

DEVITRIFICATION DIKES AND GIANT SPHERULITES FROM KLONDYKE, ARIZONA¹

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ABSTRACT

Vitrophyric rhyolite welded tuff near Klondyke, Arizona, contains thin dike-like sheets and spheroids as much as 6 feet across that have formed by devitrification of the original glassy rock. Chemical analyses show the devitrified tuff to have markedly more potash and less soda than its vitreous equivalent. Devitrification is believed to have been an autometamorphic process brought about by passage of potassium-rich fluids along fractures during welding and cooling of the tuff. A similar chemical trend is noted in some devitrified rocks of Great Britain.

INTRODUCTION

During the course of mapping the Klondyke quadrangle, Arizona, some striking devitrification features were noted in a rhyolite welded tuff. A cursory review of the literature reveals only scattered observations of similar features, and it therefore seems worthwhile to call attention to the exceptionally well-exposed examples at Klondyke.

GEOLOGIC SETTING

The Klondyke quadrangle is in Graham County, Arizona, about 55 miles northeast of Tucson. The northeast quarter of the quadrangle is occupied by parts of the north-northwesterly-trending Santa Teresa-Turnbull Mountains mass, the bulk of which is made up of sedimentary rocks of Paleozoic and Late Cretaceous age, plutonic igneous rocks of Precambrian and Tertiary age, and metamorphic rocks of Precambrian age. Along the west flank of the mountains is a thick sequence of dominantly silicic volcanic rocks of possible Late Cretaceous to early Tertiary age which either are faulted against or rest unconformably on the older rocks. The rock in which the devitrification features were noted is exposed along the east side of a gully in the center of sec. 18, T. 6 S., R. 20 E., about 2,000 feet east of the road to Imperial Mountain and 5 miles north of Klondyke. In this area the volcanic rocks are silicic lavas, flow breccias, tuffs, and welded and partly welded tuffs that strike N. 25°-30°W. and dip 55°-60°SW.

One unit of the sequence is a lens of black vitrophyre as much as 40 feet thick that is exposed for 900 to 1,000 feet along the strike (Fig. 1). The lens appears to pinch out to the northwest and is covered by alluvium at its southeast end. The vitrophyre is a hard glassy rock with subconchoidal to somewhat hackly fracture and contains scattered

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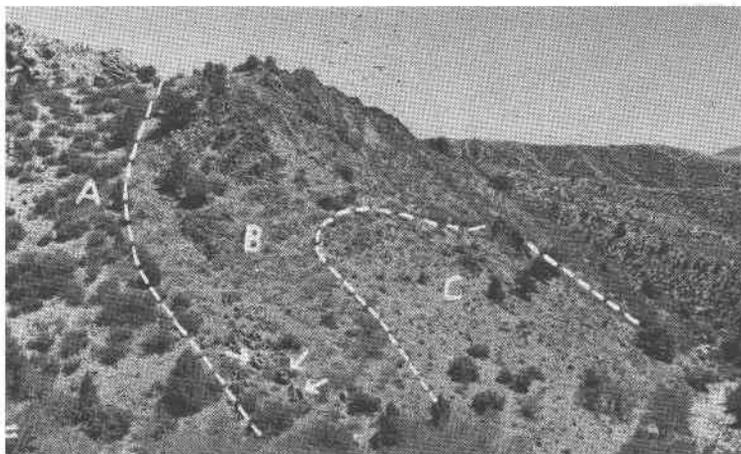


FIG. 1. Lens of vitrophyric rhyolite welded tuff (B) dipping 55° – 60° to the right and somewhat toward the observer. The lens is about 40 feet thick. It is underlain by pale red partly welded tuff (A) and overlain by grayish red welded tuff (C). The devitrification “dikes” are best exposed on the steep slope below the highest outcrop; the giant spherulites crop out along the entire slope and seem to be concentrated near the top of the vitrophyric welded tuff just beneath unit C. Arrows point to outcrops of several giant spherulites.

millimeter-sized phenocrysts of feldspar and sparse biotite and quartz. It grades downward through 15–20 feet of mottled black and red partly vitrophyric welded tuff to a sharp contact with pale red¹ partly welded rhyolite tuff 10–30 feet thick. The vitrophyre lens is overlain by grayish red solidly welded and almost completely devitrified rhyolite tuff of unknown but appreciable thickness. All these rocks are believed to be parts of a single tuff deposit, the lithologic variations being due mainly to differences in degree of welding and devitrification.

Under the microscope the vitrophyre consists of densely welded pale brown glass shards enclosing euhedral to subhedral grains of oligoclase, sanidine, and minor brown biotite and quartz, as well as sparse pumice lapilli and lithic fragments (Fig. 2).

DEVITRIFICATION DIKES

The vitrophyric welded tuff is cut by numerous steep-dipping dike-like bodies of moderate brown devitrified rock that contrast strongly with the black vitrophyre (Fig. 3) and stand out in slight relief from the vitrophyre upon weathering. These “dikes” are confined to the vitrophyre, although at least one “dike” structure is represented in the under-

¹ This and succeeding colors are from the Rock Color Chart, *National Research Council*, 1948.

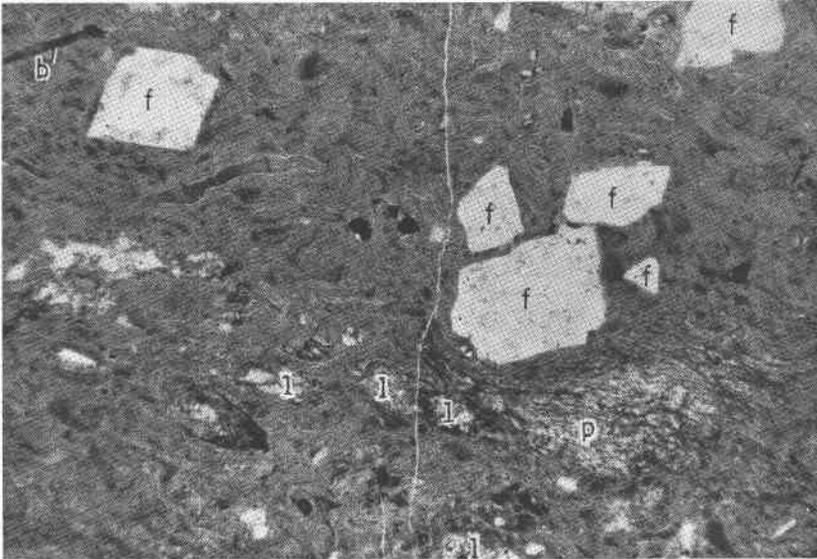


FIG. 2. Photomicrograph of vitrophyric rhyolite welded tuff. f—plagioclase; b—biotite; l—lithic fragment; p—pumice; rest of field is pale-brown glass shards. The vitroclastic texture is clearly preserved but the shards are densely welded. Plane polarized light, $\times 50$.

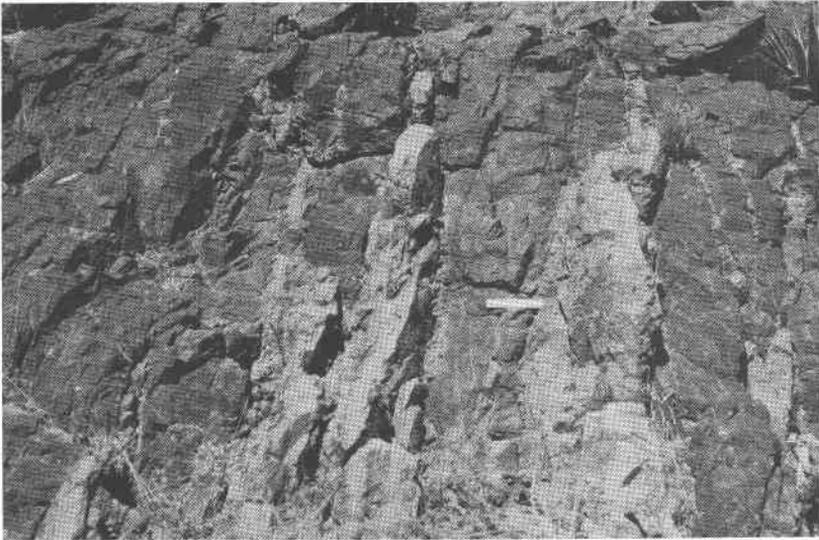


FIG. 3. Light-colored devitrification "dikes" in black vitrophyric welded tuff. Scale is $7\frac{1}{2}$ inches long, widest "dike" is about 14 inches wide. All these "dikes" pinch out uphill just above field of photograph. The vitrophyre between the two largest "dikes" is cut by several smaller "dikes" not clearly visible in the photograph.

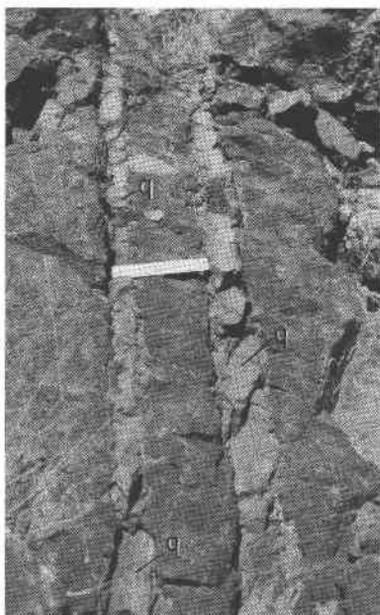


FIG. 4. Light-colored narrow devitrification "dikes" in black vitrophyric welded tuff. Scale is $7\frac{1}{2}$ inches long. Note the thin white median layer of quartz (q) in both "dikes," particularly the right-hand "dike." Left-hand "dike" continues uphill for 15-20 feet above field of photograph; both "dikes" pinch out just below field.

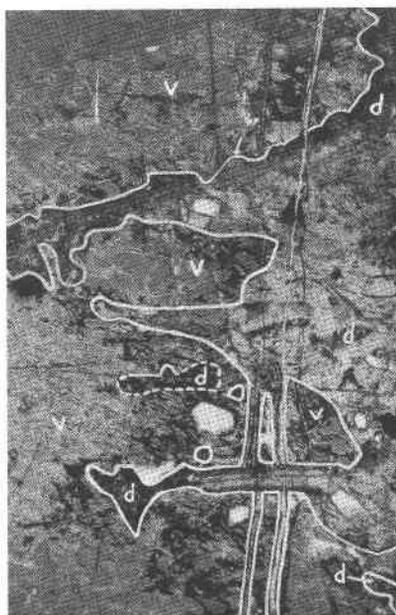


FIG. 5. Photomicrograph of irregular contact between vitrophyre (v) and "dike" of devitrified rock (d). Textures on both sides of the contact are essentially identical except where the original texture has been destroyed by growth of incomplete spherulites, as along the upper right-hand segment of the contact. Plane polarized light, $\times 33$.

lying partly welded tuff by a simple fracture. The "dikes" are rather irregular in width, ranging from a fraction of an inch to about 3 feet across; most are an inch or less wide. Near the southeast end of the vitrophyre lens, numerous ramifying "dikes" divide the vitrophyre into a mosaic of irregular blocks. All the "dikes" are divided symmetrically along their centers by a thin layer of quartz. The thickness of the quartz layer appears to be roughly proportional to the width of the enclosing "dike" but is less than 2 millimeters regardless of "dike" width.

Contacts between vitrophyre and "dikes" may be irregular with many sharp bends, re-entrants, etc., as shown in Fig. 3, or may instead be essentially straight for appreciable distances, as in Fig. 4. The contacts invariably are sharp, and no transition from stony to vitrophyric is detectable with a hand lens. Within the "dikes" themselves, however, the rock flanking the quartz core is slightly darker than that in contact

with the vitrophyre, the color changing gradually outward from moderate brown to light brown. The core rock also is more resistant to weathering than is that along the contacts, which on weathered surfaces commonly are marked by a shallow trench resulting from the disintegration of rock along both sides of the contact.

On a microscopic scale the contacts between "dike" and vitrophyre are exceedingly irregular, with narrow tongues of one rock penetrating the other (Fig. 5). The contacts are, however, quite sharp, and provide almost no evidence of any transition between the two rocks. Locally, the original vitroclastic texture has been obliterated by the formation of incomplete spherulites, but for the most part is clearly preserved in the devitrified rock. Only a few tiny islands of glassy rock have survived devitrification. Within the devitrified rock, none of the phenocrystic minerals appear to have been altered at all during devitrification.

The quartz seams along the centers of the "dikes" consist of a core of granular quartz flanked by narrow irregular selvages made up of tiny rhomb-shaped grains of adularia (?) in a fine-grained matrix that may be cristobalite or tridymite (Fig. 6); in general the minerals of the selvages are too fine grained to be identified positively in thin section. The straight sharply defined walls of the quartz seams and the complete lack of any evidence suggesting replacement of the host rock indicate that the seams must be true fissure fillings. The sequence of development appears to have been: 1) fracturing of the welded tuff to produce narrow open fissures; 2) deposition of a little very fine-grained adularia (?) and cristobalite (?) or tridymite (?) along the walls of the fissures; and 3) complete filling of the fissures by quartz. Some of the quartz was deposited early in the third stage, as witness the two grains with hexagonal outlines near the left edge of Fig. 6, which must have been deposited prior to the final filling of the fissure.

The minerals formed during devitrification are too fine grained to be identified by optical methods. A sample of devitrified tuff carefully hand picked to remove phenocrystic minerals was examined with the x-ray spectrometer by Theodore Botinelly of the U. S. Geological Survey, who reports plagioclase feldspar, quartz, cristobalite, orthoclase and mica.

Chemical analyses of a devitrification "dike" and of its immediately adjacent vitrophyric wall rock are given in Table 1, columns 1 and 2; these samples must represent essentially identical original rock. The principal chemical change accompanying devitrification obviously has been addition of potash and removal of soda; the ratio $K_2O:Na_2O$ is about 1.4 in the glassy rock and 7.7 in the devitrified rock. The devitrified equivalent also is slightly more silicic and contains about 2 per cent less

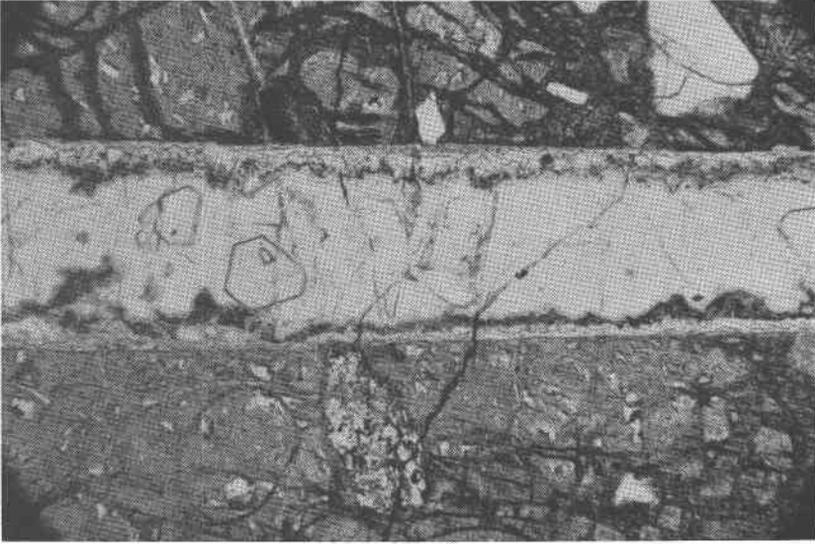


FIG. 6. Photomicrograph of median quartz seam in devitrification "dike." Wall rock is devitrified welded tuff. The quartz core, about 0.5 mm wide, is flanked by narrow irregular selvages composed of rhomb-shaped grains of adularia (?) in an irresolvable matrix that may be cristobalite or tridymite. Plane polarized light, $\times 45$.



1. Fresh vitrophyric rhyolite welded tuff, sec. 18, T. 6 S., R. 20 E., Klondyke quadrangle, Arizona. Analyst: Dorothy F. Powers, U. S. Geological Survey. Field No. 59K-S-63a; lab. no. F2676.
2. Same rock as (1), devitrified. Analyst, Dorothy F. Powers. Field no. 59K-S-63b; lab. no. F2677.
3. Average alkali rhyolite plus rhyolite obsidian. Nockolds, 1954, Table 1, col. IV.
4. Glassy leidleite (= dacite) with "sheath and core" structure, Mull, Scotland. Anderson and Radley, 1915, p. 212, col. Ia.
5. Stony (devitrified) leidleite, same locality as (4). Anderson and Radley, 1915, col. Ib.
6. Pitchstone porphyry from Cir Mhor dike, Arran, Scotland. Judd, 1893, p. 545, column III.
7. "Quartz-felsite" derived from (6). Judd, 1895, col. II.
8. Glassy leidleite, Mull, Scotland. Anderson and Radley, 1915, col. IIa.
9. Stony leidleite, same locality as (8). Anderson and Radley, 1915, col. IIb.
10. Glassy leidleite, Mull, Scotland. Anderson and Radley, 1915, col. IIIa.
11. Stony leidleite, same locality as (10). Anderson and Radley, 1915, col. IIIb.
12. Black obsidian flow, Colle de la Motte, Esterel, France. Terzaghi, 1948, Table 1, col. 11.
13. Devitrified obsidian "a few hundred feet" from (12). Terzaghi, 1948, col. 7.
14. Perlite, Wenatchee, Washington. Coombs, 1952, Table p. 202, col. 2.
15. Spherulitic breccia, presumably derived from (14). Coombs, 1952, Table p. 202, col. 3.



FIG. 7. Giant spherulite in vitrophyric welded tuff. Scale is $7\frac{1}{2}$ inches long, spherulite is about 3 feet across.

total water than the fresh rock; however, the weakly perlitic structure of the glass suggests that at least some of the H_2O^+ is not pristine, and if the original water content be taken as, say, 0.4 per cent, following Ross and Smith (1955, p. 1081-1082), and the analyses recalculated, then the silica percentages become nearly equal.

Semiquantitative spectrographic analyses by Nancy M. Conklin, U. S. Geological Survey, of 56 minor elements in the two rocks show only the following changes (data are in per cent); all are of one order of magnitude, and none is believed to be significant.

Element	Vitrophyre	Devitrified equivalent
Ba	.03	.07
Cr	.00015	.0003
Ga	.0015	.0007
Sr	.015	.03
Yb	.0003	.0007

GIANT SPHERULITES

The vitrophyric welded tuff also contains numerous spheroidal masses of devitrified rock identical lithologically with the devitrification "dikes." Field evidence, although inconclusive, suggests that the spheroids are concentrated in the upper part of the vitrophyre lens. A number are clustered near the northwest end of the lens (Fig. 1). The spheroids range in diameter from a few inches to 6 feet or more, and average perhaps 3 feet across (Fig. 7). They consist of a core of moderate brown

dense stony material encased by a thin crust, a few inches thick at most, of light-brown somewhat crumbly rock. Most spheroids observed were divided roughly in half by a thin quartz seam. One large spheroid 5–6 feet across passes uphill abruptly into a narrow devitrification “dike,” and it seems likely that others could be shown to do so if exposures were more complete.

Microscopically, the rock composing the spheroids is identical with that of the “dikes.” Although the spheroids are demonstrably not the result of the simple spherulitic crystallization responsible for the common spherulites of glassy volcanic rocks, but rather are compound—made up of a great many spherulitic, radiolitic, or axiolitic aggregates—nevertheless their origin and external form would seem to permit use of the name spherulite.

RELATED FEATURES FROM OTHER LOCALITIES

The pitchstone sills and sheets of Mull (Anderson and Radley, 1915) exhibit phenomena very similar to the devitrification “dikes” at Klondyke. These sills are commonly composed of leidlite (a rock near dacite in chemical composition). A typical sill is 11–12 feet thick and consists of a core 5 feet or so thick of glassy rock or pitchstone and margins perhaps 3 feet thick of stony devitrified rock. The transition between pitchstone and stony rock is abrupt but the stony portion does not resemble a chilled margin. The pitchstone may be split by stony partings. A feature of these rocks, first described from the Eskdale pitchstone by Geikie (1880) as “sheath and core” structure is discussed in some detail by Anderson and Radley (1915), who say (p. 210):

“The stony [devitrified] base and top of the intrusion send off arms, or, more accurately, narrow sheets of similar material, which traverse the glassy portion in a branching and sinuous manner, completely dividing it into irregular rounded cores, which are not in visible contact. In many cases the sheaths of crystalline matter, which vary from a quarter of an inch to 3 inches in thickness, show a median joint or suture-line, along which terminate numerous minute transverse joints.”

Along one median suture noted in thin section, the first mineral to form was quartz, followed by “a thin layer of some mineral having a very low refractive index; then by further quartz, and in places limonite” (Anderson and Radley, 1915, p. 213–214).

The Cir Mhor dike of Arran in western Scotland (Judd, 1893, p. 543–551) is a composite dike 12–30 feet wide with a center of highly silicic rock and selvages of andesite. The silicic dike in turn has a core of pitchstone porphyry flanked by a devitrified equivalent of the pitchstone called “quartz-felsite” by Judd. No cross-cutting devitrification features are mentioned, but the stony selvages otherwise resemble closely

the devitrification "dikes" and are considered by Judd to be results of primary devitrification, that is, devitrification taking place during consolidation of the dike (Bonney and Parkinson, 1903).

Terzaghi (1948, p. 24) noted that devitrification is limited to the immediate vicinity of cracks in an obsidian of the Esterel, France.

Spherulites as large as those from Klondyke apparently are rather rare; at least few are mentioned in the literature examined. Cross (1891; 1896, p. 298-299, Pl. 28) has described giant compound spherulites in pitchstone at the base of a rhyolite flow at Silver Cliff, Colorado; here many of the spherulites are 5 feet in diameter and some are more than 10 feet across. The large spherulites are embedded in a "white mixture of opaline silica and kaolin resulting from decomposition of the pitchstone . . .". According to Iddings (1909, p. 239-240, Fig. 77), these spherulites "appear to have formed by the rapid growth of rays of plumose spherulitic aggregates outward from a central core and the final radial growth of a denser layer forming an outer spherical shell. The whole of the inclosed rock, or magma, is not necessarily crystallized in radial arrangement. It may even be glassy in part." Fuller (1931, p. 64) noted some spherulites as much as 3 feet in diameter in the "upper laminated rhyolite" of Steens Mountain, Oregon.

CHEMICAL CHANGES ACCOMPANYING DEVITRIFICATION

Glass is generally considered to be an undercooled highly viscous (rigid) liquid (Morey, 1954, p. 28), although some investigators have referred to glass as an amorphous solid in recognition of certain changes in physical properties said to occur upon cooling when the glass attains a particular viscosity (for instance, Hawkes, 1930). X-ray diffraction studies of various glasses by Warren and others (summarized in Stanworth, 1950, p. 16-31) have shown the structure of glass to resemble that of a very distorted crystal lattice. Devitrification, or crystallization, of natural or artificial glasses may take place, provided that conditions permit the formation of stable nuclei, simply because an undercooled liquid or melt is thermodynamically unstable, and therefore may occur within a closed system; many spherulites in volcanic glasses must have formed under such conditions. Wholesale devitrification of natural glasses has been attributed to heat, pressure, circulating fluids, "power of spontaneous crystallization" or a combination of these factors (Harker, 1909, p. 226; Bonney, 1885, p. 82-95). Devitrification of the Klondyke vitrophyric tuff, however, is clearly related to fractures and must have been caused by fluids passing along the fractures. Devitrification cannot be attributed solely to heating by these fluids of the glass along the fractures, because the chemical analyses show that a marked compositional

change has occurred. Nor is it likely that the chemical changes noted could be a result of weathering or of the circulation of ground water. It is possible that devitrification was caused by later hydrothermal solutions or gases from extraneous sources, but the nearby rocks are unaltered, the "dikes" are completely different from anything I have seen or read about in hydrothermally altered volcanic rocks, and the apparent restriction of the "dikes" to the vitrophyre suggests a local source for the fluids responsible for the devitrification. The most probable source of the added potassium is the welded tuff itself or the partly welded tuff underlying it. Presumably therefore the potassium-rich fluids were erupted and transported along with the tuff, were trapped subsequently within it at the time of deposition, and later escaped along contraction cracks formed during cooling of the vitrophyre and now marked by the devitrification "dikes." Welding, fracturing, expelling of interstitial potassium-rich fluid, and devitrification all may have occurred at about the same time. Such a series of events might seem rather improbable, but apparently these devitrification features are unusual enough, at least in the Klondyke region, to have required uncommon circumstances; similar vitrophyric welded tuffs crop out over several square miles within the quadrangle, and many miles of contact are well exposed, but at no other place have these features been observed.

Paired analyses of fresh glass and its devitrified equivalent seem to be scarce in the literature, but a few are included in Table 1. A trend in the $K_2O:Na_2O$ ratio similar to although less pronounced than that in the Klondyke rocks is evident in analysis pairs 4-5, (ratio increases from 0.5 to 1.4), 6-7 (ratio increases from 1.0 to 1.3), 12-13 (ratio increases from 0.8 to 2.9), and 14-15 (ratio increases from 0.3 to 1.4). The possibility of minor original differences in these pairs of rocks cannot be excluded as confidently as for the Klondyke pair, although Judd (1893) states with assurance that (7) differs from (6) (this paper, Table 1) only in that the groundmass is devitrified.

Anderson and Radley (1915, p. 210-211) attribute the formation of the "sheaths" of "sheath and core" structure in their leidite sills to escape of some volatile substance from the devitrified margins and along joints, and present three sets of paired analyses (Table 1, columns 4-5 and 8-11) showing the devitrified rock contains about 1 per cent less water above 105° C. than the glassy rock. However, their one pair of complete analyses (Table 1, columns 4-5) shows other changes suggesting that more than simple dehydration was involved in devitrification; specifically, that potassium was added and sodium subtracted.

Terzaghi (1935, p. 378-379) has presented a variation diagram for 9 volcanic glasses and 4 devitrified volcanic glasses, all containing more

than 72 per cent silica. The diagram shows the devitrified glasses contain somewhat less soda and distinctly more potash, as well as more water, than the non-devitrified glasses. Although no pairs of analyses are given, a general trend similar to that of the Klondyke rocks is apparent.

Replacement of soda by potash accompanying devitrification was noted by Fenner (1934, p. 240–243; 1936, especially p. 262–277) in specimens of dacite pitchstone from a borehole in the Upper Basin of Yellowstone National Park. A pitchstone from a depth of 260 feet (specimen Y.P.279) contained 3.97 per cent Na_2O and 2.75 per cent K_2O , whereas a slightly devitrified but otherwise similar rock from a depth of 225 feet (specimen Y.P.267) had 3.38 per cent Na_2O and 3.59 per cent K_2O ; the ratio $\text{K}_2\text{O}:\text{Na}_2\text{O}$ increased from 0.69 in the glassy rock to 1.06 in the partly devitrified rock. Other rocks from depths of 293 to 400 feet show still higher ratios of potash to soda and also a notable increase in silica, but their original similarity to the pitchstone is less assured; some show perlitic structures but others may not have been highly glassy rocks.

Most non-devitrified natural glasses are young geologically, the great majority being of Cenozoic age (Harker, 1909, p. 225–226; Tyrrell, 1926, p. 82). The oldest one reported to date from North America seems to be a vitrophyric rhyolitic(?) welded tuff of late Late Cretaceous (Montana) age from near Wolf Creek, Montana (Barksdale, 1951). G. D. Robinson (personal communication, 1961) reports glassy rocks of about the same age from the Three Forks quadrangle, Montana. However, some are reported to be much older.

Glass of possible early Paleozoic or Precambrian age is reported from King Island, Tasmania by Scott (1951); glassy volcanic rocks are described from the Ordovician Borrowdale volcanic series of Great Britain by Mitchell (1929, p. 20; 1934, p. 424) and Hartley (1925, p. 207–208) and from Ordovician rocks near Llangynog, Wales by Cantrill and Thomas (1906, p. 242 and Pl. 24, Fig. 2); numerous occurrences of glass have been noted in andesite, basalt, and dacite of Old Red Sandstone (Devonian) age in Great Britain (Teall, 1883, p. 105, 254–255; Judd, *in* Durham, 1886, p. 427–429; Flett, 1897, p. 291; Geikie, 1897, v. 1, p. 274; Jowett, 1913, p. 475; Balsillie, 1918, p. 349; Pringle, 1948, p. 47; Macgregor and Macgregor, 1948, Table opposite p. 25; Harker, 1954, p. 166–167; Harry, 1956, p. 50); and glass has been identified in andesites of Carboniferous or Permian age in Great Britain (Geikie, 1897, v. 2, p. 45, 57; Pringle, 1948, p. 65; Macgregor and Macgregor, 1948, p. 54–55). Many of these glasses are reported in the older literature, and clear

evidence that the glass has not devitrified is commonly not given, but the existence of glass at least as old as Carboniferous seems well established (see, for instance, Judd, *in* Durham, 1886, p. 427-429). The composition and refractive index of the Tasmanian material are so unlike those of any ordinary volcanic glass that identification of this material as a true volcanic glass seems at least questionable.

These occurrences of geologically old glasses, some of which are in deformed rocks that must have been subjected to temperatures above those prevailing at the surface at the time of extrusion, appear to be rare, but they suggest that natural glasses are inherently highly stable, that they seldom if ever devitrify solely as a result of aging, and that very appreciable heat or pressure may be required to devitrify them. Various explanations have been proposed for the rare and apparently anomalous old glasses, but none seems generally valid. For instance, Hawkes (1930) points out that some of them have as much as 10 per cent water and suggests that a high water content may inhibit devitrification, but other old glasses contain only ordinary amounts of water; furthermore, the importance of water in the devitrification of natural glass at moderate temperatures is strongly emphasized by Marshall (1961). Chemical composition does not appear to be a controlling factor, as the Paleozoic glasses from England and Scotland range from rhyolitic to basaltic in composition.

CONCLUSIONS

Vitrophyric rhyolite welded tuff at Klondyke, Ariz., has devitrified along fractures, and large spherulites have formed in the upper part of the tuff. The devitrified rock is shown to contain much more potassium and markedly less sodium than its glassy equivalent. Devitrification was an autometamorphic process brought about by passage along fractures of potassium-rich fluids believed to have been trapped within or below the welded tuff at the time of emplacement. Devitrification of many other natural glasses may have had a similar deuteric origin, and indeed some such process may be the only generally operative cause of devitrification; the occurrence of geologically old non-devitrified glasses suggests that natural glasses have a high inherent stability and, once having escaped autometamorphic devitrification, may persist for a geologic era or longer.

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