

Aenigmatite From Mt. Edziza, British Columbia, Canada

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Abstract

Aenigmatite is a ubiquitous constituent of the highly fractionated, peralkaline end members of the Mt. Edziza volcanic complex in northern British Columbia. In comendite lavas and tephra it occurs as phenocrysts with aegirine, aegirine-augite and arfvedsonite, whereas it is confined to the groundmass of trachytes. This is attributed to different f_{O_2} 's during the intratelluric and groundmass stages of crystallization of comendite and trachyte.

Electron microprobe analyses indicate that both groundmass and phenocrystic aenigmatite have similar compositions that are close to those of aenigmatite from other localities. The absence of intermediate compositions between aenigmatite and rhonite suggests that solid solution between the two minerals is lacking or limited by a wide range of immiscibility.

Geological Setting

Mt. Edziza (Fig. 1) is the largest in a group of volcanic centers along a north-south zone of normal faults that cut diagonally across the Cordillera of northwestern British Columbia (Souther, 1970). The entire complex, which covers an area of 2,000 square kilometers, includes a broad spectrum of alkaline and peralkaline rocks ranging from picritic alkali olivine basalt through trachyte to sodic rhyolite (comendite). The first flows issued from a cluster of vents south of the present crater of Mt. Edziza in Late Miocene time and give K/A ages of about 9 m.y. (Wanless, personal communication). Eruptions continued periodically throughout Pleistocene and into Recent time. The youngest dated flow has a C^{14} age of 1340 ± 130 years B.P. (Souther, 1967) and a still younger, but undated pumice fall is estimated from its state of preservation to be less than 500 years old.

Three principal stages of eruption are recognized (Souther, 1972). Each stage began with the voluminous outpouring of fluid alkali olivine basalt and culminated with eruption of a relatively small volume of more acid magma. The basalt formed flat-lying shields associated with small composite cones and local piles of sub-glacial tuff-breccia and pillow lava, whereas eruptions of trachyte and rhyolite began

with explosive discharge of pumice and ended with upwelling of viscous lava as domes and short, thick flows. The latter comprise the edifice of Mt. Edziza proper, which rises 1500 meters above the surface of the basaltic shield as a steep-sided composite dome surmounted by a circular summit crater 1 1/2 km in diameter. Stage three activity was confined to satellitic vents around the periphery of the central dome. Effusion of blocky flows of olivine-rich stage-three lavas was followed by a single shower of rhyolitic pumice that brought all activity to an end.

Petrography

A full treatment of the petrochemistry of the Edziza lavas is being prepared by Souther. In summary, the basalts have the simple mineralogy typical of alkali olivine basalts: moderately zoned labradorite, clinopyroxene, olivine, and titaniferous magnetite. The mineralogy of the trachytes and rhyolites is characteristic of peralkaline rocks, and includes such soda-rich minerals as aegirine-augite, aegirine, arfvedsonite, and aenigmatite. No orthopyroxene was found in any of more than 300 thin sections examined. Average values of 70 modal analyses and 90 chemical analyses are shown in Table 1.

In general the stage I basalts are ophitic to sub-



FIG. 1. Index map.

ophitic, with laths of plagioclase (An_{70} to An_{50}), granules of olivine (FO_{72}) and titanomagnetite enclosed in deep purple titanaugite. No transitional rocks intervene between stage I basalt and stage I comendite (sodic rhyolite). The latter forms ash-flows, ash falls, and lava domes; all of which contain abundant phenocrysts of quartz, sanidine, and anorthoclase and sparse phenocrysts of aegirine-augite, aegirine, and aenigmatite. Stage II basalts commonly have an intergranular texture in which subhedral to euhedral plagioclase, strongly zoned titanaugite, olivine, and titaniferous magnetite all occur as both groundmass and phenocrystic minerals in a glassy matrix. They grade through trachybasalt—in which titanaugite is rimmed with aegirine-augite—to trachyte, in which aegirine (associated with aenigmatite and arfvedsonite) is the principal pyroxene. Stage III basalts are commonly porphyritic, with phenocrysts of plagioclase, titanaugite, and abundant olivine in a glassy or finely crystalline matrix highly charged with magnetite granules. The

TABLE 1. Average Modal and Chemical Analyses of Mt. Edziza Lavas

No. of Specimens	Stage 1 Basalt 10	Stage 1 Comendite 4	Stage 2 Basalt 10	Stage 2 Trachyte 5	Stage 3 Basalt 5
Plagioclase (An_{50} - An_{70})	54.4	---	46.0	---	45.1
Plagioclase (Sodic)	2.1	35.4	3.6	53.7	---
Anorthoclase	---	16.5	---	trace	---
Sanidine	---	12.6	---	trace	---
Quartz	---	14.8	---	---	---
Titanaugite	17.8	---	29.8	---	24.2
Olivine	5.2	---	2.2	---	15.3
Magnetite	12.7	2.6	9.8	0.5	12.8
Aegirine-augite	---	1.2	trace	9.4	---
Aegirine	---	2.0	---	4.4	---
Arfvedsonite	---	trace	---	1.9	---
Aenigmatite	---	1.1	---	12.5	---
Glass	1.9	8.6	5.1	16.5	1.9
Alteration products	5.9	5.2	3.5	1.1	0.9
SiO ₂	46.2	74.8	46.5	64.1	48.6
TiO ₂	3.06	0.16	2.88	0.46	2.11
Al ₂ O ₃	16.4	12.1	15.4	13.7	17.3
Fe ₂ O ₃	3.0	3.0*	6.2	8.5*	2.2
FeO	9.4	n.d.	6.9	n.d.	9.2
MnO	0.18	0.04	0.21	0.18	0.15
MgO	3.9	0.4	4.6	0.7	7.1
CaO	8.3	0.3	9.8	1.2	8.4
Na ₂ O	3.3	5.0	2.7	5.7	3.5
K ₂ O	1.4	3.9	0.7	4.5	1.3
H ₂ O	1.3	n.d.	1.7	n.d.	0.6
P ₂ O ₅	0.73	n.d.	0.31	n.d.	0.49
CO ₂	2.5	n.d.	0.7	n.d.	0.2

*indicates total Fe calculated as Fe₂O₃.

final, phase III rhyolitic pumice is completely vitreous.

The aenigmatite-bearing trachytes and rhyolites of Mt. Edziza are considered to be the late fractionation products of a parent alkali olivine basalt magma with the initially high content of TiO_2 and FeO and unusually low MgO that is characteristic of the Edziza shield basalts. The trachytes and rhyolites themselves lie close to the boundary between alkaline and peralkaline lavas as defined by Shand (1951) with molecular $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ equal to or slightly greater than Al_2O_3 .

Occurrence of Aenigmatite

Aenigmatite is confined, on Mt. Edziza, to trachytes and rhyolites of stage I and stage II. It is a

ubiquitous constituent of the trachytes, where it may form up to 15 percent of the rock, and occurs sporadically as a minor constituent of the rhyolites.

In holocrystalline rhyolite lavas, the aenigmatite forms tiny (± 1 mm) intergranular euhedra associated with quartz, sanidine, sodic plagioclase, anorthoclase, aegirine-augite, aegirine, and magnetite. The aenigmatite commonly exhibits sharp crystal boundaries against aegirine which may, in turn, be partly surrounded by arfvedsonite (Fig. 2 A and B). This same assemblage of minerals is found as discrete crystals enclosed in the pumiceous matrix of stage I ash falls and ashflows, one of which yielded the perfect euhedral crystals of aenigmatite described in this paper (Fig. 3). Obsidian from the base of many comendite flows is charged with tiny, oriented

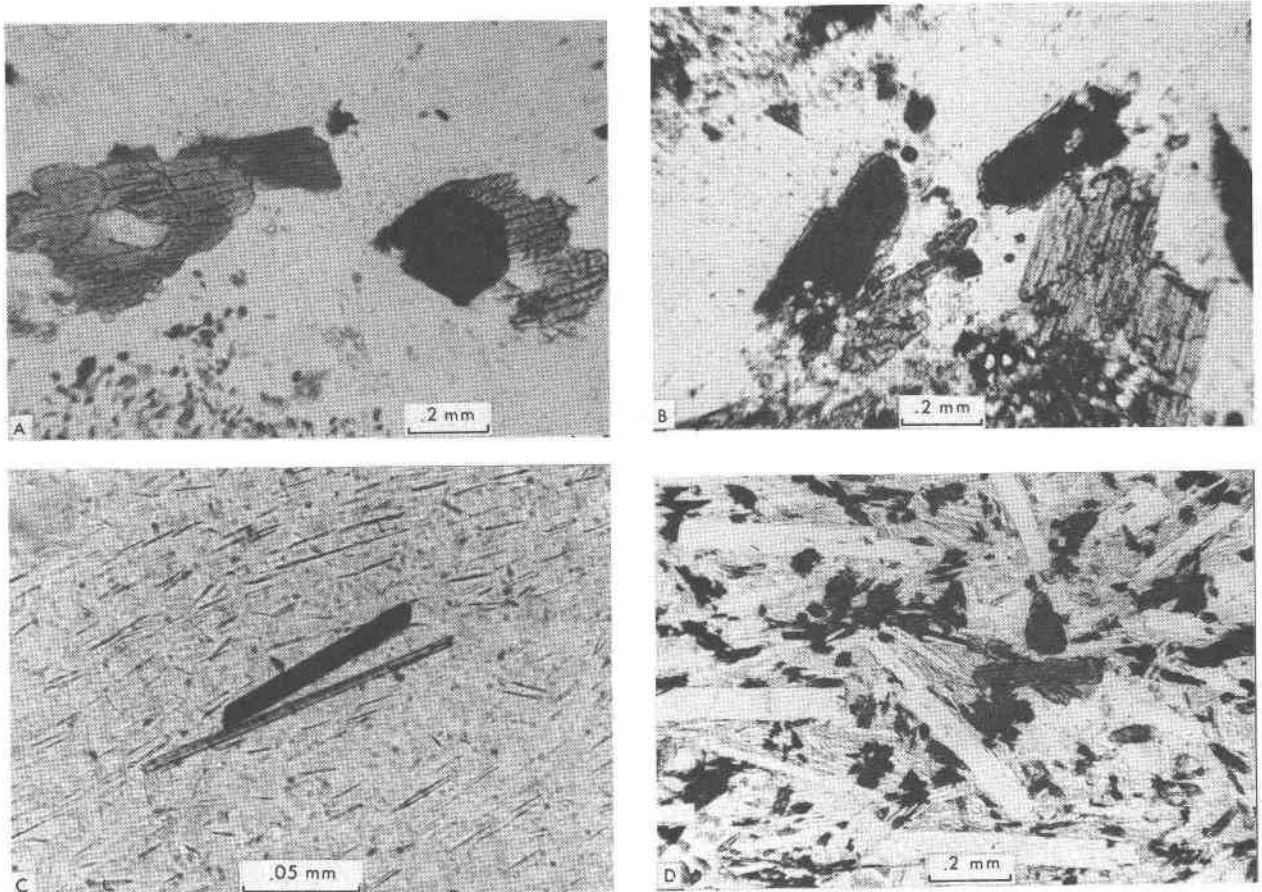


FIG. 2. Photomicrographs of aenigmatite-bearing rocks from Mt. Edziza: A. Euhedral crystals of aenigmatite (black) partly enclosed by aegirine. Aegirine crystal at left is partly surrounded by arfvedsonite (dark gray). From stage I comendite flow. B. Euhedral crystals of aenigmatite (black) completely surrounded by a narrow rim of aegirine. From stage I comendite lava dome. C. Microlites of aegirine (longer of two crystals) and aenigmatite in stage I comendite glass. From chilled base of lava flow. D. Interstitial aenigmatite (black) and aegirine (dark gray) in the vitreous groundmass of stage II trachyte. This section was used for microprobe analysis of groundmass aenigmatite (Table 4, sample 2).

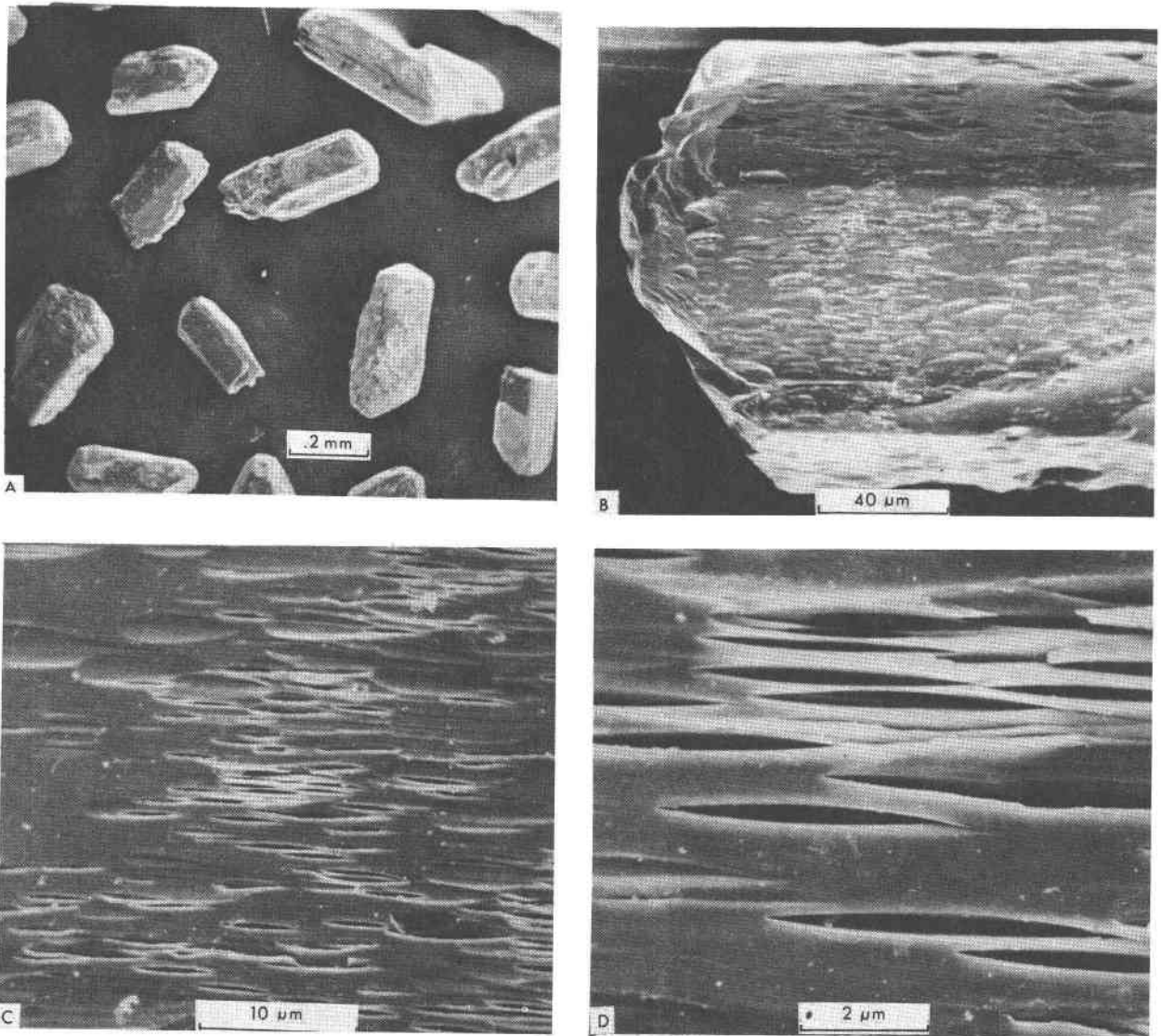


FIG. 3. Electron micrographs of aenigmatite phenocrysts from stage I comendite ash. These crystals are from the sample used for optical and X-ray study (Tables 2 and 3) and for chemical analysis (Table 4, sample 1). A. Crystals of aenigmatite after separation with methylene iodide. B. Close view of single aenigmatite crystal showing well developed (100) and (010) faces. C. Detail of crystal face (100) showing lenticular voids. Note that the voids are oriented along both cleavage directions, one in the plane of the photograph and the other at approximately right angles to it. D. Close view of lenticular voids parallel to (010).

microlites of plagioclase and slightly larger, acicular crystals of aegirine and aenigmatite which appear to have crystallized simultaneously (Fig. 2 C).

In holocrystalline trachytes, aenigmatite rarely forms phenocrysts. It occurs with aegirine and arfvedsonite in a groundmass of ragged, intergrown anhedral crystals that are interstitial to the feldspar laths (Fig. 2 D). Glassy trachyte from the chilled base of one flow contains plagioclase phenocrysts up to 2 mm long and smaller microlites of aegirine and aenigmatite. Locally the glass has spherulites

comprising radiating acicular crystals of feldspar, aegirine, and aenigmatite, obviously formed after the flow was essentially solid.

It is noteworthy that aenigmatite is found mostly as phenocrysts in the comendites and as a groundmass constituent of the trachytes. The genetic significance of this is discussed later.

Optical Properties

Due to its small size, groundmass aenigmatite was not used for the determination of optical proper-

ties. The properties listed below were measured on phenocrysts from a non-welded ash fall of highly expanded comendite pumice. The aenigmatite forms elongated prisms, 1 to 4 mm in length, with well developed faces on (100), (010), (110), and (1 $\bar{1}$ 0), and perfect cleavage parallel to (010) and (100). In thin sections of phenocrysts the cleavage traces appear as sinuous or undulatory dark bands which, under the electron microscope, are seen to be lenticular voids aligned along both cleavage directions (Fig. 3 C, D). The voids have average dimensions of about 0.5 \times 5.0 microns. They may be analogous to the pores in "light wolframite" (Escobar *et al.*, 1971) which are attributed to incorporation of water and gasses during crystallization. Similar voids were not observed in the groundmass aenigmatite.

Optical properties of the analyzed phenocrystic aenigmatite are given in Table 2. The optic plane is parallel to (010). Both groundmass and phenocrystic aenigmatite have very strong absorption and are almost opaque in the Z direction. Dispersion is strong with $r < v$ and, in some sections, an anomalous bluish-grey interference color is noted. The refractive indices are very high and were measured by the immersion method, using standard glass powders in methylene iodide with dissolved phosphorous and sulfur (Sueno, 1933). Because of its strong pleochroism and high refractive indices the error of measurement was high.

X-Ray Analysis

X-ray powder spectrographs of aenigmatite were obtained at 30 kV, 20 mA, scanning speed of 1/2 deg. 2 θ per minute, scale factor and a time constant 8. An external quartz standard was used for calibration. The average d value from four determinations is given in Table 3, column 1. Kelsey and

TABLE 2. Optical Properties of the Phenocrystic Aenigmatite from Mt. Edziza

		Pleochroism	
α	1.800 \pm 0.005	X	light yellowish brown
β	1.813 \pm 0.005	Y	reddish brown
γ	1.88 \pm 0.01	Z	deep reddish brown - black
$c \wedge Z$	43°	Absorption	X<Y<Z
Optic plane parallel to (010)			
$2V_Z$ obs 52°			
$2V_Z$ calc 49°			

TABLE 3. X-Ray Powder Data for Aenigmatite

Mt. Edziza		Kola		Mt. Edziza		Kola	
d Å	I	d Å	I	d Å	I	d Å	I
8.11	80	8.11	VS(1)	2.073	25	2.073	W
		7.43	VW	2.010	25	2.007	MW
		6.38	VW	1.976	15	1.973	VVW
4.84	30	4.82	W	1.948	15	1.947	VVW
4.41	20	4.40	W	1.911	20	1.912	VW
4.20	25	4.20	W			1.802	VWB
3.708	30	3.704	MW			1.772	VVW
3.491	25	3.484	W	1.732	20	1.731	WB
3.152	100	3.144	VS(2)	1.678	10	1.680	W
2.940	45	2.939	MS	1.632	25		
2.813	25	2.806	VW	1.625	25	1.627	M
2.754	25	2.753	VW	1.611	20	1.610	W
2.707	75	2.705	S(3)			1.590	VVW
2.658	20	2.658	VVW	1.558	10	1.560	VVW
2.546	60	2.545	S	1.518	20	1.514	W
2.453	20	2.462	VW	1.495	25	1.498	MW
2.417	35	2.413	M	1.480	25	1.484	MW
2.345	15	2.347	VW	1.478	20		
2.307	15	2.310	VW	1.471	30		
2.193	10	2.197	VVW	1.468	35	1.468	MB
2.120	60	2.119	MS	1.465	35		

Mt. Edziza: Present study
Kola: Kelsey and McKie (1964)

McKie (1964) made a careful X-ray analysis of aenigmatite and determined the unit-cell dimensions. The results of the present study are in good agreement with their values, except for a few peaks of weaker intensity. From the shape and dimensions of the unit-cell, the pattern of aenigmatite is unindexable. Kelsey and McKie determined only three peaks with larger d -spacings as follows: 8.11 Å, 001 and 010; 7.43, 0 $\bar{1}$ 1; 6.38, 111. Of these, the second and the third peaks are missing in the aenigmatite under investigation.

Kelsey and McKie (1964) suggested that aenigmatite is triclinic, and its structure is based on silicate chains of pyroxene type cross-linked by Ti⁴⁺ and Fe²⁺. More recently Canillo *et al.* (1971), in their detailed study of the structure of aenigmatite, showed that its silicate chains are of sapphirine type, composed of pyroxene-like chains, and that formation of twins, frequently observed in volcanic aenigmatite, is interpreted as due to the quenching effect of crystallization under rapid cooling.

The Edziza aenigmatite was analyzed by Mr. A. G. Plant of the Geological Survey of Canada, using a Materials Analysis Company electron microprobe operated at 20 kV and with a specimen current of 0.035 μ A. Three phenocrysts from stage I comendite and ten grains from the groundmass of stage II trachyte were selected for analysis. Each phenocryst was analyzed at ten spots approximately equally spaced in a traverse across the grain to check for zoning or inhomogeneity. They are unzoned and homogeneous, and all three grains are chem-

ically identical. The groundmass aenigmatite, though too fine-grained for analysis of more than one or two spots per grain, also proved to be fairly uniform in composition. Average data from all points (Table 4) show the phenocrystic and groundmass aenigmatites to be similar in composition, except that the latter is appreciably lower in TiO₂ and slightly higher in SiO₂ and FeO than the former. The 6.95 percent TiO₂ of the groundmass aenigmatite is, in fact, the lowest recorded for any aenigmatite except that from the Khushagol intrusive which has 6.80 percent TiO₂ (Mitrofanov and Afanas'eva, 1966).

Fe₂O₃ contents were calculated after the method proposed by Finger (1972) with the following results:

Phenocrystic aenigmatite		Groundmass aenigmatite	
Total Fe as FeO 41.1		Total Fe as FeO 42.3	
Fe ₂ O ₃	4.0	Fe ₂ O ₃	4.9
FeO	37.5	FeO	39.9

Atomic proportions (Table 4) were calculated using these values.

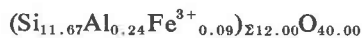
The structural formula was first given as metasilicate by Gossner and Spielberger (1929) and Kostyleva (1930), and later Fleischer (1936) proposed X₄Y₁₃(Si₂O₇)₆, in which X = Na, K, Ca; Y = Fe²⁺, Fe³⁺, Mn, Mg, Ti, Al; and (OH) content is not essential. From detailed examination of unit-cell dimensions, density, and chemical composition, Kelsey and McKie (1964) found that the unit-cell should contain O₄₀ instead of O₄₂, and gave the formula:



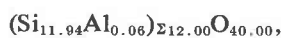
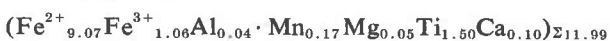
X = Ca, Na, K; Y = Fe²⁺, Fe³⁺, Mn, Mg, Ti, Al, Ca; and Z = Si, Al, Fe³⁺, or more specifically, for their crystal:



The phenocrystic aenigmatite from Mt. Edziza has the formula



and the groundmass aenigmatite,



both of which are in good agreement with the gen-

eral formula of aenigmatite given by Kelsey and McKie. Moreover, it is seen from Table 4 that aenigmatites from different localities have very similar compositions. Comparison of the two formulas for Edziza aenigmatites indicates that low Ti content of the groundmass aenigmatite is compensated for by increased Fe³⁺. The genetic significance of this is discussed in the following section.

Genetic Significance

Aenigmatite is considered to be a typical constituent of peralkaline lavas or plutonic rocks in which soda predominates over alumina, in some cases over even the sum of alumina and ferric oxide. The aenigmatite-bearing rocks of Mt. Edziza have molecular (Na₂O + K₂O) ≥ Al₂O₃ > Na₂O. They are thus peralkaline but with a lower content of soda than some of the rocks from which aenigmatite has been described. The relatively high TiO₂ content of Edziza lavas may have been a factor in the formation of aenigmatite.

It is noteworthy that the groundmass aenigmatite is lower in TiO₂ than aenigmatite occurring as phenocrysts. A similar relationship was noted by

TABLE 4. Chemical Composition of Aenigmatites from Various Localities

	1	2	3	4	5	6
SiO ₂	40.7	41.7	41.02	39.62	41.41	41.30
TiO ₂	8.3	6.95	8.92	9.66	8.30	7.43
Al ₂ O ₃	0.72	0.29	0.94	0.64	0.00	0.67
Fe ₂ O ₃	n.d.	n.d.	1.31	4.64	4.46	3.75
FeO	41.1	42.3	38.84	33.92	35.87	36.52
MnO	0.85	0.71	1.16	2.46	1.78	1.01
MgO	0.11	0.11	0.07	1.65	1.35	1.27
CaO	0.50	0.32	0.45	0.44	0.00	0.32
Na ₂ O	7.2	7.2	7.36	7.20	6.87	7.39
K ₂ O	0.03	0.11	0.06	0.04	0.04	0.08
H ₂ O	n.d.	n.d.	n.d.	0.05	0.00	n.d.
Cl	n.d.	n.d.	n.d.	0.02	n.d.	n.d.
Total	99.51	99.69	100.13	100.34	100.08	99.74
Si	11.67	11.94	11.73	11.26	11.79	11.80
Al	0.24	0.06	0.27	0.21	-	0.20
Fe ³⁺	0.09	-	-	0.53	0.21	-
	12.00	12.00	12.00	12.00	12.00	12.00
Al	-	0.04	0.05	-	-	0.02
Fe ³⁺	0.77	1.06	0.28	0.47	0.74	0.81
Mg	0.05	0.05	0.03	0.70	0.57	0.54
Ti	1.79	1.50	1.92	2.07	1.78	1.60
Fe ²⁺	9.00	9.07	9.29	8.06	8.54	8.72
Mn	0.21	0.17	0.28	0.59	0.43	0.24
Ca	0.15	0.10	0.14	0.11	-	0.07
	11.97	11.99	11.99	12.00	12.06	12.00
Ca	-	-	-	0.02	-	0.03
Na	4.01	4.00	4.08	3.97	3.79	4.09
K	0.01	0.04	0.02	0.01	0.02	0.03
	4.02	4.04	4.10	4.00	3.81	4.15
O	40.00	40.00	40.00	39.90	40.00	40.00
OH	-	-	-	0.10	-	-
	40.00	40.00	40.00	40.00	40.00	40.00

1 Mt. Edziza (phenocryst) (this study) 2 Mt. Edziza (groundmass) (this study) 3 Pantelleria (Carmichael, 1962) 4 Kola (Kelsey and McKie, 1964) 5 Greenland (Kelsey and McKie, 1964) 6 Nandewar (Abbott, 1967)

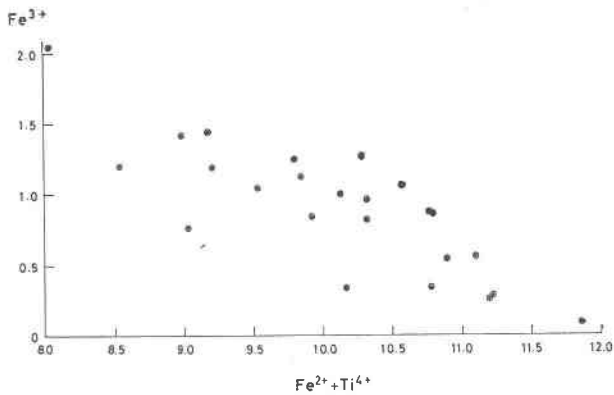


FIG. 4. Relation between Fe^{3+} and $\text{Fe}^{2+} + \text{Ti}^{4+}$ cations in unit formula of aenigmatites.

Abbott (1967) in the aenigmatite-bearing trachyte from Nandewar, New South Wales. He attributes the low TiO_2 content of groundmass aenigmatite to extraction of Ti from the liquid by precipitation of titanomagnetite or other Ti-bearing minerals in the phenocrystic stage of crystallization. This explanation is consistent with the petrography of the Edziza rocks, many of which contain early formed phenocrysts of both titanomagnetite and titanaugite. Also, the chemical formulae suggest that Ti is replaced by Fe^{3+} in the groundmass aenigmatite.

In the syenites and monzonites of Morotu, Sakhalin, Yagi (1953) described a complex zonal growth of aenigmatite, aegirine-augite, arfvedsonite, and aegirine in that order from the core to the margin. Similar zoning is not so well developed in the Edziza rocks; however, the order of crystallization (aenigmatite, aegirine-augite, arfvedsonite) deduced from partially mantled crystals, is the same. The presence of feldspar, aegirine (or aegirine-augite), and aenigmatite microlites in obsidian from the chilled margins of aenigmatite-bearing flows suggests that the crystallization of these three minerals began simultaneously. Subsequent mantling of aenigmatite euhedra by aegirine-augite and arfvedsonite indicates that crystallization of the latter two minerals continued after crystallization of aenigmatite.

Carmichael (1962) found an antipathetic relation between the amount of aenigmatite and that of fayalite and ilmenite, suggesting that aenigmatite may form by the reaction of fayalite and ilmenite with sodium-rich liquid. Although no evidence has been found to indicate this reaction, Lindsley and Haggerty (1971) described an interesting occurrence of aenigmatite in the pegmatoid of Picture Gorge basalt of Oregon, U.S.A., which is the first

reported occurrence of this mineral in basaltic rocks. There aenigmatite locally and selectively replaces ilmenite lamellae in ilmenomagnetite formed simultaneously with or later than sodium-rich clinopyroxenes. All these relationships support very late stage formation of aenigmatite.

Experimental studies of aenigmatite have been carried out in several laboratories. Ernst (1962) formed "Ti-free aenigmatite" at the f_{O_2} of wustite-magnetite buffer, but not at that of the fayalite-magnetite-quartz buffer. The synthesized crystals have properties very similar to those of natural aenigmatite, and this clearly indicates that Ti is not essential. Ernst tentatively gave the formula $\text{Na}_4\text{Fe}^{2+}_7\text{Fe}^{3+}_6\text{Si}_{12}\text{O}_{42}$ to this Ti-free analogue, following Fleischer's formula, but this should now be expressed by $\text{Na}_4\text{Fe}^{2+}_8\text{Fe}^{3+}_4\text{Si}_{12}\text{O}_{40}$ after Kelsey and McKie's formula. Formation of "Ti-free aenigmatite" raised the question of whether or not there is a solid solution series between $\text{Na}_4\text{Fe}^{2+}_{10}\text{Ti}_2\text{Si}_{12}\text{O}_{40}$ and $\text{Na}_4\text{Fe}^{2+}_8\text{Fe}^{3+}_4\text{Si}_{12}\text{O}_{40}$. Figure 4 indicates a reciprocal relationship between the number of Fe^{3+} cations and the total (Fe^{2+} plus Ti) cations in the unit formula. This, and the fact that low Ti in the groundmass aenigmatite from Edziza is compensated by increased Fe^{3+} , supports the possibility of a solid solution series between the two above-mentioned end members through replacement of $\text{Fe}^{2+} + \text{Ti} \rightleftharpoons 2 \text{Fe}^{3+}$. The Ti content of aenigmatite is, however, rather limited, ranging between 1.50 and 1.90 cations per unit formula in all but a few analyses (Fig. 5). This means that the replacement of $\text{Fe}^{2+} + \text{Ti} \rightleftharpoons 2 \text{Fe}^{3+}$ is valid only for a limited range of Ti, and only aenigmatites moderately rich in Ti content

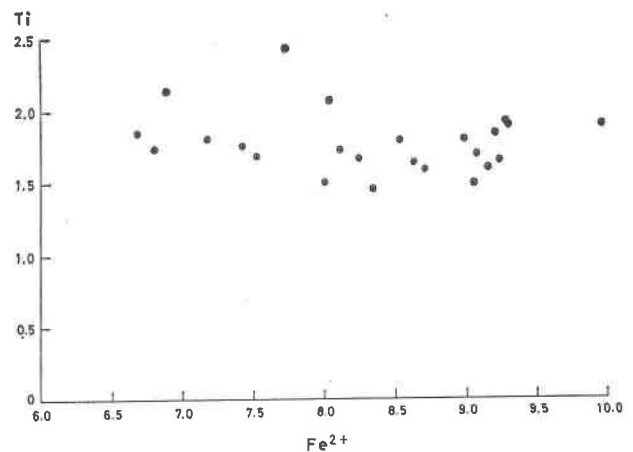


FIG. 5. Relation between Ti and Fe^{2+} cations in unit formula of aenigmatites.

do form in nature, even though a Ti-free analogue has been formed in the laboratory. Therefore magma with a relatively high Ti content is considered essential for the formation of aenigmatite in nature.

Following Ernst's experiments, Thompson and Chisholm (1969) synthesized aenigmatite of idealized composition. The conditions were as follows: Aenigmatite was formed within 48 hours from the oxide mixtures at 700°C, $p_{\text{H}_2\text{O}} = 1$ kbar and $f_{\text{O}_2} =$ iron-wustite buffer. From the occurrence of aenigmatite in the pantellerites from Pantelleria, Nicholls and Carmichael (1969) indicated that aenigmatite may be stable at oxygen fugacities even three orders of magnitude above the Ni-NiO buffer, but Lindsley (1971) experimentally showed that aenigmatite will dissociate into assemblages of acmite, titaniferous magnetite, and quartz under the f_{O_2} of Ni-NiO buffer. When these decomposed materials were hydrothermally heated under the f_{O_2} of fayalite-magnetite-quartz buffer, aenigmatite was again formed. From these results Lindsley (1971) estimated that the stability curve for aenigmatite should lie between the f_{O_2} values given by Ni-NiO and fayalite-magnetite-quartz buffer curves at 750°C and 500 bars. The fact that aenigmatite can form from its anhydrous starting materials in evacuated silica-glass tubes at atmospheric pressure suggests that f_{O_2} rather than total pressure has the greater influence on the stability of aenigmatite.

Although we have no direct determination of f_{O_2} values in these alkalic rocks, Fudali's (1965) estimation is relevant to the present discussion. Fudali found that f_{O_2} ranges from 10^{-9} to $10^{-6.5}$ atmosphere for basalts and andesites of the Cascades at their liquidus temperatures and that there is a strong tendency for the f_{O_2} to increase with increasing SiO_2 content. From these data it is reasonable to consider that f_{O_2} increases from trachyte to comendite and that it also increases from the intratelluric to the groundmass stage within the same magma as crystallization proceeds. Therefore, the presence of aenigmatite in the groundmass of trachyte and in the phenocrysts of comendite suggests that the f_{O_2} 's at these stages are just suitable for the formation of aenigmatite, whereas f_{O_2} 's are either too low in the intratelluric stage of trachyte or too high in the groundmass stage of comendite.

Relation between Aenigmatite and Rhonite

Rhonite was originally described by Soellner (1907) from southern Rhon, Germany, and has

been found in various mafic to intermediate alkalic rocks as a primary mineral or as an alteration product of amphiboles. Rhonite has been regarded as isostructural with aenigmatite, because of similarities in optic properties and crystal morphology. Fleischer (1936) suggested that rhonite is isomorphous with aenigmatite through substitution of CaAl for NaSi and that the two minerals are end members of a solid solution series of plagioclase type. Cameron, Carmen, and Butler (1970) recently discussed the substitution between aenigmatite and rhonite and, following Fleischer's suggestion, expressed intermediate members by the formula



The amount of Si calculated by this formula is, however, always greater than that present, from which they concluded that if rhonite and aenigmatite do form a solid solution series, then they should have a more complex substitution than CaAl for NaSi.

In order to investigate the relation between the two minerals, all existing chemical data, including Ernst's Ti-free aenigmatite are plotted in Ca-Na-K and Fe-Mg-Ti diagrams (Figs. 6 and 7), in which Fe is the total of Fe^{2+} and Fe^{3+} . The diagrams indicate that aenigmatite and rhonite have their own fields, each of limited compositional range, and that there are no intermediate compositions. Incorporation of Ti-free aenigmatite does not materially change the compositional range of aenigmatite.

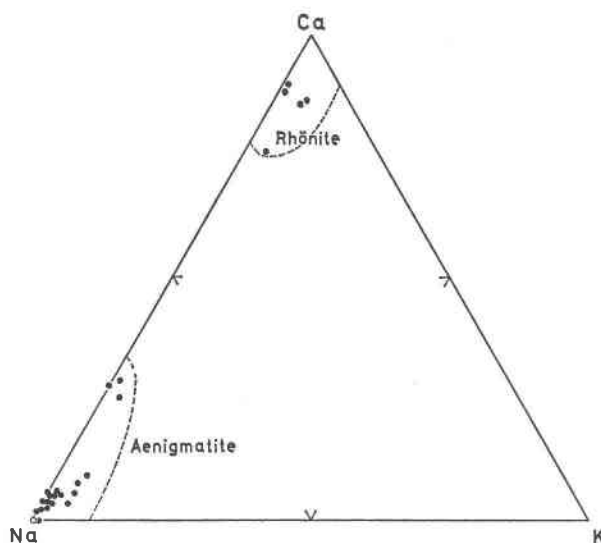


FIG. 6. Plot of aenigmatite and rhonite on Na-Ca-K diagram.

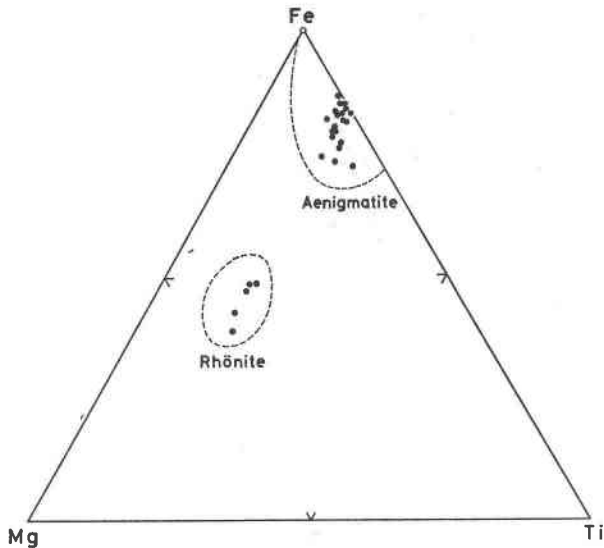


FIG. 7. Plot of aenigmatite and rhonite on Fe-Mg-Ti diagram.

Tomita (1934) described a zonal structure comprising a rhonite core grading outward through rhonite-aenigmatite to an aenigmatite margin in the teschenite from Oki, Japan. Conversely, rhonite cores separated by sharp boundaries from aenigmatite margins in the monzonites and syenites from Morotu, Sakhalin (Yagi, 1953), suggest that the two minerals must, if they form a solid solution series, have a wide range of immiscibility. This is further supported by the lack of zoning in relatively large phenocrysts and also by the similarity in composition of phenocrystic and groundmass aenigmatites from Mt. Edziza.

Grunhagen and Seck (1972), in their study of rhonite from metaphonolite of Puy de Saint-Sandoux, indicated the following two possibilities: (1) There is a miscibility gap between aenigmatite and rhonite. (2) Though a complete series of solid solutions is thermodynamically stable, conditions favorable for their formation do not exist in natural magmas. They consider the second possibility more likely in view of complex substitutions between the two minerals. Experimental study of the compositions of pure rhonite and those intermediate between aenigmatite and rhonite under various conditions is expected to throw light on this problem.

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