

POTASH-RICH ROCKS OF THE ESTEREL, FRANCE*

RUTH D. TERZAGHI

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ABSTRACT

An apparently fresh, vitreous obsidian of the Esterel region has a normal chemical composition, whereas analyzed specimens of devitrified obsidian and of rhyolite are abnormally rich in potash and/or silica. The contrast between the composition of the fresh obsidian and that of the other rhyolitic rocks of the region, as well as microscopic features of the rhyolite and devitrified obsidian, suggest that these rocks owe their abnormal composition to hydrothermal enrichment in potash and/or silica.

INTRODUCTION

The term *potash-rich rock* is applied to any igneous rock whose normative feldspar content corresponds to a point in the orthoclase field of the feldspar equilibrium diagram (Bowen, 1928, Doggett, 1929). The problematical nature of the origin of these rocks was first discussed by Bowen (1928) who suggested a manner in which they might result from crystallization-differentiation. Other hypotheses of their origin were presented by the writer (Terzaghi, 1935).

Final conclusions regarding the origin of these rocks can be drawn only on the basis of field and laboratory investigations of individual occurrences. Studies of this kind which have already been made indicate that potash-rich rocks may originate in more than one way. The earliest of these studies dealt with some volcanic rocks of the Yellowstone Park region (Fenner 1936) and demonstrated the secondary origin of a considerable part of the potash contained in some of these rocks. Another mode of origin of potash-rich rocks has been indicated by Esper S. Larsen and Esper S. Larsen, 3rd (1938), who showed that potash-rich rhyolites of the San Juan region can be explained as a result of fractional crystallization involving the separation of a single alkalic feldspar richer

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in soda then the liquid phase. The present article deals with a group of potash-rich rocks which, like those of the Yellowstone region, owe their abnormal chemical composition to hydrothermal alteration.

The rhyolites and obsidian which are the subject of this article have been mapped and described by Albert Michel-Lévy (1911) to whose publication the reader is referred for a detailed account of them. The general description of the field relations, given in the next section, is based on this work. Megascopic secondary features, such as veins and druses, and other details of occurrence, were observed by the writer during three weeks spent in the field. The description of microscopic features is based on the writer's examination of over one hundred thin sections of Esterel rocks in the Mineralogical Laboratory of the Sorbonne. These were very kindly placed at the disposition of the writer by Professor Michel-Lévy, whose courtesy and helpfulness she acknowledges with gratitude. Thanks are also due to Mr. LeRiche of the same laboratory for taking the photomicrographs which illustrate this article.

GENERAL DESCRIPTION

The Esterel is a region of low mountains and hills, roughly 16 km. by 25 km. adjacent to the Mediterranean coast, between Cannes and St. Raphael. It is mapped topographically on the eastern part of the Fréjus sheet and the western part of the Cannes sheet, both of which were published by the Geographical Service of the French Army in 1933. The scale of both maps is 1/50,000.

Schist outcrops in the northern part of the region. It is overlain by sandstones and bituminous shales of Carboniferous age. Fluorite occurring in these was being mined at the time of the writer's visit in 1939. An angular unconformity separates the Carboniferous rocks from those of Permian age, which are gently folded. The latter include terrestrial sandstone, shale, and conglomerate, a few small intrusive bodies of dark-colored igneous rock, and the rhyolites and obsidian which are the subject of this article. The oldest of the rhyolitic rocks is the platy rhyolite porphyry or *porphyre tabulaire* of Michel-Lévy; closely associated with it is the slightly younger red rhyolite porphyry (*porphyre amarante*); the youngest of the three extrusive rocks of the area is a spherulitic rhyolite (*pyroméride*) which has vitreous and devitrified facies.

VEINS AND DRUSES IN RHYOLITES

The presence of veins and druses throughout the rhyolitic rocks of the Esterel indicates that the extrusion of these rocks was followed by a period in which hot aqueous solutions, and possibly gases, were abundant.

Veins of the commonest type are twenty centimeters or less in thickness and consist of dense, fine-grained reddish brown material. Microscopic examination shows that this material is a mixture consisting of an amorphous substance, probably opal, calcite, minute red particles which appear to be hematite, and one or more minerals having a low birefringence, which are too fine-grained for microscopic determination. Some of the largest of these veins are associated with lens-shaped masses of a clay mineral, one to two centimeters in thickness.

Quartz veins and druses occur locally in all of the rhyolites. Magnetite is found in the central part of some of the druses in the red porphyry and a kaolinite-like substance occupies the central part of quartz druses in some of the rhyolite dikes.

Relatively volatile minerals are not uncommon in the rhyolites. In the Maure-Vieille valley, the writer found fluorite in vugs in a rhyolite dike which represents a vent of the youngest flow, as well as in vesicular rhyolite porphyry of the oldest flow. Galena was found in cavities in a devitrified glass.

SPHERULITIC RHYOLITE AND OBSIDIAN

Introduction

The spherulitic rhyolite and obsidian represent the youngest flow of the region. The composition of these is better known than that of the older porphyry, owing to the larger number of analyses which have been made, and they will therefore be discussed first.

Chemical Composition

Nine analyses of the spherulitic rhyolite and obsidian, as well as two of the porphyry, were made by Pisani and published by Michel-Lévy in 1911. These are given in Table 1 and the norms in Table 2. Figure 1 shows the normative feldspar content of the rocks, and Fig. 2 the normative orthoclase, plagioclase, quartz, and corundum.

Clearly unaltered rock outcrops at only one¹ of the six localities from which specimens were taken for analysis. The composition of this rock, a vitreous obsidian, therefore provides the one reliable indication of the original composition of the lava of the youngest flow, to which it belongs. The composition of this rock (Analysis No. 11) is normal. The molecular ratio of potash to soda is only 0.5, and the rock is therefore not potash-rich. The molecular proportion of alumina is exactly equal to the sum

¹ Colle de la Motte; this locality, not indicated on the 1933 topographic map, is reached by a path which branches eastward from the Reyran valley road at a point 5.3 km. from Fréjus, and follows the south side of the *colle* (hill).

TABLE 1. ANALYSES OF RHYOLITES AND OBSIDIANS
(Michel-Lévy, 1911)
Analyst, Pisani

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
TiO ₂		0.20	0.13		0.08		0.06	0.13	0.06	0.05	0.06
SiO ₂	88.40	82.61	81.80	81.20	78.11	77.10	76.40	76.25	75.90	74.60	72.20
Al ₂ O ₃	4.85	8.30	7.65	9.40	11.50	10.64	10.60	11.10	11.43	11.23	10.75
Fe ₂ O ₃	1.61	2.54	1.88	1.35	1.60	1.55	1.40	1.68	1.70	1.52	0.89
FeO.....		0.45	0.70					0.45	0.30		0.80
CaO.....		0.26			0.51			0.39		0.45	0.45
MgO.....	0.39		0.64	0.77	0.25	1.05	0.38	0.26	0.26	0.25	0.65
K ₂ O.....	2.45	2.98	2.75	4.55	6.26	5.98	7.45	7.85	6.40	8.71	3.17
Na ₂ O.....	0.54	1.44	2.97	2.45	0.54	0.64	2.57	1.16	2.47	1.61	3.95
Loss on ignition.....	1.30	0.75	1.01	0.70	1.90	2.50	1.60	1.00	0.89	1.70	7.32
Total.....	99.54	99.53	99.53	100.42	100.75	99.46	100.46	100.27	99.41	100.12	100.24

- (1) Spherulitic rhyolite, flow, Grand Defends-Boulouris.
- (2) Platy porphyry, flow, Chemin Auriasque.
- (3) Spherulitic rhyolite, dike, Logement des Cantoniers.
- (4) Spherulitic rhyolite with residue of obsidian, flow, Colle de la Motte.
- (5) Spherulitic rhyolite, flow, Col des Sacs.
- (6) Devitrified obsidian, flow, west side, Collet Redon.
- (7) Devitrified obsidian with transition to spherulitic rhyolite, flow, Colle de la Motte.
- (8) Porphyry, Mont Vinaigre.
- (9) Spherulitic rhyolite, dike, Mont Vinaigre, 500 meters south of Duchesse.
- (10) Devitrified obsidian, north of summit of Mont Pelet.
- (11) Black obsidian, flow, Colle de la Motte.

TABLE 2. NORMS OF OBSIDIANS AND RHYOLITES
(Numbers refer to analyses given in Table 1)

	1	2	3	4	5	6	7	8	9	10	11
Q	75.30	62.22	53.10	46.32	48.18	47.70	35.82	37.98	36.60	31.98	34.74
or	14.51	17.79	16.68	27.24	37.25	35.58	44.48	46.70	37.81	51.71	18.90
ab	4.56	12.05	23.58	20.96	4.72	5.24	12.58	9.96	20.96	8.91	33.54
an		1.39			2.50			1.67			2.22
C	1.30	2.14		0.46	3.06	2.89			0.41		
ac			1.39				3.70			4.16	
ns							1.22				
di								0.22		1.30	
wo										0.23	
hy	1.00		1.60	4.01	3.11	5.24	1.00	0.60	0.70		2.13
mt		0.70	1.86					0.93	0.70		1.39
il		0.46	0.30		0.15		0.15	0.30	0.15		0.15
hm	1.68	2.08	0.64					1.06	1.28		

of the alkalis plus lime, and the silica content is 72 per cent, or, after deducting loss on ignition, 78 per cent.

The composition of the other analyzed specimens varies through an extremely wide range, and nearly all of them are strikingly different in composition from the vitreous obsidian. An abnormally high potash content and a high potash-soda ratio characterize most members of the

group, including a devitrified glass (No. 7) and a rhyolite (No. 4) collected within a few hundred feet of the outcrop of fresh obsidian. Some of the analyzed specimens are distinguished by a very high silica content, and by an excess of alumina over the sum of the alkalis plus lime, which corresponds to corundum in the norm and to secondary sericite, chlorite, and clay minerals in the mode. It appears highly improbable that the original composition of rock representing a single flow could be characterized by variations of such magnitude and kind. Furthermore, the presence of normative corundum is in itself an indication that the rocks are altered. On the basis of chemical composition alone it would therefore be difficult to escape the conclusion that the majority of the analyzed specimens represent altered rock.

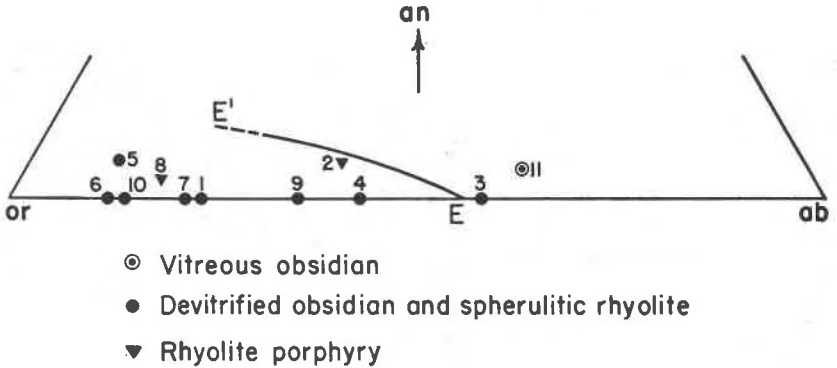


FIG. 1. Normative feldspar content of rhyolitic rocks of the Esterel.

Line $E-E'$ represents the probable position of the orthoclase-plagioclase field boundary. Numbers refer to analyses given in Table 1.

Inspection of Fig. 2 suggests that the differences between the composition of the vitreous obsidian (No. 11) and that of the other rhyolitic rocks can be explained as the result of one or more of several different alteration processes, including replacement of lime and/or soda by potash (Analyses 7, 9, and 10), replacement of feldspar by quartz (Analyses 1, 3, 4, 5, and 6) and the alteration of feldspar to sericite or a clay mineral (Analyses 1, 5, and 6). Microscopic features which suggest that these processes have in fact taken place will be described in the following paragraphs.

Evidence of Alteration of Devitrified Obsidian

The writer has noted elsewhere (Terzaghi 1935) that there are no potash-rich vitreous obsidians among the rocks of which analyses are

given in Washington's tables (1917) whereas there are several potash-rich devitrified obsidians from various parts of the world. This fact suggests that both the high potash content and the crystalline character with which it is associated may be due to the same cause, presumably

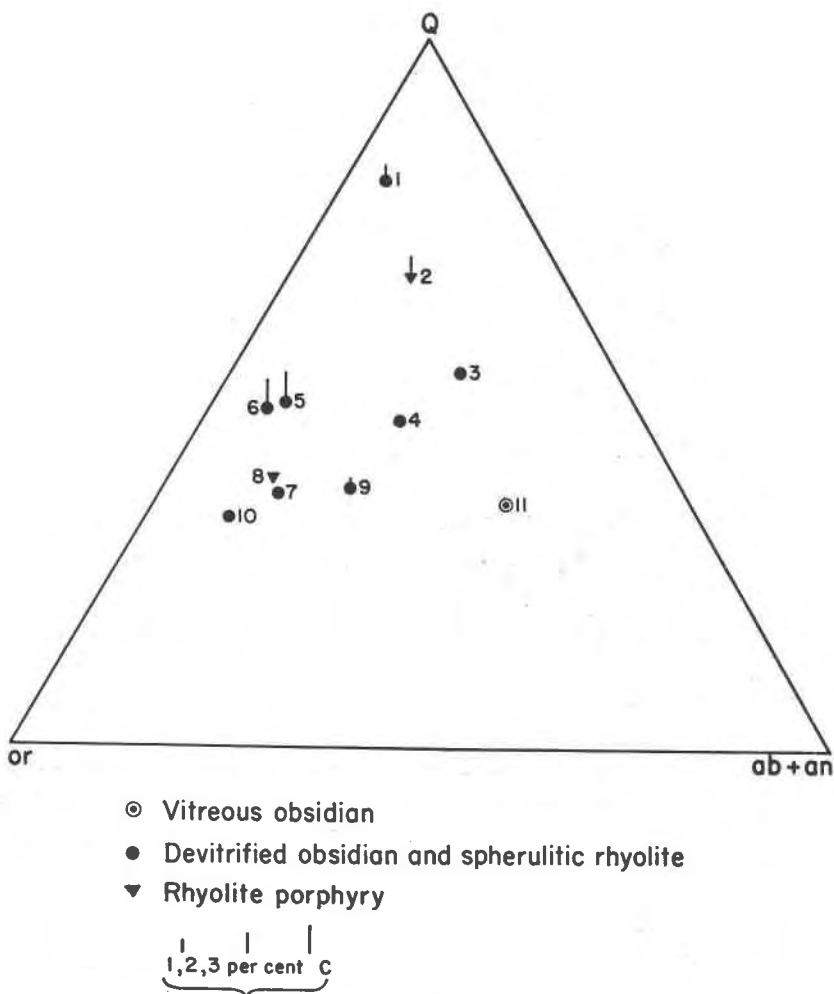


FIG. 2. Normative quartz, orthoclase, plagioclase, and corundum content of rhyolitic rocks of the Esterel.

Quartz, orthoclase, and plagioclase content, recomputed to 100 per cent, are shown in the triangular diagram; the percentage of corundum in the norm is indicated by the length of the vertical line attached to the symbol representing each of the specimens which contain normative corundum.

hydrothermal alteration. This statement does not, of course, imply that devitrification cannot take place without the aid of percolating solutions; it does, however, point to the necessity of a careful examination of devitrified obsidians for evidence of alteration. Such evidence is found in devitrified obsidian of the Esterel and will be described below.

Field evidence of a causal relationship between alteration by percolating solutions and devitrification is found in the limitation of devitrification to the immediate vicinity of cracks in an obsidian outcropping in the gully located by the co-ordinates 958W and 141.4N on the Fréjus sheet.

Evidence of another kind is found in the thin section of which a part is shown in Plate 1, Fig. 1. In the rock which this section represents, crystallization evidently took place in three distinct stages. In the first stage, crystallites formed and accumulated, apparently in random orientation, in spheroidal agglomerations whose shape suggests that the lava was still in motion during this stage. A part of such an agglomeration is visible in the photomicrograph. The second stage of crystallization is represented by feebly polarizing, plume-like structures present in the crackled material occupying a wedge-shaped area in the central part of the photomicrograph. (These structures are not visible in the photomicrograph, which was taken in ordinary light.) The appearance of these suggests that active flow had ceased when they developed. Their formation evidently preceded the chilling which led to the development of perlitic cracks in the completely amorphous lava. The third and last stage of crystallization is represented by relatively well-developed individuals of alkalic feldspar occurring in the material which exhibits perlitic cracks. These crystals are not visible in the photomicrograph (Pl. 1, Fig. 1), but similar ones, commonly with a rhombic cross section, are plainly seen in Plate 1, Fig. 2. Their formation appears to have followed that of the perlitic cracks, and we may therefore conclude that they developed when the lava had already hardened. In spite of the rigidity of the glass in which they formed, these crystals are much larger and better developed than those formed in earlier stages when the lava was fluid. In order to account for their relative perfection, it is necessary to suppose that their development was aided by aqueous solutions percolating through the cracks in the obsidian and it appears most probable that they originated by the replacement of vitreous material. The solution which deposited them did not attack the crystalline material already present, probably because it was less soluble and contained fewer or smaller cracks than the adjacent vitreous material.

Plate 1, Fig. 2, shows part of a thin section of devitrified obsidian from another locality (Colle de la Motte). Like the specimen of devitrified glass shown in Fig. 1 (Pl. 1), this contains relatively well developed crys-

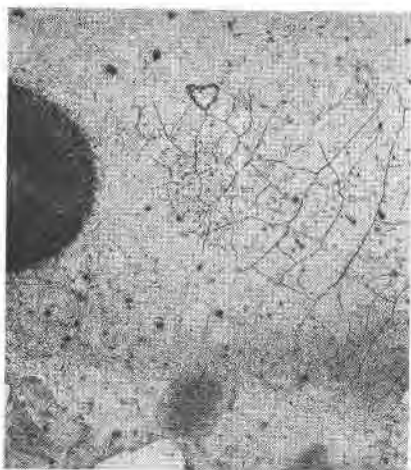


FIG. 1.—Devitrified Obsidian.

Perlitic cracks characterize originally glassy portions, whereas irregular cracks occur where incipient crystallization preceded final chilling. Ordinary light. $\times 20$.



FIG. 2.—Devitrified Obsidian.

Rhombic masses of pink alkalic feldspar occupy masses surrounded by perlitic cracks. A veinlet of alkalic feldspar may be seen at the left-hand side. Ordinary light. $\times 41$.

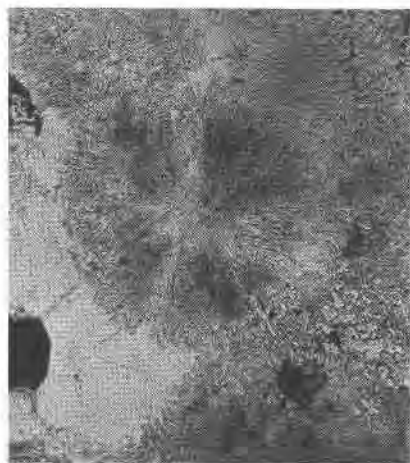


FIG. 3.—Spherulitic Rhyolite.

Spherulites are locally replaced by quartz. The clear mineral is quartz, large stippled areas represent a clay mineral, and black areas, magnetite in part altered to hematite. Ordinary light. $\times 76$.

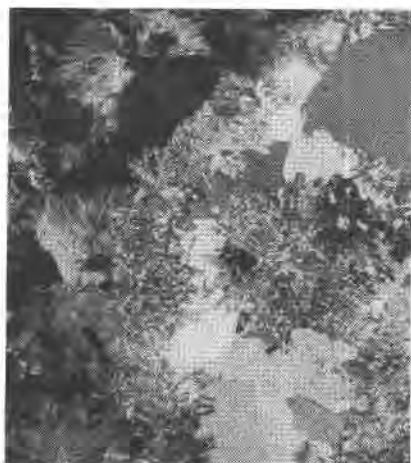


FIG. 4. Spherulitic Rhyolite.

Feldspar in the spherulites is in part sericitized and in part replaced by quartz in the vicinity of a pocket or veinlet containing quartz and sericite. Crossed Nicols. $\times 19$.

tals of alkalic feldspar, interpreted as an effect of hydrothermal alteration. A veinlet consisting chiefly of alkalic feldspar, visible adjacent and parallel to the left-hand side of the photomicrograph, is likewise attributed to percolating hydrothermal solutions. In connection with the microscopic evidence that this obsidian has been enriched in alkalic feldspar, it is of interest to note that an analyzed specimen of devitrified obsidian from the same locality contains 7.45 per cent K_2O , in contrast to 3.17 per cent K_2O contained in the fresh vitreous obsidian from an adjacent outcrop.

Evidence of Alteration of Spherulitic Rhyolite

In most localities, the spherulitic rhyolite appears to be altered. The feldspar phenocrysts are generally dull, the rock commonly has a bleached appearance, and in places it is in part altered to a white powder. Even in new road cuts and in quarries, it is generally so decomposed along cracks and joints that it is impossible to obtain a good hand specimen.

Details found in some of the thin sections suggest the nature of the alteration processes. Plate 1, Fig. 3, shows a spherulitic rhyolite in which the spaces between spherulites are occupied by coarse-grained quartz, small quantities of a fine grained clay mineral, and magnetite locally altered to hematite, all apparently of hydrothermal origin. The spherulites are in part replaced by quartz. As a result of alteration, this rock was enriched in quartz and ferric oxide. Analysis No. 4 represents a spherulitic rhyolite from the same locality. A comparison of the norm of this rock with that of the vitreous obsidian suggests that it has been enriched in silica and that soda and lime have been in part replaced by potash.

Similar phenomena are illustrated by Plate 1, Fig. 4, which shows part of a thin section of a spherulitic rhyolite. The feldspar contained in the spherulites has been locally replaced by quartz and in part sericitized in the zone contiguous to the elongated interstitial masses consisting of sericite and coarse grained secondary quartz. The net effect of the alteration of this rock was the removal of soda, the addition of silica and possibly of potash, and an increase in the molecular ratio of alumina to alkali-plus-lime.

The rock shown in Plate 2, Fig. 1, has also been enriched in quartz and sericite, but the resulting texture is different from that shown in Plate 1, Fig. 4. Each of the rounded areas in the groundmass represents a spherulite almost completely replaced by a single quartz individual. Locally the groundmass contains sericite. As shown in the photomicrograph, sericite also occurs in a veinlet intersecting a quartz phenocryst,

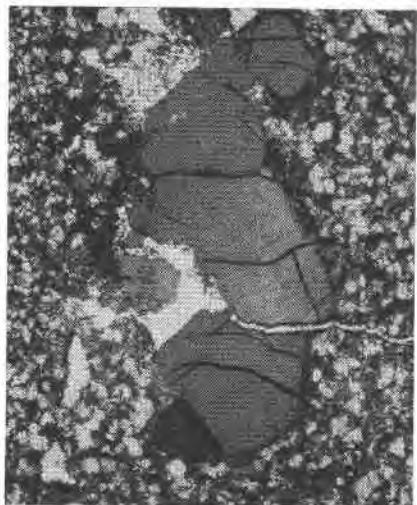


FIG. 1.—Spherulitic Rhyolite.

Showing veinlet of sericite cutting quartz phenocryst. Crossed Nicols. $\times 33$.

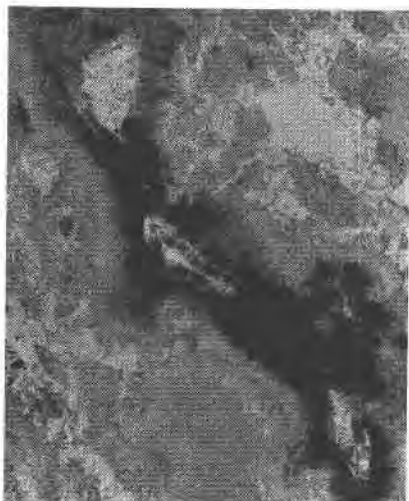


FIG. 2.—Spherulitic Rhyolite.

Showing veinlet of hematite-stained alkalic feldspar with quartz in center. Ordinary light. $\times 19$.

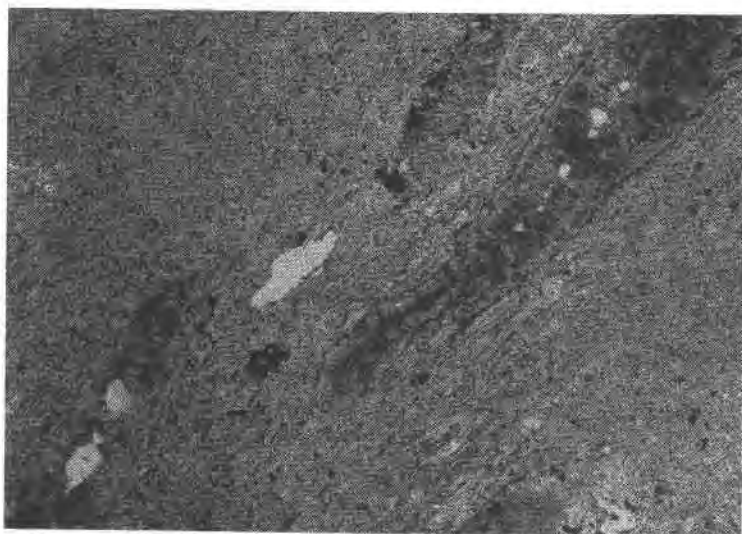


FIG. 3.—Platy Porphyry.

Showing vesicles filled with secondary alkalic feldspar and quartz. Ordinary light. $\times 48$.

PLATE 2. Photomicrographs of Rhyolite.

and in a cavity within the same phenocryst. Other phenocrysts not shown in the photomicrograph have been completely replaced by sericite and quartz, possibly accompanied by other secondary minerals.

Plate 2, Fig. 2, shows part of a thin section of a rock which has undergone at least two stages of alteration. The first involved partial replacement of the groundmass by minute quartz veinlets and alteration of feldspar to clay mineral. This process was followed by the deposition of alkalic feldspar in irregular veinlets, one of which is shown in the photomicrograph. Analysis No. 6 represents a devitrified obsidian from the same locality. This rock is richer in silica and potash than the unaltered rock (No. 11) and contains normative corundum. It has therefore probably undergone the same alteration processes as the rock shown in Plate 2, Fig. 2.

Microscopic veinlets of quartz and opal are common in the spherulitic rhyolite. They appear to represent a later stage of alteration than do the replacement processes described in the preceding paragraphs.

RHYOLITE PORPHYRY

There are few outcrops of perfectly fresh rhyolite porphyry. In most localities, the phenocrysts are dull and in some places they have been completely altered to a clay mineral. Locally the rock is pale green and is readily crumbled.

An inspection of the thin sections shows that the phenocrysts of alkalic feldspar are commonly partly altered to a granular material characterized by low index of refraction and low birefringence, or, more rarely, to sericite. Plagioclase was not found in any of the thin sections examined but in places the red porphyry contains masses of a white kaolinite-like material having a rectangular or a rounded cross section, from 1 to 3 mm. in greatest dimension. These may represent completely altered plagioclase phenocrysts.

The porphyry generally contains elongated vesicles lined by fibers most of which consist of alkalic feldspar. The centers of many of the vesicles are filled with quartz and, in at least one locality, calcite. In the platy porphyry, the vesicles range in width from a few hundredths of a millimeter to several millimeters, and in length from about one tenth millimeter to ten millimeters. They constitute as much as 30 per cent of some specimens. Plate 2, Fig. 3, representing a part of a thin section of platy porphyry, shows some of these vesicles. In the red porphyry, the feldspar-lined vesicles are not longer than 0.1 mm. and in most specimens of this rock those which are readily visible constitute less than five per cent of the rock.

In some specimens of porphyry, quartz occupying the central part of the vesicles appears locally to have replaced feldspar. In a few such

specimens, the secondary feldspar is altered to an opaque brown substance, probably consisting of iron-stained clay mineral.

The microscopic features described in the preceding paragraphs suggest that the porphyry has been subjected to the same alteration processes as the spherulitic rhyolite, i.e., potash enrichment in some localities and in others, enrichment in silica and impoverishment in both alkalis owing to alteration of feldspar to a clay mineral. The chemical analyses support this conclusion. One of these (No. 8) represents a specimen of red porphyry in which the secondary feldspar is relatively fresh. This rock is characterized by an abnormally high potash content (7.85 per cent). The other analysis (No. 2) represents a specimen of platy porphyry in which much of the feldspar has been altered to clay mineral. As would be expected, the total alkalis in this rock are low, and the molecular ratio of alumina to the sum of the alkalis plus lime is greater than one. Potash is considerably in excess of soda, possibly owing to selective leaching of soda.

CONCLUSIONS

The abundance of veins and druses, some of which contain relatively volatile constituents, indicates that hot solutions and possibly gaseous emanations were active in the region after the eruptions of rhyolitic lava took place. Few of the rocks of rhyolitic composition remained completely unchanged by these solutions, but the nature of the reactions between solutions and rocks is most clearly indicated by microscopic features of the spherulitic rhyolite. These show that under some conditions alkalic feldspar was completely dissolved and replaced by quartz; under others, at least a part of the alkali content of the feldspar was removed and the residue crystallized *in situ* as sericite or as a clay mineral. Under still other conditions, alkalic feldspar, or sericite, or a clay mineral was deposited as a vein mineral. The deposition of notable quantities of quartz accompanied the deposition of clay mineral and of sericite, whereas in general only a small quantity of quartz was deposited contemporaneously with secondary feldspar. Some of the rhyolitic rocks have undergone first leaching of feldspar followed by deposition of feldspar or sericite or a clay mineral; some have been subjected to only one of these processes.

The presence in potash-rich altered rocks of secondary alkalic feldspar and of vein sericite of extraneous origin strongly suggests that a considerable part of the large quantity of potash contained in many of the altered rocks was acquired during alteration. The source of the secondary potash was possibly two-fold. Some of it may have been introduced by hydrothermal solutions or gaseous emanations originating from an underlying body of magma. Another part of the potash was probably derived by local leaching of the rhyolite itself. The quantitative impor-

tance of this source is indicated by the fact that about one fourth of the thin sections examined bear clear evidence of more or less advanced replacement of spherulites by quartz, like that illustrated by Plate 1, Fig. 3. The potash thus leached from the rhyolite in one place was carried on in solution and was available for potash enrichment elsewhere.

These conclusions regarding the dual origin of the secondary potash in the Esterel region are in general agreement with those presented by Allen (1934, 1935), Allen and Day (1934) and by Fenner (1936) in their studies of the thermal waters and the altered rhyolite of the Yellowstone Park region. In this area, the rhyolite is still in the process of alteration by thermal water containing alkali halides and bicarbonates. The halides are believed to originate as gaseous emanations from an underlying body of magma, whereas the presence of bicarbonates is attributed to a reaction between dissolved carbon dioxide of magmatic origin and alkalis leached from rhyolite.

Irrespective of whether the alkalis contained in the thermal waters of the Esterel were of magmatic origin or derived by the leaching of already solidified rock, it is not probable that the quantity of potassium in solution was in excess of that of sodium. Hence the question arises as to whether these waters were capable of effecting a substitution of potassium for sodium in the rock through which they passed. An affirmative answer to this question has been provided by Fenner (1936) who found that substitution of potassium for sodium in the rocks of the Yellowstone region "goes on until the waters are so depleted of potassium and enriched in sodium that the ratio of the two becomes 1:34."

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