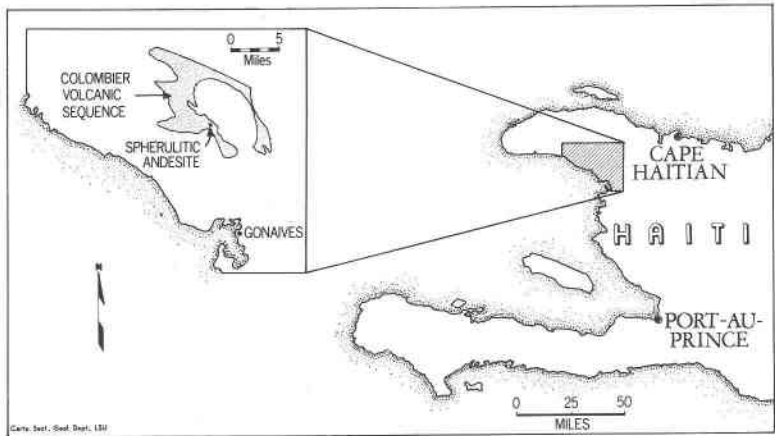


FIG. 1. Location of the Colombier volcanic sequence and the spherulitic andesite described here.

spherulitic andesite is somewhat more mafic than most flows in the sequence. The spherulites are found as bands, apparently concentrated along lines of flow, and isolated individuals in all parts of the flow. The diameter of the spherulites ranges from 1.0 to 2.3 mm, but most are about 1.3 mm in diameter.

#### DESCRIPTION OF THE SPHERULITES AND GROUNDMASS

Spherulites examined in thin section appear to have a crude radial structure defined by feldspar laths and interfibrillar material (Fig. 2a), although the feldspar cannot be positively identified because of its small grain size. Under high magnification, the fibrous nature of the spherulite can be seen best (Fig. 2b), and it is also possible to distinguish anhedral masses and subhedral to euhedral grains of biotite up to  $5 \mu$  in

TABLE 1. MODAL ANALYSES OF SPHERULITIC ANDESITE (M-180) AND OTHER ANDESITES FROM THE COLOMBIER VOLCANIC SEQUENCE

	Pyroxene Andesite M-180	Pyroxene Andesite M-175	Hornblende Andesite M-186		M-180
Plagioclase	26	33	20	Phenocrysts	37
Orthopyroxene	5	tr	tr	Spherulites	16
Clinopyroxene	8	5	tr	Groundmass	47
Hornblende	—	—	6		
Magnetite	2	3	2		
Groundmass	59	59	71		

diameter between the fibers (Fig. 2c). Although this biotite is a minor component of the spherulites, it is much more abundant in the spherulites than in the groundmass and gives the spherulites their characteristic light brown color. Observations of the cathodoluminescence during electron microprobe analysis revealed that the spherulites luminesce light blue-green and contain individual plagioclase fibers, which are about  $10\ \mu$  wide and up to  $100\ \mu$  in length, with bright blue luminescent borders. The composition of these fibers, as determined with the micro-

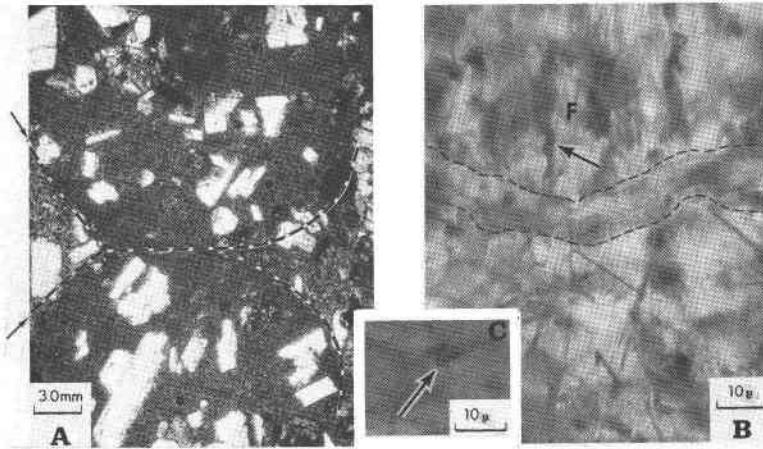


FIG. 2. (a) Two spherulites with straight mutual boundary and unaligned plagioclase and pyroxene phenocrysts, some of which cross the spherulite boundary. (b) Spherulite-groundmass boundary showing feldspar fibers (F) with inter-fibrillar biotite masses (arrow) in the spherulite and unaligned plagioclase and rods of hornblende in the groundmass. The border zone is delineated by dashed lines. (c) Euhedral biotite grain (arrow) in inter-fibrillar area of spherulite.

probe ranges from a core of approximately  $An_{40}$  to a narrow potassium feldspar (anorthoclase?) rim. Less than 25 percent of the spherulites is composed of the plagioclase fibers. The remainder of the spherulites consists dominantly of a material with the composition of potassium feldspar, which appears fibrous in cathodoluminescence. We have interpreted these observations to indicate that the spherulites consist of an open aggregate of crudely radiating plagioclase fibers with abundant inter-fibrillar potassium feldspar and some biotite. Hematite, a few hornblende (?) needles, and apatite form small grains scattered through the spherulites.

The groundmass, in which the spherulites are contained, appears in thin section to consist of randomly oriented feldspar fibers with a small

amount of interstitial hematite, apatite, and small needles of hornblende. The hornblende needles, which are very scarce in the spherulites but abundant in the groundmass, appear to be the groundmass analog of the biotite which is abundant in the spherulite and almost completely absent from the groundmass. The cathodoluminescence of the groundmass differs from that of the spherulites in that only the plagioclase fibers luminesce clearly. The remaining approximately 75 percent of the groundmass is dominantly a cryptocrystalline material which from reconnaissance probe analyses contains up to 2 percent total iron as FeO.

Both the spherulites and groundmass contain phenocrysts of plagioclase and ortho- and clinopyroxene. No difference between the primary magnetite of the spherulites and that of the groundmass was detected in polished section. Many of the phenocrysts are only partly included in the spherulites.

In most places, the border between the spherulites and groundmass is a band about 10  $\mu$  wide. The band consists dominantly of a weakly birefringent, pale greenish-yellow mineral with anomalous interference colors, which forms plates oriented perpendicular to the spherulite surface. The optical properties and the high calcium content obtained in microprobe analyses suggest that the mineral in these peripheral bands is a calcic brittle mica or pumpellyite. In some places, a very narrow band of a tangentially-oriented, greenish-brown, platy mineral, thought to be a low-potassium biotite, is found between the brittle mica (?) band and the spherulite.

#### CHEMICAL COMPOSITION OF THE SPHERULITES AND GROUNDMASS

The compositions of the spherulites and groundmass, compared in Figure 3, were obtained by atomic absorption analysis of spherulite and groundmass separates, both of which contained phenocrysts. Because the phenocrysts are randomly distributed within the andesite, any difference in the two analyses can be assumed to represent a compositional difference between the spherulite and groundmass. The results of these analyses indicate potassium is partitioned strongly into the spherulite whereas sodium and magnesium are depleted in the spherulite. Calcium is not clearly partitioned into either part of the andesite.

Electron microprobe analyses verified this partitioning of elements and clarified the nature of the border that surrounds the spherulites. Typical traverses shown in Figures 4 and 5 illustrate the sharp change in potassium content of the matrix from about 9 percent K<sub>2</sub>O in the spherulites to about 2 percent K<sub>2</sub>O in the groundmass. The approximately constant calcium content of the matrix is also shown. The con-

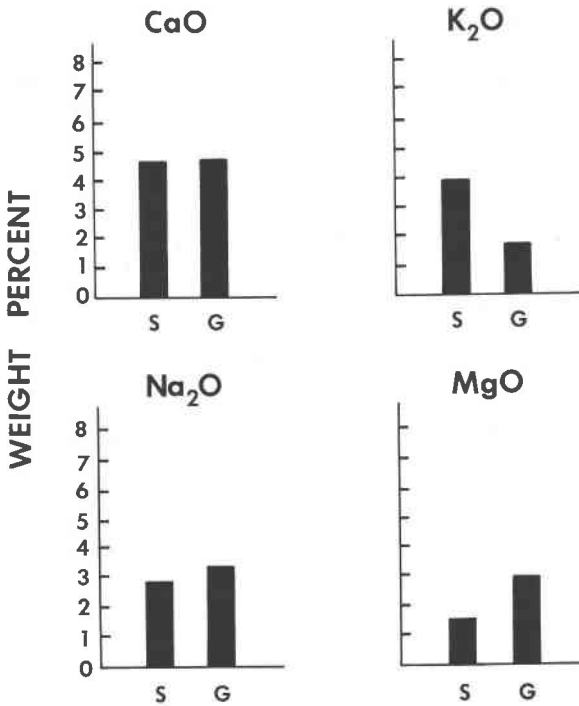


FIG. 3. Compositions of the spherulites (S) and groundmass (G).  
Both analyses include phenocrysts.

centration of potassium in the potassium feldspar and biotite-rich inter-fibrillar areas of the spherulite contrasts strongly with the concentration of calcium in the plagioclase fibers. The upper two potassium and calcium traverses illustrate the concentration of calcium and depletion of potassium in the border zone, whereas the lower traverse illustrates the more unusual two-phase border zone consisting of a relatively potassium-poor biotite inner zone and a calcium-rich brittle mica or pumpellyite outer zone. The border zone is also enriched in silicon, iron, and titanium and is depleted in aluminum, as indicated by reconnaissance microprobe traverses. A distinct enrichment of silicon in the spherulites and titanium in the groundmass was also detected. Iron appeared to be present in approximately equal amounts in both the spherulites and groundmass.

#### CRYSTALLIZATION OF THE SPHERULITES

By relating observations of spherulite formation in polymers to studies of crystallization in metals (Elbaum, 1959), Keith and Padden have

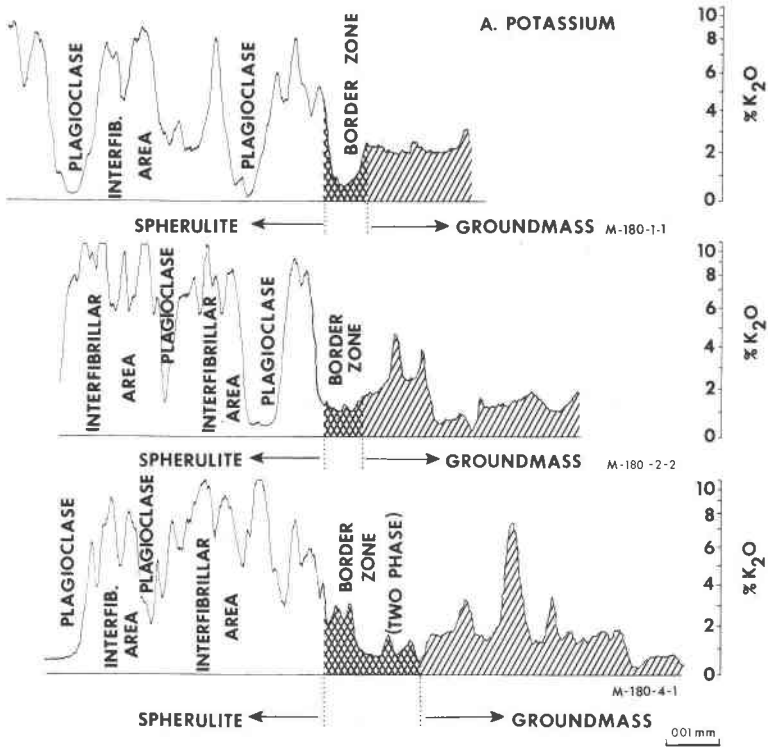


FIG. 4. Electron microprobe potassium traverses across spherulite-groundmass contact. The traverses are oblique to fibers and border zone and therefore do not show true dimensions.

proposed (1963), and partly verified (1964a, b), a theory of spherulite formation. These investigators have pointed out that all spherulite-forming melts are multicomponent systems which crystallize slowly and have low diffusion rates. They indicate that, as these melts crystallize, the components not included in the growing phase accumulate at the crystal-liquid interface, thereby lowering the liquidus temperature of the melt in this region. Because the area near the growing crystal would be less supercooled than the more distant melt with smaller amounts of impurities, protrusions on the surface of a growing crystal should develop more rapidly than planar surfaces, thereby causing a fibrous habit to develop, (Keith and Padden, 1963). Lateral crystallization and consequent widening of the fibers is restricted by the high impurity content of the residual interfibrillar melt which lowers both the liquidus temperature and nucleation rates. Keith and Padden have shown that the thickness,  $\delta$ , of the impurity-rich layer is defined by

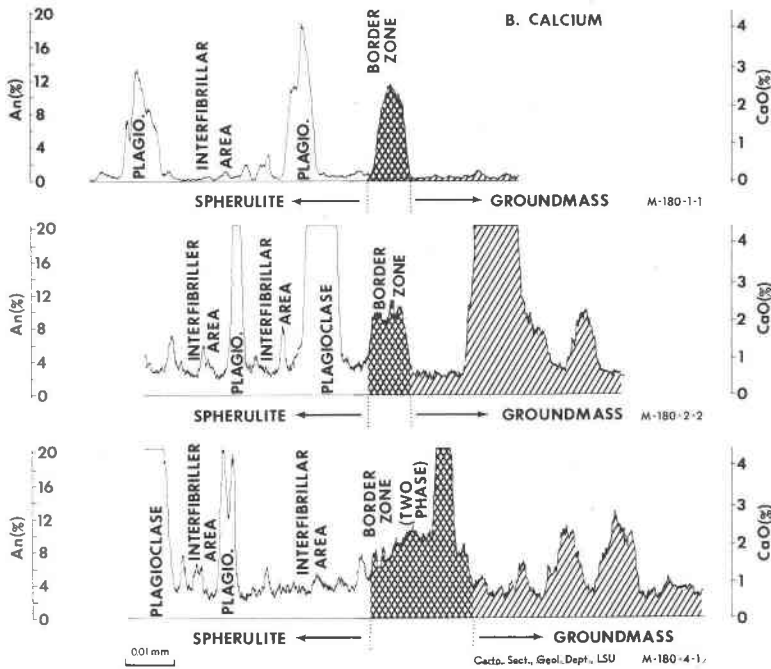


FIG. 5. Electron microprobe calcium traverses across spherulite-groundmass contact. The traverses are oblique to fibers and border zone and therefore do not show true dimensions.

$$\delta = D/G$$

where  $D$  is the diffusion coefficient of the impurity and  $G$  is the growth rate of the spherulite. They have also indicated that the diameter of the resulting fibers will be approximately equal to  $\delta$ .

According to this interpretation of spherulite growth, potassium and magnesium are impurities which were expelled into the interfibrillar areas of the spherulite as the plagioclase fibers grew. The strong partitioning of sodium into the groundmass and the concentration of calcium in the border zone suggest that sodium and some calcium were also expelled from the spherulite. Apparently, potassium was sufficiently concentrated in the interfibrillar melt to allow nucleation of potassium feldspar and biotite, thereby fixing most of the potassium in the spherulite. The small amount of potassium that did not form these minerals was concentrated as the inner biotite border found around some spherulites. Sodium, magnesium, iron, titanium and the excess calcium, which did not nucleate stable phases within the interfibrillar areas, were con-

sequently expelled as potassium feldspar and biotite crystallized and were concentrated in the border zone of the spherulite.

Calcium is strongly concentrated in the spherulite border zone (Fig. 4). This suggests that it was expelled from the spherulites; however it shows no preferential concentration in the groundmass (Fig. 3). The explanation for this might be that only a small amount of calcium was expelled from the spherulite and this was all retained in the border zones.

The relatively low potassium concentration in the groundmass does not agree well with the interpretation of spherulite formation given above. The absence of a negative concentration gradient around the spherulites makes it unlikely that the spherulite depleted the groundmass in potassium. Instead, it is more plausible that the potassium content of the rock was originally high and that most of this potassium was retained in the spherulites whereas it was lost from the groundmass after spherulite formation. Although minor potassium feldspar and some potassium-rich borders on plagioclase were detected by microprobe analyses, no evidence could be found in the groundmass for the past or present existence of an abundant potassium-bearing phase. This suggests that the potassium was removed before the groundmass had devitrified, and therefore relatively early in the cooling process. Thus, the potassium could have been strongly partitioned into either a late escaping volatile phase or percolating groundwater through a process similar to that discussed by Scott (1968). The possibility that potassium escaped from the groundmass indicates that the distribution of elements observed in the spherulitic andesite is influenced by secondary processes, as well as by the primary process of spherulite formation.

The Agate Point obsidian, which was the subject of a controversy between Tanton (1925), Bain (1926), and Greig (1928), contains spherulites with borders similar to those described here. In an investigation in which he concluded that the spherulites were cognate xenoliths, Bain painstakingly analyzed the groundmass, spherulites, and border zone (including phenocrysts). The results of his analyses, calculated as water free, are shown in Figure 6. Calcium, potassium, iron, magnesium, and possibly aluminum were expelled during crystallization of these spherulites, whereas sodium and silicon were apparently retained. The relatively minor degree of partitioning shown by these elements may be a function of the low diffusion rates in highly siliceous melts. The distribution of the elements, however, agrees with that predicted by Keith and Padden for a case in which the dominant phases forming in the spherulite are quartz and sodic plagioclase, rather than inter-



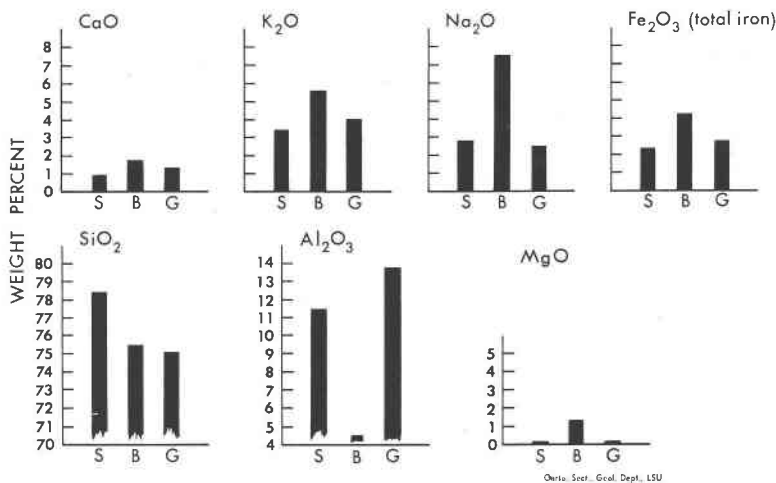


FIG. 6. Compositions of spherulites (S), border zone (B), and groundmass (G) of the Agate Point vitrophyre. Analyses are calculated as water free from data of Bain (1926).

mediate plagioclase, potassium feldspar, and biotite as in the andesite described here.

#### GROWTH RATE OF THE SPHERULITES

The width,  $\delta$ , of the impurity-rich border zone in the spherulitic andesite averages about  $10 \mu$ . The diffusion coefficient,  $D$ , of the impurities in the melt can be estimated by extrapolating the data obtained by Towers and Chipman (1957) for the diffusion coefficient of calcium to the probable temperature of formation of the spherulites which can be estimated by considering morphology and distribution of the spherulites and the cooling history of the flow. The diameter,  $\delta$ , of the plagioclase fibers is approximately constant from center to rim of individual spherulites and from spherulite to spherulite throughout the flow. Thus, the ratio  $D/G$  must have been constant during spherulite formation. This condition would have been fulfilled if  $D$  and  $G$  remained individually constant during spherulite formation or if they varied equally with time. Keith and Padden (1964a) have shown that for any change in temperature, changes in  $D$  in polymer melts will be much greater than changes in  $G$ , and it seems likely that this will be the case in spherulite-forming silicate melts. Therefore,  $D$  and  $G$  must have remained constant, which requires that spherulite formation have taken place at approximately constant temperature. This would have been possible only during the earliest phase of cooling at about  $900\text{--}1000^\circ\text{C}$ ,

or very late in the cooling history at 200–300°C. Because the diffusion rate in the andesite glass would have decreased with temperature and reached a very small value at 200–300°C, it is most likely that spherulite formation took place at 900–1000°C. The extrapolated value of  $D$  for this temperature range is  $2 \times 10^{-9}$  cm<sup>2</sup>/sec, which gives an estimated growth rate,  $G$ , of about  $10^{-6}$  cm/sec, or a total growth time of 1 to 2 days.

Greig (1928) has reported that spherulites up to 3/4 in. in diameter formed in artificial glass in about two days which suggests a slightly greater growth rate than that estimated here. In experiments on the devitrification of rhyolite glass at temperatures of 240–650°C and water pressures up to 4 kbar, Lofgren (1967) reported devitrification rates of  $10^{-7}$  cm/sec in the presence of alkali-rich solutions in contrast to devitrification rates of  $10^{-10}$  cm/sec in the presence of pure water. Although the conditions of Lofgren's experiments differ greatly from those at which the spherulites described here are thought to have formed, his results indicate that an alkali-bearing fluid phase facilitates spherulite growth. This fact, as well as the high temperatures estimated for spherulite formation in the andesite emphasize the previously suggested possibility that the low potassium content of the groundmass could be the result of the escape of a potassium-bearing fluid during and after spherulite formation.

#### CONCLUSIONS

The results of this study indicate that spherulite formation in silicate melts results in the partitioning of elements between the spherulite and groundmass as well as the concentration of "impurity" elements into areas between fibers in the spherulite and in a peripheral zone around the spherulites. These features have been noted in polymer melts and have been predicted to be in other spherulite-forming systems (Keith and Padden, 1963). The spherulites described here formed at about 900 to 1000°C and grew at the rate of  $10^{-6}$  cm/sec.

#### ACKNOWLEDGMENTS

G. K. Billings and R. E. Ferrell furnished helpful advice during the atomic absorption and X-ray diffraction analyses. G. E. Lofgren kindly called the writers' attention to the publications of Keith and Padden referred to in this paper and along with S. A. Heath and R. E. Ferrell, provided stimulating discussion and criticism of the ideas presented here.

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*Manuscript received, February 19, 1968; accepted for publication, July 23, 1968.*