

SULFIDE SPHERULES IN VESICLES OF DREDGED PILLOW BASALT¹

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ABSTRACT

Virtually all samples of fresh, submarine, pillow basalt dredged from the ocean floor contain spotted vesicles in their outer glassy margins. The spots also occur in vesicles in some drastically quenched lava erupted subaerially. The spots are minute spherules ranging from 0.2 to 2.5 microns in diameter, which are rather evenly spaced at 1 to 8 microns apart on the vesicle walls. Electron microprobe analyses indicate that the spherules are composed primarily of Fe, S, Cu, and Ni.

The spherules apparently form by diffusion of Fe, Cu, and Ni from the basalt melt toward pre-existing vesicles. The vesicles themselves were probably formed by exsolution of a volatile phase deficient in water and composed primarily of sulfur and carbon compounds; in pillows of average water content, water is too soluble in basalt melt to exsolve at depths greater than a few thousand meters. Reaction of S with Fe, Cu, and Ni presumably produced droplets of an immiscible sulfide liquid, which quenched upon continued cooling and formed the spherules on the vesicle walls.

A similar mechanism may account for the formation of larger, chemically similar, sulfide globules (up to 0.5 mm in diameter), which have been found in fresh basalt pillows as well as in surface lava flows. They may form at a melt-volatile interface within a subsurface magma reservoir and then be reincorporated into the melt prior to eruption on the surface.

INTRODUCTION

A study of thin sections of fresh pillow basalts dredged from several oceans reveals that curious spotted vesicles are a widespread, if not ubiquitous, feature of such rocks. These vesicles are best developed in the outer glassy rim of the pillows, where they are nearly spherical and are enclosed by pale-brown sideromelane. Further into the pillow, they become more irregular in shape and are enclosed either in opaque glass charged with feathery crystallites or in microcrystalline groundmass materials.

The walls of the spotted vesicles are covered with rather evenly spaced spherules, from 0.2–2.5 μm in diameter. These spherules are composed primarily of iron, sulfur, and copper.

In addition to the spherules in vesicles, some submarine lavas contain much larger globules (5–500 μm in diameter) which are chemically similar. Throughout this paper, the term *spherules* will be used for the small sulfide masses in vesicles, and *globules* will be used for the larger masses in the body of the rock, generally surrounded by basalt glass in the outer parts of pillows.

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OCCURRENCE

Spherule-lined vesicles are most common in sideromelane glass in drastically quenched volcanic rocks. They are best seen in the outer glass skin of subaqueously erupted pillow basalts containing small vesicles. If the vesicles are small compared with the thickness of the thin section, then the chances are greater that part of the vesicle wall will be inclined to the plane of the section and more of the spherules on the vesicle wall will be visible.

Most of the spherule-lined vesicles examined are from deep-water submarine basaltic pillows, but they have been found in the rims of several pillows produced in meltwater ponds by subglacial eruptions in Iceland. Structural and stratigraphic features indicate that the water depth at the time of eruption of these pillows was as shallow as 170 meters (J. G. Jones, written communication, 1969).

Pillows produced by flow of the 1801 lava into the sea on the west cape of the Island of Hawaii contain no clearly defined spherules in their vesicles, although vesicle walls show a minute patterned texture.

Sideromelane glassy ash produced by littoral explosions where aa lava flows enter the sea was examined for spotted vesicles. They are not present in the ash of the 1840, 1868, or 1919 littoral cones on the Island of Hawaii.

The glassy outer crust of several air-quenched pahoehoe lava flows on the Island of Hawaii was found to lack the spotted vesicles. However, spherule-lined vesicles were found in basaltic spatter and pumice from lava fountains in several recent eruptions of Kilauea Volcano, Hawaii, and Robert L. Smith reported (written communication, 1969) spherules in vesicles of the glassy crust of the 1959 Kilauea Iki lava lake in Hawaii. Some samples of pumice from the 1961 summit eruption of Kilauea Volcano contain the characteristic spherules. The spots are extremely small, generally 0.1 to 0.2 microns in diameter, and hence at the lower size limit of those identified in pillows.

The spotted vesicles have not been found in the quenched oozes that rise in holes drilled in the recent lava lakes on Kilauea Volcano.

Finally, Robert L. Smith also reported that a search of several glassy rocks of more siliceous composition revealed the spherules in only one sample: a dacite bomb from the 1875 eruption of Askja Volcano, Iceland.

These occurrences suggest that the spotted vesicles are present in rocks (1) that are drastically quenched either by air or water, and (2) in which the original magmatic gas has not had a chance to escape, either because of confining water pressure or proximity to the erupting vent.

Sulfide globules are much larger than the spherules (up to 0.5 mm in diameter) and are not associated with vesicles. They have been found in

the outer glassy rims of some pillows, in oozes which have moved into holes drilled in the crust of lava lakes in Hawaii (Skinner and Peck, 1969), and in some prehistoric lava flows in Hawaii (Desborough, *et al.*, 1968).

DESCRIPTION

Spherule-lined vesicles range from 10 μm to several millimeters in diameter. The walls of the vesicles are covered with spherules (Figure 1) that range from about 0.2 to 2.5 μm in diameter and are spaced approximately equal distances apart, the average spacing ranging from 1 to 10 μm from vesicle to vesicle. Under high magnification, the spherules generally look circular (spherical) or slightly irregular, but details of shape cannot be resolved because of their small size. They are opaque or dark yellow brown or red brown, but these colors are questionable because of optical effects inherent in viewing objects of this small size. Under reflected light some of the spherules show surfaces which reflect light brilliantly.

When a vesicle wall is cut perpendicular to the plane of section, individual spherules appear to be half embedded in glass, and half protruding into the vesicle.

In vesicles containing the larger spherules, a second "generation" of smaller spherules about one-fifth the diameter of the larger is commonly present in the area between the larger ones (Figures 1 B, C).

The sulfide globules found in pillow basalts are up to 0.5 mm in diameter and are hence vastly larger than the spherules (Figure 2). They are not associated with vesicles but occur as nearly perfect spheres surrounded by sideromelane. In polished section, the outer surfaces of the globules appear smooth and sharp, and internally they appear to be composed of a single mineral phase.

Electron photomicrographs (Figure 1B) show that the spherules are rather perfect spheres embedded about half way into the glass of the vesicle walls. Preparation of a plastic replica for electron microscopy resulted in dislocation of about half of the spherules from their sockets. The spherules do not appear to have any crystal faces. The vesicle sides of the spherules are quite smooth, whereas the glass pits in which they lie show a minute hummocky surface.

In a given vesicle, the size and spacing of the spherules are remarkably constant. However, these dimensions vary from one vesicle to another within the same sample and from sample to sample. Size and spacing are controlled mainly by the rate of cooling, a function of the distance of the vesicle from the rim of the pillow (that is, from the cooling surface). In all pillows studied, the size and spacing of the spherules show a systematic

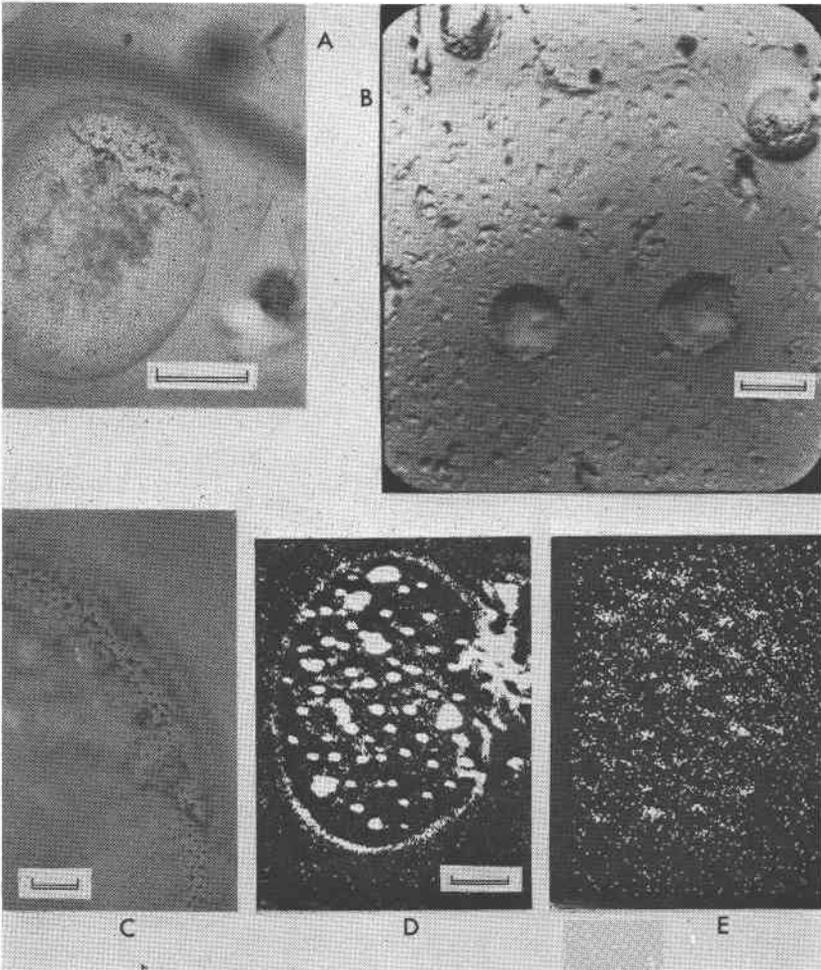


FIG. 1. Photomicrographs of spotted vesicles from dredged pillow basalt.

- A. Sample D-22. Mid-Atlantic Ridge near 60° N Lat. Depth, 930–1025 m. Scale is 100 μm long; small olivine crystal on right.
- B. Sample 29-11-1a. Juan de Fuca Ridge off Washington state. Depth, 2400–2520 m. Electron photomicrograph of platinum-shaded replica. The two circular shapes in center are replicas of spherules themselves, while the two circular shapes on top are replicas of pits from which the spherules have been plucked. Scale is 1 μm long.
- C. Sample D-22. Same vesicle as A. Note tiny spherules between larger spherules. Scale is 20 μm long.
- D. Sample 29-11-a. Juan de Fuca Ridge off Washington state. Electron beam scanning photograph showing back scattered electrons. Brightness is proportional to mean atomic number. Scale is 10 μm long.
- E. Sample 29-11-a. Electron beam scanning photograph showing same area as D. Brightness is proportional to sulfur content. Scale same as D.

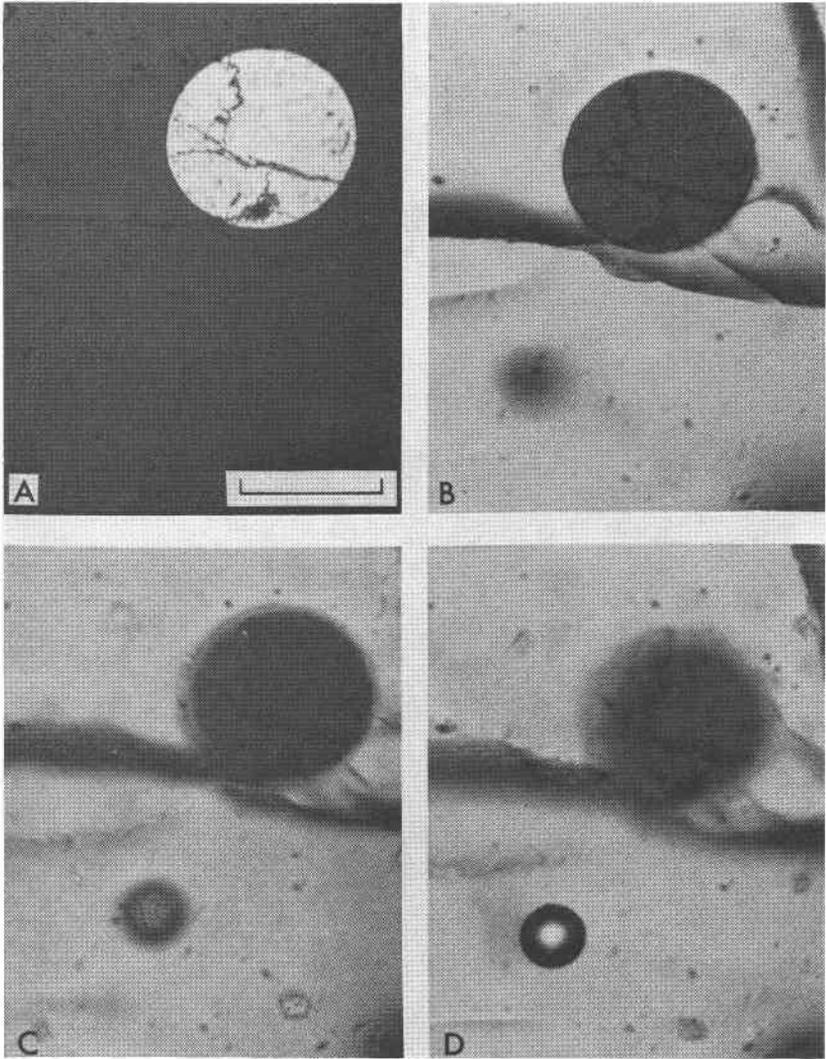


FIG. 2. Photomicrograph of polished thin section showing a spherule lined vesicle and a sulfide globule from a basalt pillow (Sample 29-15-7a) collected from 1350-1400 m depth on the Juan de Fuca Ridge (Table 2). All photographs are of the same area taken under different lighting and focus conditions; scale is 50 microns long. A, reflected light, sulfide globule in top center. B, largely transmitted light. C, transmitted light, deeper focus than B showing small vesicle near bottom with regularly arranged sulfide spherules. D, still deeper focus than C showing outer tooth-like fringe of vesicle resulting from spherules extending partly into surrounding sideromelane.

increase progressing inward from the outer rim (Figure 3). Within 2 mm of the outer pillow rim, the spherules in vesicles are commonly less than $0.5\ \mu\text{m}$ in diameter and are spaced about $2\text{--}3\ \mu\text{m}$ apart, but 8 mm from the outer rim, the spherules are typically about $2\ \mu\text{m}$ in diameter and are spaced $5\text{--}6\ \mu\text{m}$ apart.

The vesicles themselves show no systematic increase in size inward from the pillow rim, at least in the outer 1 cm zone of transparent glass. They may, however, become slightly more abundant inward from the pillow rim.

Other factors that affect the size and spacing of the spherules are the size of the containing vesicle, the depth of eruption, and the chemistry and volatile content of the enclosing basalt. However, the effect of rate of cooling (as measured by distance from the pillow rim) is so dominant that the other factors can be evaluated only by statistical treatment of many measurements on different samples.

Calculations of the volume of spherule material within the vesicles show that more material is present within vesicles that are deeper within the pillows. The volume of spherule material can be compared by calculating its thickness if all the spherules were evened out to form a continuous layer lining the vesicle. For example, by using the data for sample 1712 and assuming that the spherules are spherical and are arranged on a rectangular grid, we find that nearly 10 times more material is present in the spherules 8 mm in from the pillow rim than in those 2 mm in from the pillow rim (Figure 3). Even if the spherules become flatter (less spherical) as they become larger, almost certainly more spherule material is present in the vesicles which contain larger spherules. This suggests that the increase in size and spacing inward from the pillow rim is the result not simply of slower condensation and nucleation of the volatile component within the vesicles, but instead, of slower cooling that allows more complete diffusion of elements toward the vesicles, and more complete reaction of these elements with those already in the vesicles.

CHEMISTRY

Spherules were analyzed with the electron probe microanalyzer. Beam scans were made on entire sectioned vesicles in uncovered, polished thin sections, but concentrations of individual elements in the spherules are masked by the presence of the basaltic glass of the vesicle wall. Back scattered electron beam scanning photographs (Figure 1D) show that the mean atomic number of the spherules is considerably higher than that of the enclosing basaltic glass. Sulfur is the only element that clearly shows a concentration within the spherules relative to the surrounding basaltic glass in beam scanning images (Figure 1E).

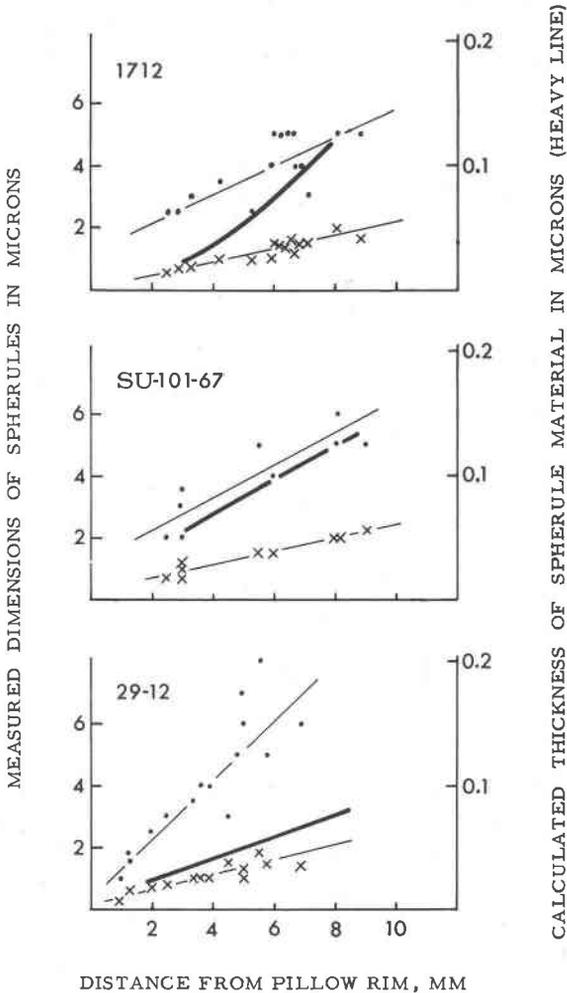


FIG. 3. Dimensions of spherules within vesicles from dredged pillow basalts plotted against the distance inward from the pillow rim. Crosses, measured diameter of spherules; dots, measured average spacing of spherules; heavy line, calculated thickness of spherule material if it were evened out in a continuous layer on the vesicle wall. Sample 1712: depth 4680 m, east rift zone ridge of Kilauea volcano, Hawaii. Sample SU-101-67, depth 2690–3000 m, north ridge Roca Partida, Revillagigedo Islands, Mexico. Sample 29-12, depth 2300–2740 m, Juan de Fuca Ridge off Washington State.

An attempt to scrape the spherules out of the vesicles with a micro-needle failed, probably because the spherules are half embedded in the vesicle walls. The spherules do not appear to dissolve in toluene or concentrated nitric acid when uncovered thin sections are treated; however,

the difficulty of optically distinguishing spherules from the pits in which they are seated makes these observations inconclusive.

Individual spherules were obtained by painting polished uncovered thin sections with liquid collodion and peeling off the dry collodion, to which some of the spherules adhered. Squares of collodion containing spherules were cut from the peel, placed on a polished Be probe mount, and washed with amyl acetate while being observed under the microscope.

The microprobe analyses (Tables 1 and 2) were made utilizing different combinations of excitation potential and specimen current. Intensities of $K\alpha$ X-ray lines were integrated over 20 seconds using LiF, ADP, and KAP crystals, and sealed and flow proportional counters.

The seven analyses of spherules (unpolished surfaces) shown in Table 1 were made using pyrite as a standard for Fe and S, synthetic plagioclase (An_{60}) for Ca, and pure-element standards for Mg, Al, Si, Cu, and Ni.

TABLE 1. MICROPROBE ANALYSES OF SPHERULES FROM VESICLES IN PILLOW BASALTS

	1	2	3	4	5	6	7
Vesicle	—	—	1a	1a	1a	3	3
Excitation potential (kV)	15	15	20	15	15	20	20
Specimen current set on Be std. (μA)	.02	.02	.005	.01	.02	.005	.005
Normalized weight percent [n.d., not determined]							
MgO	—	0.5	—	—	—	—	—
Al ₂ O ₃	—	1.0	—	1.0	0.5	—	—
SiO ₂	0.5	0.5	1.0	6.0	2.0	0.6	1.0
CaO	—	1.5	—	1.0	0.5	—	—
S	47.0	33.0	37.5	32.0	31.5	39.5	35.5
Fe	49.5	63	55.0	54.0	61.5	54.0	56.0
Cu	n.d.	n.d.	6.5	6.0	4.0	6.0	7.0
Ni	3.0	trace	n.d.	n.d.	n.d.	n.d.	0.5
Total, original analysis	58.43	31.42	60.04	38.64	30.62	27.25	23.29
Diameter of spherule, μm	n.d.	n.d.	2.3	2.3	2.3	1.2	1.2
Mole Ratio (Fe + Cu + Ni):S	0.64	1.09	0.92	1.06	1.19	.86	1.01

1. Sample 29-11-1a. Juan de Fuca Ridge off Washington State. Depth, 2,400–2,520 m.
 2–7. Sample D-22. Mid-Atlantic Ridge near lat 60°N. Depth, 930–1,025 m.

TABLE 2. MICROPROBE ANALYSES OF SULFIDE GLOBULES IN PILLOW BASALTS
Normalized weight percent (except col. 5)

	1	2	3	4	5
Fe	53.8	57.3	55.9	54.8	53.60
Cu	9.5	7.6	9.2	9.4	10.83
Ni	.9	1.6	1.5	1.2	1.57
S	35.8	33.5	33.4	34.6	33.13
Total, original analysis	89.3	92.3	85.0	90.6	99.13
Apparent diameter of globule in thin section, μm	6.5	7.7	5.3	7.0	63
Mole Ratio (Fe+Cu+Ni):S	1.01	1.12	1.12	1.07	1.13

Instrumental conditions: 15 kV excitation potential, 0.01 microamps specimen current set on sulfide standard

1-3. Sample 29-12-5a. Juan de Fuca Ridge off Washington State. Depth, 2,400 m.

4, 5. Sample 29-15-7a. Juan de Fuca Ridge off Washington State. Depth, 1,350-1,400 m.

Background corrections were made, but other corrections were not attempted because of the small size and unpolished surface of the samples. The spherule analyses must be considered as qualitative estimates only.

Five analyses of sulfide globules in polished thin sections of the pillow basalts were made using synthetic sulfide standards prepared by Gerald K. Czamanske (Table 2). Ni, Fe, and S contents were compared with a standard composed of $\text{Ni}_{1.89}\text{Fe}_{59.20}\text{S}_{38.92}$ (weight percent), and Cu was compared with a standard composed of $\text{Cu}_{34.36}\text{Fe}_{32.62}\text{S}_{33.01}$. Corrections for background, instrumental drift, absorption, atomic number, and fluorescence were made by means of a computer program written (and later modified) by M. H. Beeson (1967; written communication, 1970).

Only one of the analyses (No. 5, Table 2) totals approximately 100 percent. The others do not because of the small size of both the spherules (unpolished) and globules (polished) (Page, *et al.*, 1968). Other microprobe analysts (White, 1964; White, *et al.*, 1966; and Bayard, 1967) have found that in some systems the ratio of intensities for two elements remains the same regardless of the size of the sample. Analyses in such systems can thus be normalized to 100 percent with some confidence. This has been shown to be true for iron and sulfur in pyrite on the basis of $K\alpha$ X-ray line intensities (N. Page, oral communication, 1970) and is probably true for iron and sulfur in these samples.

Fe, S, Cu, and Ni are the characteristic elements in both spherules and the larger globules. In addition, some spherules contain minor or trace amounts of Al, Mg, Si, and Ca. These elements are probably contained

in fragments of sideromelane clinging to the surface of the spherules and have therefore been calculated as oxides in Table 1. Traces of Si, Ca, K, and Ti were detected in the largest globule (sample 29-15-7a, Table 2).

Microprobe traverses across the globules indicate a single homogeneous phase. The small size of the spherules makes it impossible to determine if more than one phase is present.

ORIGIN

The sulfide spherules apparently formed by diffusion of Fe, Cu, and Ni from the basalt liquid toward the vesicles, which had formed slightly earlier, and by reaction of these elements with sulfur within the vesicles. The volatile phase which formed the vesicles was probably composed primarily of compounds of S, C, O, and H, by analogy with analyses of Hawaiian volcanic gases (Heald, *et al.*, 1963). But H₂O is probably not a major constituent in the deeper pillow vesicles since the solubility of water in basalt (Hamilton, *et al.*, 1964) would preclude exsolution at pressures greater than about 2,000 meters, if original water content were less than 1 percent (Moore, 1965). Hence, the main vesicle-forming phases in the deeper pillows are probably dominated by compounds of S and C. Concentrations of Fe, Cu, and Ni near the vesicle walls apparently reached a level where an immiscible liquid sulfide phase formed upon reaction with the S within the vesicle.

Formation of vesicles was so rapid that it was almost unaffected by the rate of cooling of the melt during formation of the pillow. Vesicles do not show a systematic increase in size across the outer 1 cm of the pillows in the zone in which the spherules increase in volume (Figure 3), although vesicles are rare in the outermost 1 mm. The inward increase in volume shown by spherules in vesicles is interpreted to reflect slower cooling which permitted more complete diffusion of elements to the vesicle walls and more complete reaction with S within the vesicles. This diffusion and reaction were stopped by quenching of the outer part of the pillow.

The spherules probably did not form by simple condensation, on vesicle walls, of part of the volatile phase in the vesicle because (1) the spherules are clearly embedded in the walls (Figure 1B), (2) they contain Ni and Cu in amounts that are unlikely in the volatile phase, and (3) the amount of material within vesicles varies.

Calculations of conductive heat flow from the surface of a semi-infinite solid (Carslaw and Jaeger, 1959, p. 59) show that the time required to cool a pillow from 1200° to 500°C with the outer surface held at 0°C, and with diffusivity of 0.007, is 10 seconds at a surface 2 mm inside the outer rim, 40 seconds at 4 mm, 95 seconds at 6 mm, and 155

seconds at 8 mm. These times are roughly proportional to the volumes of spherule material (Figure 3), which indicates the importance of cooling rate in spherule formation.

Increase in size and spacing of the spherules inward from the pillow rim is presumed to result from slower cooling and formation of wider spaced nucleation centers. Although the increase in spacing may result partly from continued expansion of the vesicles after nucleation of the spherules began, expansion cannot account for the increase in size of the spherules.

The spherules form only in drastically quenched lavas because rapid cooling and increase in viscosity prevent the rise and escape of the vesiculating gas phase along with the elements which have diffused into that phase. Furthermore, the spherules are best developed if eruption (and exsolution) takes place under high confining pressure (as with submarine eruptions) and thus produces a volatile phase of relatively high density.

Spherule-lined vesicles are not well developed in air-quenched lava flows, or in flows that erupt on land and pour into the sea and produce pillows, because much of the volatile phase escapes during flowage over the ground surface, and the volatiles that remain expand to such an extent that their density is low. The poorly developed spherules that occur in spatter and pumice from lava fountains perhaps form because drastic air quenching near the vent traps some of the higher density volatiles. Because of volatile retention, one would expect the bulk sulfur content of basalt erupted subaqueously to be higher than that of the same basalt erupted subaerially.

The composition of both spherules and globules is similar though the globules contain more Cu and less Fe. The globules and spherules have about the same bulk composition as do polymineralic sulfide grains found in subaerial Hawaiian basaltic lava flows (Desborough, *et al.*, 1968) and in basaltic oozes which flowed into a drill hole in the crust of Alae lava lake, Hawaii (Skinner and Peck, 1969). The basalts in these two occurrences have not been subjected to drastic quenching as have the pillow basalts, and consequently what one may presume to have been sulfide globules have unmixed upon slower cooling into intergrown aggregates of Cu-Fe-S monosulfide solid solution (pyrrhotite?), magnetite, and Fe-Ni sulfide (Desborough *et al.*, 1968) or to pyrrhotite, chalcopyrite, and magnetite (Skinner and Peck, 1969).

Because the globules and spherules appear to represent quenched, homogeneous, sulfide liquids, the temperature of quenching can be estimated from the determined compositions (Tables 1 and 2). Work on the system Cu-Fe-S by Grieg, Jenson, and Merwin (1955) indicates that a homogeneous sulfide melt with the Fe/Cu and metal/S ratios of the

globules and spherules must have been quenched at 1050–1075°C. Recent work by Craig and Kullerud (1969) indicates that the low Ni contents determined will not substantially change this temperature estimate.

The restriction of the spherules to the melt-volatile interface raises questions about the origin of the larger, but chemically similar, sulfide globules that are present in the glass and groundmass of some pillows. These globules are not associated with vesicles and are chemically similar to the polymineralic grains which occur in subaerial Hawaiian basalts (Skinner and Peck, 1969; Desborough, *et al.*, 1968). The fact that basalt pillows collected at depths as great as 5,000 meters contain some small vesicles (Moore, 1965, Table 3; Engel and Fisher, 1969, p. 1138) indicates that the basalt melt is saturated with a volatile phase at 0.5 kilobars pressure and that exsolution takes place. This pressure is greater than that in the upper part of the shallow magma reservoirs beneath some active volcanoes. Fiske and Kinoshita (1969) have shown that the reservoir beneath Kilauea Volcano may be as shallow as 2 km. Hence, volatiles will exsolve under these conditions and may be important in deforming the volcano prior to eruption. Some of the volatiles may be trapped in places where elements can diffuse toward the melt-volatile interface to produce immiscible sulfide liquids on a scale larger than that which occurs within the vesicles in pillows. Such sulfide liquids may be reincorporated within the melt and may be carried to the surface during eruptions as the larger sulfide globules.

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