An aenigmatite–richterite–olivine trachyte from Puu Koae, West Maui, Hawaii

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Abstract

The Puu Koae trachyte forms a conspicuous bulbous dome on the north shore of West Maui. This trachyte has a peraluminous composition, but contains alkali amphibole, aenigmatite, iron-rich olivine, and sodic clinopyroxene. This mineralogical association indicates that the trachyte crystallized from a peralkaline melt, and that its composition changed at the time of crystallization by loss of sodium. The conclusion is that peralkaline salic liquids have been produced at one stage of the evolution of the island of Maui.

Introduction

The geology of West Maui has been described by Stearns and Macdonald (1942). West Maui is a mainly basaltic volcano, the rocks of which, known as the Wailuku volcanic series, are almost entirely tholeiitic. The youngest flows, however, unquestionably belong to the alkali suite. The Wailuku series is "overlain by a thin cap of mugearite and trachyte named the Honolua volcanic series." Postdating the Honolua series are a few basanite eruptions, the Lahaina volcanic series (Macdonald and Katsura, 1964). The Puu Koae trachyte, the subject of this note, belongs to the Honolua series. A sample collected at Puu Koae contains aenigmatite, alkali amphibole, olivine, and a sodium-rich pyroxene, a type of mineralogical association not hitherto reported from the Hawaiian archipelago. Mentions of alkali-rich minerals can be found in the literature. Washington (1923, p. 107), for example, noted the possible presence of colorless (?) acmite in the Puu Anahulu trachyte from the island of Hawaii, though this finding has never been confirmed. Macdonald (in Stearns and Macdonald, 1942) noticed the presence of a "riebeckite-like" alkali amphibole in some trachyte and "andesites" from West Maui, and in particular in the Puu Koae trachyte, where he found it accompanied by abundant acmite. In spite of these brief observations, no definite peralkaline lava is known in Hawaii, and a recent survey of the occurrences of peralkaline silicic rocks in the oceanic islands (Baker, 1975) understandably does not even mention the archipelago.

Description

The Puu Koae trachyte forms an obvious bulbous dome which is a well-known landmark on the northwestern coast of the island of Maui. The sample examined was taken from the southeastern side of the dome. In hand specimen the lava has a chalky uninviting aspect which certainly justifies the fact that the outcrop is singled out as a good opportunity for the observation of erosional features, in particular the etching of the rocks by ocean spray (Stearns and Macdonald, 1942). The rock appears completely crystallized, with obvious white feldspar grains in a brownish spotted groundmass.

Under the microscope, it shows a typical trachytic texture, most alkali feldspar laths being oriented in the same general direction. There is an obvious size discontinuity between the largest (2mm × 0.3mm) and the smaller feldspar crystals. All the phenocrysts have lamellar polysynthetic twinning (Fig. 1), as do most of the groundmass crystals. Feldspar is, of course, the major constituent of the lava. In any petrographic thin section there are usually a few rather large (0.5mm × 0.3mm) olivine crystals (Fig. 2), fresh but for a narrow and continuous iron-oxide rim. More numerous are sections of alkali amphibole that can reach 0.7mm in length (Fig. 3); these amphibole crystals are usually partly molded around large feldspar laths, but can also show regular crystal outlines. Their polychroism is quite variable, in color as well as in intensity, both within a single crystal and from crystal to crystal. Aenigmatite is abundant, forming mostly small (0.15mm × 0.05mm) crystals;
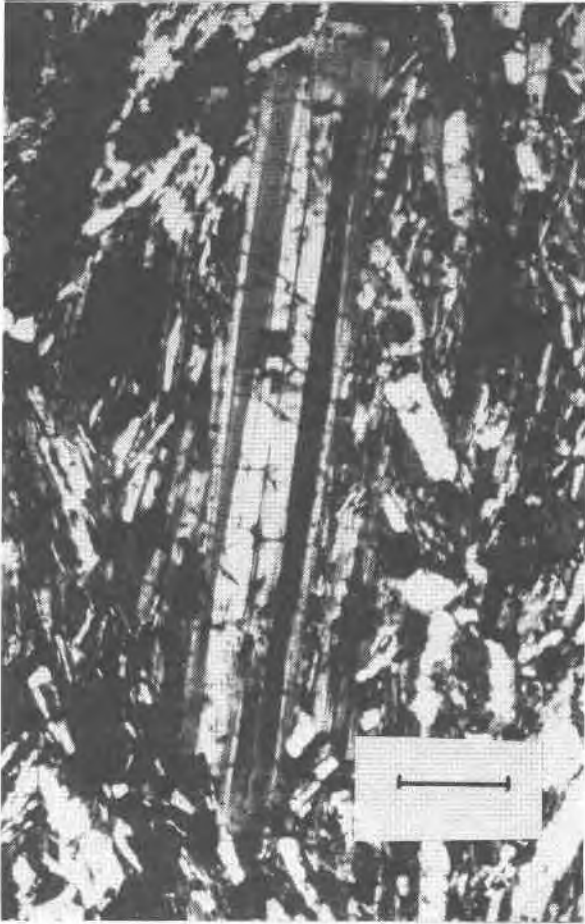
Fig. 1. Oligoclase phenocrysts, with regular crystal outline and polysynthetic twinning. Length of the bar is 0.15mm.

Mineralogical composition

All minerals have been analyzed on the Geophysical Laboratory automated electron microprobe (Finger and Hadidiacos, 1972), with natural or synthetic minerals as standards.

Feldspars

Both large phenocrysts and groundmass feldspars were analyzed, and Figure 4 shows the range of compositions found in terms of albite, anorthite, and orthoclase end-members. Particular emphasis was put on the unusual Ca-rich phenocryst composition, so that the number of points in the diagram is in no way related to the modal proportions of the two varieties of feldspars in the rock. Table 1 contains analyses of the two types of compositions.

The phenocrysts correspond to an oligoclase with 5 to 6 percent Or in solid solution. They are consistently rimmed by alkali feldspar whose composition is similar to that of groundmass feldspars. They do not give any evidence of being xenocrysts, nor do

clinopyroxene is very rare, forming minute prisms (less than 0.02 mm), usually developed around unidentified rusty grains. Patches of interstitial brown isotropic material are present and may perhaps be altered glass. Magnetite forms small- or medium-sized (0.2mm) crystals with regular outlines.

The order of crystallization cannot be unequivocally determined. Textural relationships nevertheless indicate that the large feldspar phenocrysts (oligoclase), olivine, and magnetite were followed by alkali amphiboles; among these richterite, with weak pleochroism, appeared before arfvedsonite. Sodic pyroxene was, after alkali feldspar and aenigmatite, the last phase to crystallize.

Mention should also be made of two former phenocrysts, one hexagonal in shape, the other an elongated rectangle, that have been entirely altered to finely-granular iron ore, and could be pseudomorphs after biotite.
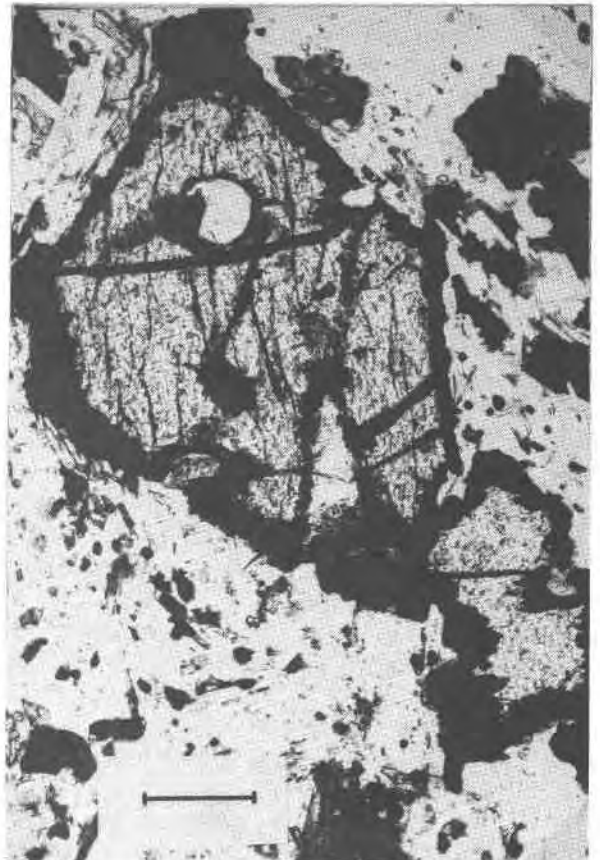

Fig. 2. Olivine crystal, rimmed by iron oxides. Length of the bar is 0.10mm.
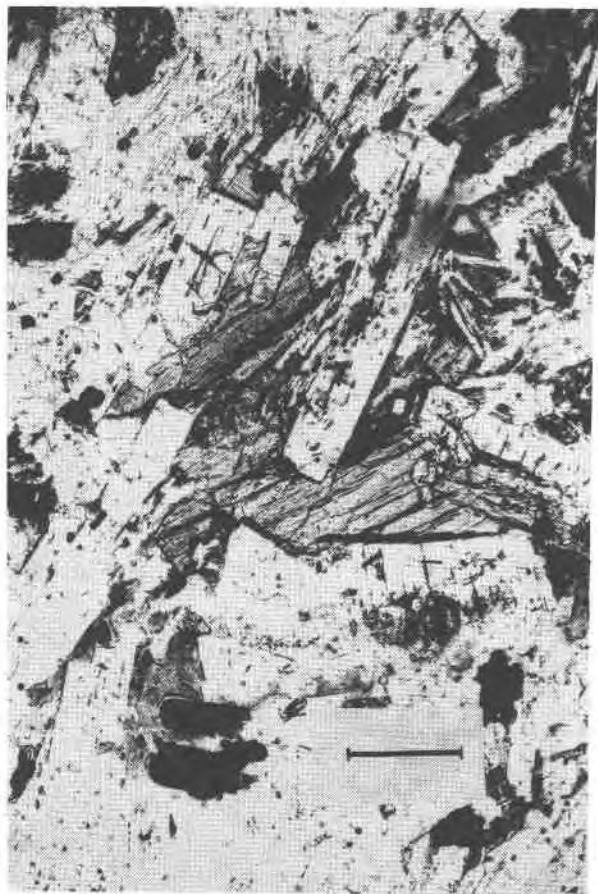
Fig. 3. Richterite (grey) and alkali feldspar laths. Length of the bar is 0.10mm.

they show any indication of corrosion (Fig. 1). The groundmass feldspar, on the other hand, is a potassium-bearing albite. The last-formed crystals, the richest in potassium, contain virtually no Ca and cluster around $Or_{25}Ab_{75}$ to $Or_{30}Ab_{70}$. They do not reach the most frequent composition found in peralkaline rocks ($Or_{35}Ab_{65}$; Bailey, 1975). The spread of compositions found is strikingly similar to that reported by Keil *et al.* (1972) for feldspars in a trachyte from the Ukumehame dome, also from West Maui. It appears from Macdonald and Katsura's reported analyses that their sample C 128 (from Puu Koae) and sample C 116 (from Ukumehame) have very similar bulk compositions. However, the alumina-deficient phases described here have not been recorded in the Ukumehame trachyte.

Olivine

Table 2 gives analyses of the two crystals of iron-rich olivine found in the Puu Koae trachyte. No

optical variations in birefringence were observed, and the differences in compositions between the center and the edges of the crystals are very small. There is a positive correlation between FeO, MnO, and CaO, these elements being inversely correlated with MgO. The composition varies from $Fo_{30}Fa_{64}Te_6$ to $Fo_{27}Fa_{66}Te_7$, the high tephroite content being somewhat unusual. The MnO content of olivines from the Mount Suswa trachytes and phonolites, for instance, varies between 3.1 and 3.8 percent (Nash *et al.,* 1969), for similar fayalite values. However, Barker and Hodges (1977) have recently found in nepheline syenites similar or higher MnO percentages in olivines containing 77 to 87 percent fayalite in solid solution.

Aenigmatite

Aenigmatite has frequently been reported in oversaturated peralkaline rocks. Analyses tabulated by Sutherland (1975) show very little compositional variation in this mineral in extrusive rocks. Analyses reported in Table 3 appear to be higher in MnO, Al_2O_3, and MgO, and lower in TiO_2 than most recorded so far in volcanic rocks. The high manganese values are in keeping with the high MnO content of all the other iron-bearing phases analyzed in the Puu Koae trachyte. Variations between crystals are small, but it would appear (Fig. 5) that low TiO_2 values are associated with high MnO, and perhaps high total iron. New analyses listed by Barker and Hodges (1977; appendix Table 3) show variable Ti and Mn contents but do not conform to the pattern found in Puu Koae. It appears that analyses are still not numerous enough to support a particular substitution scheme for volcanic aenigmatites.

However, a consideration of published analyses (Sutherland, 1975; Yagi and Souther, 1974; Borley, 1976) seems to indicate a higher TiO_2 content in aenigmatites from rocks with a high content of normative quartz, the highest TiO_2 content (10.23 percent) being recorded in a peralkaline granite with 33.56 percent normative quartz (Borley, 1976; Jacobson *et al.,* 1958).

Richterite–arfvedsonite amphiboles

Alkali amphibole is the most abundant iron-bearing phase in the Puu Koae trachyte and shows the greatest chemical variation. The polychroism visible in thin section is much deeper in the iron-rich last-formed arfvedsonite than in the richterite; richterite forms large crystals, whereas arfvedsonite forms either small crystals or rims the earlier-formed richterites. Colors vary from pale yellow to purplish-pink
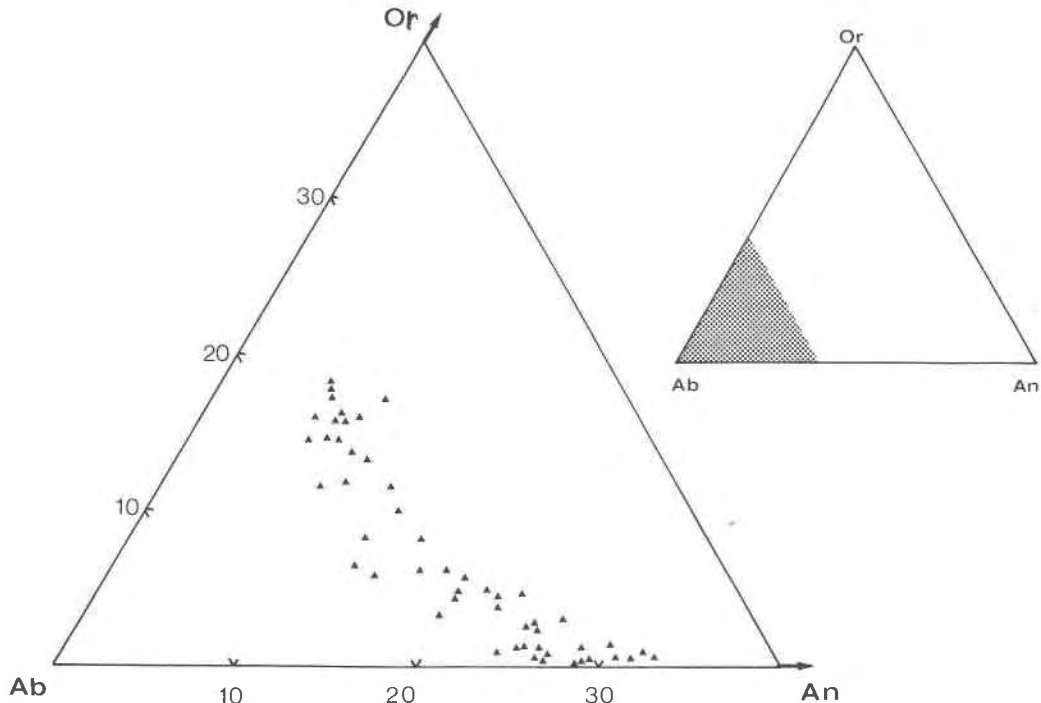
Fig. 4. Electron microprobe analyses of feldspars represented in terms of their Ab, An, and Or contents (mole percent).

in richterites to dark greenish-blue in the arfvedsonite. Table 4 lists representative analyses of the range of compositions found, and Figure 6 illustrates the variations found, which span the greater part of the richterite–arfvedsonite series of compositions. Particular effort was made to find out if there was a complete series between the two end-members; it appears from the 29 analyses made that there are indeed two clusters, corresponding to richterite and to an amphibole containing 60 to 70 percent of the arfvedsonite component. Fluorine has been found in similar amphiboles from oversaturated peralkaline lavas (Nicholls and Carmichael, 1969), but was not determined in the course of the present study.

Clinopyroxenes

Clinopyroxene is rare and forms very small euhedral crystals. The minute size of the grains prevented a precise analysis; however, compositions found would indicate the presence of hedenbergite with 50 percent acmite in solid solution as well as the existence of pure acmite. Fodor *et al.* (1975) reported analysis of clinopyroxenes in the Ukumehame trachyte. They are very different from those found in Puu Koae, and are solid solutions between diopside and hedenbergite. This could be interpreted as in-

dicating that the Ukumehame trachyte is not peralkaline.

Iron–titanium oxides

Iron–titanium oxides are relatively abundant in the trachyte, sometimes forming euhedral crystals of variable size. They are rich in TiO_2 and MnO (Table 5). In spite of their high ulvöspinel content (above 60 mole percent), they are free of exsolution textures. They are similar in this respect to some of the magnetites found in the peralkaline lavas from Mount Suswa (Nash *et al.*, 1969). Small magnetite crystals are sometimes included in aenigmatite, but there appears to be no special or necessary spatial relationship between these two phases, and no evidence of a reaction relationship.

Chemical composition of the Puu Koae trachyte

Table 6 lists a new analysis of the Puu Koae trachyte, along with the analysis previously published by Macdonald and Katsura (1964; specimen C 128). The striking peculiarity of these analyses is their peraluminous character. From all previous knowledge, and as forcefully stated by Macdonald (1975), "the most obvious indication of peralkalinity is the modal presence of certain index minerals, of which alkali

Table 1. Electron microprobe analyses of feldspars

	1	2	3	4
SiO_2	63.39	66.63	66.44	66.76
Al_2O_3	22.52	18.91	20.51	18.69
Fe_2O_3 *	.16	.63	.36	.50
CaO	3.75	.17	1.41	.12
Na_2O	8.83	8.41	9.40	8.38
K_2O	1.00	4.66	2.54	4.82
BaO	.26	.04	.21	.00
Total	99.91	99.46	100.88	99.26
Si	2.816	2.985	2.924	2.996
Al	1.178	.998	1.063	.987
Fe^{3+}	.005	.021	.011	.016
Ca	.178	.008	.065	.005
Na	.760	.731	.802	.728
K	.056	.265	.142	.275
Ba	.004	.000	.002	.000

* Total iron as Fe_2O_3

1 - Center of oligoclase phenocryst
2 - Edge of same
3 - Center of microphenocryst
4 - Small groundmass crystal

Table 2. Electron microprobe analyses of olivines

	1	2		1	2
SiO_2	33.08	32.54	Si	.995	.996
FeO *	49.07	51.25	Fe^{2+}	1.234	1.313
MgO	14.25	11.83	Mg	.639	.540
CaO	.41	.54	Ca	.012	.017
MnO	4.82	5.29	Mn	.123	.136
Total	101.63	101.43			

* Total iron as FeO

1 - Center of crystal
2 - Edge of crystal

Table 3. Electron microprobe analyses of aenigmatite

	1	2	3
SiO_2	40.25	41.75	40.50
Al_2O_3	1.25	.56	1.11
FeO *	39.74	40.36	41.09
MgO	1.71	1.25	1.57
CaO	.41	.18	.34
Na_2O	7.35	7.43	7.27
MnO	2.02	2.56	2.14
TiO_2	6.78	5.07	5.57
Total	99.51	99.16	99.36
Si	11.383	11.856	11.458
Al	.417	.187	.370
Fe^{3+}	1.963	2.027	2.331
Fe^{2+}	7.436	7.558	7.390
Mg	.721	.529	.662
Ca	.124	.055	.103
Na	4.030	4.090	3.988
Mn	.484	.616	.513
Ti	1.442	1.083	1.185

* Total iron as FeO
  K, V, and Cr below detection limits.

Structural formulas calculated assuming 28 cations and 40 oxygens.

pyroxene, alkali amphiboles, and aenigmatite are the most common." As far as is known these index minerals can crystallize only from a liquid with a peralkaline chemistry[1]. Two possibilities have to be considered: either the liquid was originally peralkaline, or else the early crystallization of a peraluminous phase gave it a secondary peralkaline chemistry. This latter possibility must be entertained when, as is the case of the Puu Koae trachyte, a rock with a peralkaline mineralogy contains plagioclase pheno-

[1] An exception to this rule are the pure acmite crystals deposited on the inner surface of vugs, in some basalts for example, that can be considered as deposited by a vapor phase (*e.g.* Smith and Lindsley, 1971, p. 285). But the texture of the Puu Koae trachyte does not support such an origin for its constituent alkali–iron-bearing minerals.
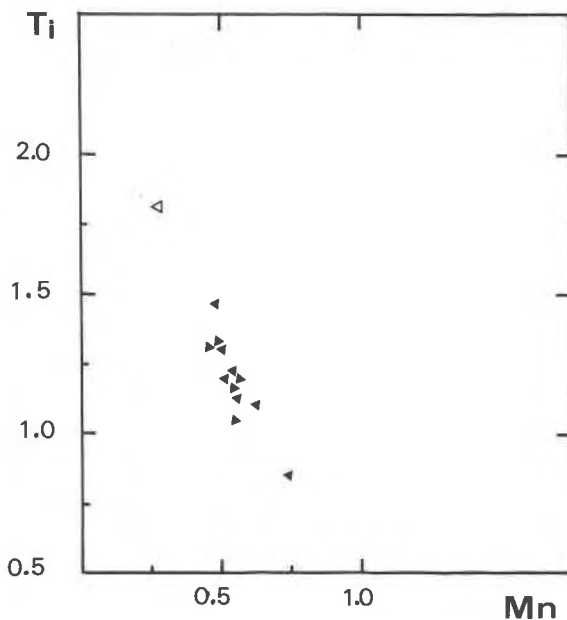
Fig. 5. Variation of Ti *versus* Mn in analyzed aenigmatites from Puu Koae. Open triangle is cossyrite from Pantelleria (in Zies, 1966).
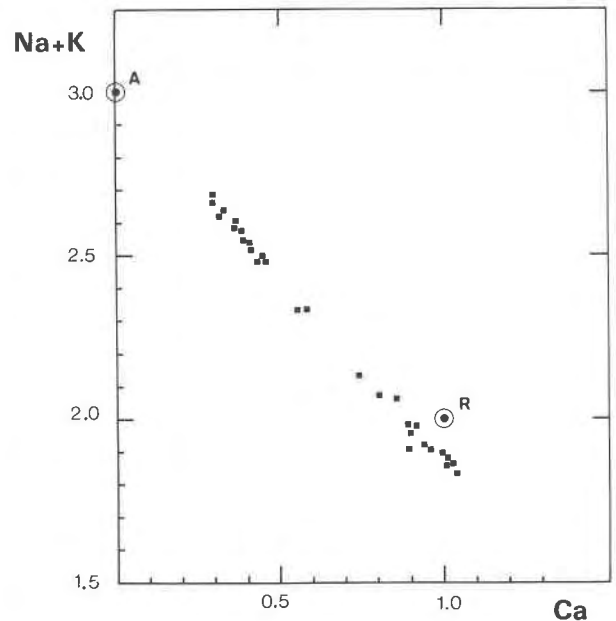

Fig. 6. Variation of (Na + K) *versus* Ca in alkali amphibole analyses from Puu Koae. Electron microprobe analyses have been recalculated on the basis of 23 oxygen atoms; no correction was made to account for the obvious presence of ferric iron in arfvedsonite. A = arfvedsonite; R = richterite.

crysts; the appearance of feldspar containing a certain amount of the anorthite molecule (the plagioclase effect) could induce a deficit in Al_2O_3 with respect to alkalis. Such a process has been described in a phonolite by Carmichael (1964) and mentioned by Villari in a trachyte from Pantelleria (1975, p. 712).

However, the observed modal abundance of oligoclase in the Maui trachyte (Table 6) is insufficient to account for the appearance of the typical peralkaline minerals. The unusual composition of the feldspar phenocrysts nevertheless does suggest that the peralkaline character of the initial liquid could have been

Table 4. Electron microprobe analyses of richterite and arfvedsonite

	1	2			
SiO_2	51.01	51.37	Si	7.598	7.867
Al_2O_3	1.91	1.11	Al	.332	.197
FeO *	16.60	22.37	Fe^{2+}	2.067	2.862
MgO	12.69	8.32	Mg	2.815	1.896
CaO	6.50	1.82	Ca	1.036	.296
Na_2O	5.48	8.20	Na	1.583	2.435
K_2O	1.21	1.18	K	.227	.229
MnO	1.09	1.72	Mn	.135	.220
TiO_2	1.48	1.45	Ti	.162	.166
Total	97.96	97.54			

*Total iron as FeO

1 - Richterite ;   2 - Arfvedsonite.

Table 5. Electron microprobe analysis of titanomagnetite

SiO_2	.21
Al_2O_3	.30
Fe_2O_3*	26.10
FeO*	48.05
MgO	.24
TiO_2	21.59
MnO	2.77
Total	99.26

Percentage ulvospinel = 62%

Percentage magnetite = 38%

*FeO and Fe_2O_3 calculated from total iron as determined by electron microprobe analysis, and the structural formula.

Table 6. Chemical composition, CIPW norms and modal analysis of the Puu Koae trachyte

	1	2		1	2
SiO_2	59.82	60.85	Q	1.74	1.04
Al_2O_3	18.07	18.51	Or	20.15	21.28
Fe_2O_3	4.06	3.10	Ab	62.37	60.93
FeO	1.71	2.08	An	3.16	6.89
MgO	0.53	0.58	Hy	1.32	2.13
CaO	0.90	1.77	He	1.19	
Na_2O	7.37	7.20	Mt	4.16	4.49
K_2O	3.41	3.60	Il	1.48	1.23
MnO	0.28	0.27	Ap	.46	.67
TiO_2	0.78	0.65	C	1.10	.24
P_2O_5	0.20	0.29			
H_2O +	2.07	0.47			
H_2O -	0.55	0.42			
Totals	99.75	99.81			

Modal Analysis :	
Oligoclase (phenocrysts)	3.8%
Alkali feldspars (groundmass)	88.1%
Magnetite	2.1%
Aenigmatite	2.4%
Alkali Amphiboles	2.8%
Clinopyroxene	.8%
Olivine	< .1%

1 - Puu Koae trachyte. New analysis M. Lenoble and N. Vassard, Paris, 1977

2 - Puu Koae trachyte; sample C. 128 (Macdonald and Katsura, 1964)

less pronouned than that indicated by the bulk composition of peralkaline rocks in which plagioclase is typically absent.

The probable conclusion is that the liquid from which the trachyte crystallized was peralkaline, that its composition was modified at the time of crystallization and probably after, and that the present bulk rock composition does not adequately represent this liquid. Macdonald and Bailey (1973) and Baker and Henage (1977), among others, have summarized some of the effects of crystallization on peralkaline compositions, listing among the major changes the loss of sodium. The analyses listed in Table 5 show that addition of less than 1.5 percent Na_2O would be enough to give the Puu Koae trachyte a mildly peralkaline composition. This amount is well within the range of sodium losses reported on samples from Pantelleria by Macdonald and Bailey (1973, p. N2); the mechanism could be expulsion of sodium-rich fluids (Baker and Henage, 1977).

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