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AENIGMATITE FROM THE GROUNDMASS OF A PERALKALINE TRACHYTE

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INTRODUCTION

Previous chemical analyses of aenigmatite (Fleischer, 1936; Carmichael, 1962; Kelsey and McKie, 1964; Mitrofanov and Afanas'eva, 1966; Zies, 1966) are of phenocrysts from the pantellerites of Pantelleria, the Kola Peninsula, and Greenland, and the alkali syenites of the East Sayan Mts. The aenigmatite reported here is an interstitial mineral in the groundmass of a peralkaline trachyte, and it was analyzed to determine whether there are any significant differences between this type of aenigmatite and that occurring as phenocrysts.

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OCCURRENCE

The host peralkaline trachyte (analysis and norm, Table 1) is from a continental alkaline volcanic province in the Nandewar Mountains of New South Wales, Australia, where it occurs as a dome in a complex consisting of flows, plugs, domes and coulees of alkaline rocks ranging from olivine basalts, hawaiites, benmoreites, trachytes, and comendites to alkali rhyolites (Abbott, 1965). The trachyte is porphyritic with phenocrysts of alkali feldspar ($\beta=1.531$, $2V_X=56$–$60°$) set in a groundmass of feldspar laths with trachytic flow structure. Analyses of two feldspar fractions yielded compositions of $Or_{37.4}Ab_{61.4}An_{1.2}$ and $Or_{40.3}Ab_{58.9}An_{0.8}$; the former corresponding approximately to the phenocrysts and the latter to the groundmass feldspars. Between the feldspar laths of the groundmass are minor quartz, green aegirine-augite ($\beta=1.758$, $2V_X=88°$; approximate composition $Ac_{50}Hd_{50}$, Deer, Howie, and Zussman, 1963, p. 87), arfvedsonitic riebeckite (α = dark blue-green, β = pale violet-brown, γ = dark green, $2V_X=71°$), and deep red-brown aenigmatite. Sparse titanomagnetite ($a_0=8.38$ Å) is often rimmed with aenigmatite in a manner suggestive of a reaction rim.

TABLE 1. CHEMICAL ANALYSIS AND CIPW NORM OF AENIGMATITE TRACHYTE, NANDEWAR MOUNTAINS, NEW SOUTH WALES

SiO_2	65.59		Q	3.34
TiO_2	0.41		or	32.92
Al_2O_3	16.45		ab	53.61
Fe_2O_3	2.11	di	wo	0.45
FeO	1.62		en	0.07
MnO	0.08		fs	0.42
MgO	0.14	hy	en	0.28
CaO	0.36		fs	1.74
Na_2O	7.02		ac	5.11
K_2O	5.57		il	0.78
Rb_2O	0.01		mt	0.50
P_2O_5	0.07		ap	0.17
ZrO_2	0.09		cc	0.09
H_2O^+	0.18		H_2O	0.18
H_2O^-			Rest	0.10
CO_2	0.04			
Total	99.74		Total	99.76

$$\text{Peralkalinity ratio} \left(\frac{Na^+ + K^+}{Al^{3+}}\right) = 1.07$$

Analyst: M. J. Abbott.

PROPERTIES

The aenigmatite in the trachyte is extremely fine grained, and the rock was crushed to less than 300 mesh for separation. After washing to remove the fine dust, the powder was passed slowly through a Franz isodynamic separator. The aenigmatite was concentrated further by passing the ferromagnesian enriched fraction repeatedly through a micropanner using carbon tetrachloride as the suspending fluid, the final separation and purification being made by repeated centrifuging in Clerici solution. The mineral was cleaned by heating in a solution of 10% oxalic acid, thus removing adhering magnetite and thallium.

TABLE 2. CHEMICAL ANALYSIS AND OPTICAL PROPERTIES OF AENIGMATITE SEPARATED FROM NANDEWAR MOUNTAINS TRACHYTE (TABLE 1)

SiO_2	41.30	Refractive indices (±0.015)
TiO_2	7.43	$\alpha=1.81$
Al_2O_3	0.67	$\beta=1.82$
Fe_2O_3	3.75	$\gamma=1.90$
FeO	36.52	Pleochroism
MnO	1.01	X=pale yellow brown
MgO	1.27	Y=red brown
CaO	0.32	Z=dark brown
Na_2O	7.39	Absorption
K_2O	0.08	$X<Y<Z$
H_2O^+	n.d.	Elongation positive
H_2O^-	nil	
Total	99.74	

Analysts: A. J. Easton and M. J. Abbott.

The new chemical analysis is presented in Table 2, together with determinable optical properties. The problems of wet chemical analysis pointed out by Zies (1966), in particular the determination of alumina, were avoided by using a combination of gravimetric (SiO_2, FeO, and MgO, by A. J. Easton), flame photometric (Na_2O, by A. J. Easton), and X-ray fluorescence techniques (TiO_2, Al_2O_3, total Fe, MnO, CaO, and K_2O, by M. J. A.). The X-ray fluorescence analysis was performed using an unpublished method made available by Dr. K. Norrish, C.S.I.R.O., Adelaide. H_2O^+ was not determined because pure material was scarce, and also because it has been shown (Kelsey and McKie, 1964; Zies, 1966) that essential water is absent.

The structural formula, calculated on the basis of 40 anions per unit cell, is given in Table 3, and it agrees well with the generalized formula

TABLE 3. STRUCTURAL FORMULAE OF AENIGMATITES, CALCULATED ON THE BASIS OF 40 ANIONS PER UNIT CELL

	1	2	3	4
(4) Si^{4+}	11.796	11.737	11.581	11.527
Al^{3+}	0.204	0.081	0.337	0.473
Fe^{3+}		0.182	0.082	
$\Sigma 4$	12.000	12.000	12.000	12.000
(6) Al^{3+}	0.022			0.043
Fe^{3+}	0.806	0.379	0.784	1.239
Mg^{2+}	0.541	0.209	0.176	0.174
Ti^{4+}	1.596	1.880	1.605	1.454
Fe^{2+}	8.724	9.221	9.159	8.347
Mn^{2+}	0.244	0.279	0.242	0.137
Ca^{2+}	0.067	0.032	0.034	0.606
$\Sigma 6$	12.000	12.000	12.000	12.000
(8) Ca^{2+}	0.031	0.137	0.201	0.527
Na^{+}	4.093	3.853	4.961	3.098
K^{+}	0.029	0.014	0.018	0.015
$\Sigma 8$	4.153	4.004	5.180	3.640
Anions				
OH^{-}		0.057	0.173	0.057
$O^{=}$	40.000	39.943	39.827	39.943
Molecular Ratio $\frac{100\ Fe^{3+}}{Fe^{2+}+Fe^{3+}}$	8.5	5.7	8.6	12.9

1. Aenigmatite from Nandewar Mts., anal. Table 2.
2. Cossyrite from Pantelleria (Zies, 1966, Table 1).
3. Aenigmatite from alkali syenite, E. Sayan Mts. (Mitrofanov and Afanas'eva, 1966).
4. Aenigmatite from alkali syenite, E. Sayan Mts. (Mitrofanov and Afanas'eva, 1966).

proposed by Kelsey and McKie (1964), *viz*: $X_4^{VIII}\ Y_{12}^{VI}\ Z_{12}^{IV}\ (O,OH)_{40}$, and it is also quite similar to the structural formulae calculated from other recent analyses (Kelsey and McKie, 1964; Zies, 1966).

The alumina is very low, as in all other recent analyses, but unlike those quoted by Kelsey and McKie (1964, Table IV, I and II) and Zies, (1966, structural formula calculated by present author, this paper Table 3) it is sufficient to satisfy the small deficiency of silicon in tetrahedral sites. Because of the crystal chemical difficulties of fitting Fe^{3+} into sites of tetrahedral co-ordination, it is suggested that the Fe^{3+} recorded in tetrahedral sites in these analyses is a result of slight errors in the determination of alumina.

The late-formed interstitial aenigmatite described here is similar to the aenigmatites recently analyzed by Kelsey and McKie (1964), and Zies (1966), but the TiO_2 is lower than in most of the phenocryst material with the exception of that analyzed by Mitrofanov and Afanas'eva (1966), whose analyses differ in several respects from those in Kelsey and McKie (1964). The structural formulae calculated by the present author from the analyses of the East Sayan Mountains aenigmatites (Mitrofanov and Afanas'eva, 1966) are set out in Table 3. No. 3 has a large excess of 8-fold coordinated ions over the theoretical 4 per unit cell, with high Na; No. 4 has relatively low TiO_2 (6.80%) and high CaO (3.72%) with a deficiency of 8-fold coordinated ions. The low titanium contents of both aenigmatites is possibly due to the reported modal abundance of the mineral (from 7% to 12% in some rocks), the total titanium content of the rocks being insufficient to form high-Ti aenigmatite.

The X-ray powder data of the Nandewar aenigmatite are very similar to those produced by Kelsey and McKie (1964, Table II), and also to those for the Ti-free synthetic aenigmatite produced by Ernst (1962, p. 715, Table 13).

PARAGENESIS

Aenigmatite occurs commonly in the groundmass of peralkaline trachytes and phonolites, as well as phenocrysts in pantellerites. The following conditions appear to be necessary for its formation: (1) Relatively high concentrations of TiO_2, (2) peralkalinity and (3) low oxygen fugacity.

The host trachyte of the aenigmatite (Table 1) contains 0.41 percent TiO_2. The pantellerites analyzed by Carmichael (1962, Table 6) have approximately the same content of TiO_2, ranging from 0.35 to 0.60 percent. The aenigmatite phenocrysts (with the exceptions noted above) have higher TiO_2 than the groundmass aenigmatite reported here. It appears that where aenigmatite crystallizes early it accepts titanium very readily, as suggested by Kelsey and McKie (1964); but late-stage crystallization will yield an aenigmatite with lower titanium because some has already been removed by titanomagnetite, aegirine-augite, or alkali amphibole. The fact that Ernst (1962) produced an aenigmatite synthetically in a Ti-free system indicates that a high titanium concentration is not absolutely essential to form the mineral. The TiO_2 in analyzed aenigmatites varies from 9.66 percent (Kelsey and McKie, 1964, Table 3, I) to 6.80 percent (Mitrofanov and Afanas'eva, 1966).

All aenigmatite-bearing rocks have a molecular excess of Na_2O+K_2O over Al_2O_3, with acmite in the norm. Some of the pantellerites from Pantelleria (Washington, 1913; Carmichael, 1962) have a molecular excess of Na_2O alone over $Fe_2O_3+Al_2O_3$ and have normative sodium metasilicate; but the presence of the latter is not considered essential for the crystallization of aenigmatite (Zies, 1960).

The host trachyte from the Nandewar Mountains has a peralkalinity ratio (agpaicity index) of 1.07 (defined in Table 1); other aenigmatite-bearing trachytes from the province have ratios ranging from 1.10 to 1.14. Clearly, peralkalinity is necessary for the formation of aenigmatite.

In his experimental study of the composition $Na_2O\cdot 5FeO_x\cdot 8SiO_2\cdot xH_2O$, Ernst (1962) found that aenigmatite existed with acmite and quartz at oxygen fugacities defined by the magnetite-wüstite and wüstite-iron buffers at water pressures up to 1,000 bars and temperatures from 650°C to 800°C. Although the addition of titanium to this simple system probably extends the stability field of aenigmatite (Kelsey and McKie, 1964), its general geometry is not expected to change. The oxygen fugacities at which aenigmatite was produced experimentally are lower than those at which magnetite and titanomagnetite can exist stably so that aenigmatite is the only phase which will accept large amounts of titanium and ferrous iron.

The ferromagnesian assemblages in the aenigmatite trachytes examined from the Nandewar Mountains are:

1. Titanomagnetite - sodic ferrohedenbergite($Ac_{10}Hd_{84}Di_6$) - aenigmatite - riebeckite-arfvedsonite solid solution.
2. Titanomagnetite - hedenbergite - acmite solid solution (approx. $Ac_{50}Hd_{50}$) - aenigmatite - riebeckite - arfvedsonite solid solution.
3. Titanomagnetite - hedenbergite - acmite solid solution - aenigmatite - arfvedsonite.

The assemblage titanomagnetite-fayalite-aenigmatite which is common in many trachytes, is equivalent to assemblage 1, with calcium so low that hedenbergite cannot form. Assemblages 2 and 3 probably formed at higher oxygen fugacities than assemblage 1 as shown by the change of composition of the clinopyroxene from a sodic ferrohedenbergite (with most of the iron as Fe^{2+}) to a hedenbergite-acmite solid solution (with the iron equally partitioned between Fe^{2+} and Fe^{3+}). If this is so, then the presence of aenigmatite in assemblages 2 and 3 indicates that aenigmatite is stable over a wider range of oxygen fugacities in natural Ti- and Ca-bearing systems than in the synthetic system investigated by Ernst (1962). The great influence of oxygen fugacity on the ferromagnesian assemblage and in particular on the presence or absence of aenigmatite is shown by the presence of the assemblage titanomagnetite—aegirine-augite in the same trachyte flow as the assemblage 1 above. The two assemblages are probably related by some reaction as:

$$\underset{\substack{\text{Titanium-rich}\\ \text{magnetite}}}{6(\mathrm{TiFeO_3\cdot Fe_3O_4})} + 12\mathrm{SiO_2} + \underset{\substack{\text{Acmite-hedenbergite solid}\\ \text{solution}}}{12(\mathrm{NaFe^{3+}Si_2O_6\cdot CaFe^{2+}Si_2O_6})}$$

$$\rightleftharpoons \underset{\text{Aenigmatite}}{3(\mathrm{Na_4Fe^{2+}_{10}Ti_2Si_{12}O_{40}})} + \underset{\text{Hedenbergite}}{12(\mathrm{CaFe^{2+}Si_2O_6})} + \underset{\text{Magnetite}}{2\,\mathrm{Fe_3O_4}} + 5\mathrm{O_2}$$

The reaction of fayalite and ilmenite or fayalite and ulvospinel with a sodium-rich liquid to give aenigmatite, as proposed by Carmichael (1962), is the corresponding reaction for Ca-free systems.

Titanomagnetites rimmed with aenigmatite have been observed in several trachytes from the Nandewar Mountains. This indicates a possible reaction of titanomagnetite with a peralkaline sodium silicate liquid to yield aenigmatite under conditions of low oxygen fugacity. The breakdown products of aenigmatite under controlled conditions of oxygen fugacity are to be further investigated.

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NUCLEI OF PLEOCHROIC HALOS IN BIOTITES OF SOME SIERRA NEVADA GRANITIC ROCKS

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The concentric ring structure of pleochroic halos in biotite has been studied in very great detail (Hirschi, 1920; Kerr-Lawson, 1927, 1928;

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