MINERALOGICAL MAGAZINE, JUNE 1976, VOL. 40, PP. 595–8

Ænigmatite from an Ægirine–Riebeckite granite, Liruei Complex, Nigeria

G. D. BORLEY

Dept. of Geology, Imperial College of Science and Technology, London, S.W.7

SUMMARY. Ænigmatite occurs as a trace constituent of the Ægirine–Riebeckite Granite of the Liruei Complex, Younger Granite Province of Nigeria. It is enriched in Ti and Mg and depleted in Si, Al, and Ca relative to many other ænigmatites. Relative to coexisting ægirine and arfvedsonitic riebeckite it is enriched in Ti and depleted in Fe^{3+}. Conditions required for formation of the mineral appear to have been high Ti concentration in a peralkaline magma of low T and f_{O_2}. The composition of the Nigerian ænigmatite confirms that there is only limited miscibility between rhönite and ænigmatite although in certain circumstances the two may have a paragenetic relationship.

ÆNIGMATITE is a relatively uncommon mineral, its main occurrence being as a groundmass or phenocryst phase in peralkaline plutonic and volcanic rocks. In rocks of this type it has been reported since the 19th century, but more recently it has been described as present in the syenites of Sakhalin (Yagi, 1953), the obsidians of Pantelleria (Carmichael, 1962), the Nandewar volcanics of New South Wales (Abbott, 1967), the Mayor Island pantellerites (Ewart *et al.*, 1968), the pantelleritic tuffs of Ethiopia (Gibson, 1970), the intrusions of the Tugtutoq Complex of South Greenland (Upton *et al.*, 1971), the rocks of the Diablo Plateau area of Trans Pecos Province (Hodges and Barker, 1973), and from Mt. Edziza, British Columbia (Yagi and Souther, 1974).

Various structural formulae have been proposed for the mineral, the earliest being that of Fleischer (1936): $Na_4Fe_9^{2+}Fe_2^{3+}Ti_2Si_{12}O_{42}$. This formula was based on a consideration of analytical and unit-cell data by Fleischer who suggested a general formula $2[X_4Y_{13}(Si_2O_7)_6]$ for the unit-cell. A different formula has been suggested by Kelsey and McKie (1964) and Cannillo *et al.* (1971): $Na_4(Fe_{10}^{2+}Ti_2)Si_{12}O_{40}$. Calculation of this formula was based on a determination of the number of oxygen atoms per unit-cell and it appears to be generally accepted.

Fleischer (1936) also proposed that ænigmatite was an end-member of an ænigmatite–rhönite series, rhönite being formed by substitution of CaAl for NaSi. Rhönite is rarer than ænigmatite but it does occur in some silica-poor basic and intermediate rocks such as the teschenites of Oki Island (Tomita, 1934), the melasyenites of Big Bend National Park, Texas (Cameron *et al.*, 1970), the melaphonolite of the Auvergne (Grunhagen and Seck, 1972), and the alkalic rocks of Sakhalin (Yagi, 1953). A plot of analyses of ænigmatite and rhönite by Yagi and Souther (1974) suggests that the two minerals have limited compositional ranges and that there is probably a wide immiscibility gap between them. This gap persists even when the ænigmatite is Ti-depleted like that reported by Hodges and Barker (1973). The paragenetic relationship between the two minerals is still obscure but will be commented on in a later section of the paper.

Present occurrence of ænigmatite. The ænigmatite discussed in this paper comes from a peralkaline Ægirine–Riebeckite Granite in the Liruei Complex, which is one of the Younger Granite Complexes of Nigeria. Ænigmatite is a trace constituent in this Granite as it is in one or two other peralkaline granites of the Province, and its presence was only discovered during mineral separation and subsequent examination of many thin sections. It coexists with ægirine in which it may occur as small, scattered, grains, and with arfvedsonitic riebeckite. Optically, the ænigmatite is typical, having a reddish-brown colour and high refractive indices.

TABLE I

	1	2	3	4	5
SiO_2	47·45	50·05	39·71	40·7	39·62
TiO_2	1·61	1·58	10·23	8·3	9·66
Al_2O_3	0·66	0·45	0·13	0·72	0·64
Fe_2O_3	12·65	29·95	3·27	—	4·64
FeO	21·41	2·89	37·03	41·1*	33·92
MnO	0·98	0·33	1·20	0·85	2·46
MgO	0·03	tr	1·49	0·11	1·65
CaO	2·88	1·91	0·20	0·50	0·44
Na_2O	6·62	12·59	6·9	7·2	7·20
K_2O	1·82	0·28	0·24	0·03	0·04
	100·00†	100·03	100·40	99·51	100·27

*Electron-probe analysis—total iron as FeO.

†Total includes: Li_2O 0·42; ZrO_2 0·28; ZnO 0·33; P_2O_5; 0·08; total H_2O 1·92; F 1·40; Cl 0·07. Total is minus 0·61 oxygen ≡ F, Cl.

	3	4	5
Atomic ratios of ænigmatite calculated to 40 oxygen:			
Si	11·36	11·67	11·26
Al^{iv}	0·03	0·24	0·21
Fe^{3+}	0·60	0·09	0·53
	12·00	12·00	12·00
Al^{vi}	—	—	—
Fe^{3+}	0·12	0·77	0·47
Mg	0·64	0·05	0·70
Ti	2·19	1·79	2·19
Fe^{2+}	8·82	9·00	8·06
Mn	0·29	0·21	0·59
Ca	—	0·15	0·11
	12·06	11·97	12·00
Ca	0·07	—	0·02
Na	3·81	4·01	3·97
K	0·07	0·01	0·01
	3·95	4·02	4·00

1.	Arfvedsonitic-riebeckite	From Ægirine-riebeckite granite, Liruei Complex, Nigeria.
2.	Ægirine	
3.	Ænigmatite	
4.		from Mt. Edziza lava (Yagi and Souther, 1974).
5.		from Kola Peninsula (Kelsey and McKie, 1964).

Analysis and composition. The ænigmatite was analysed by wet chemical methods as were the coexisting pyroxene and amphibole; analyses of all three minerals are given in Table I, together with analyses of two other ænigmatites for comparison.

Compared with ænigmatites from elsewhere the Nigerian mineral is enriched in Ti and Mg and depleted in Si, Al, and Ca. Its Ti content is particularly noteworthy, being a little higher than that of the Ti-rich ænigmatite from Kola, discussed by Kelsey and McKie (1964). Relative to its coexisting minerals the Nigerian ænigmatite is enriched in

Ti and depleted in Fe^{3+}, which is in accordance with the suggestion of Kelsey and McKie that ænigmatite acts as a Ti 'sink' and that its crystallization should be followed by that of Ti-poor pyroxene or amphibole. The composition of the Nigerian mineral provides further evidence that with few exceptions ænigmatite has a narrow compositional range and shows only limited miscibility with rhönite.

The conditions required for formation of ænigmatite in both silicic and silica-poor peralkaline rocks, and its stability range, are still imperfectly known. In his experimental work on the stability of riebeckite–arfvedsonite solid solutions Ernst (1962) showed that ænigmatite was a stable anhydrous phase at low P_{fluid} and very low f_{O_2}. The more recent, and preliminary, experimental data of Lindsley (1971) demonstrate that ænigmatite is stable at about 750 °C at 500 bar pressure and at an oxygen fugacity higher than suggested by Ernst—somewhere between the nickel–nickel-oxide and quartz–magnetite–fayalite buffers. A moderate oxygen fugacity appears to be considered by many geologists (Kelsey and McKie, 1964; Abbott, 1967; and Yagi and Souther, 1974) to be necessary for the crystallization of ænigmatite, as well as peralkaline conditions and a high concentration of TiO_2 in the parent magma. Carmichael (1962) suggested that ænigmatite might form by the reaction of fayalite and ilmenite (or ulvöspinel) with a soda-rich liquid, but there appear to be few petrographic data that support this as a general possibility. An antipathetic relationship between Fe–Ti oxides and ænigmatite is, however, suggested by many authors and certainly Fe–Ti oxides are generally lacking in the peralkaline Younger Granites in Nigeria. Marsh (1975) has considered the thermodynamics of reactions involving ænigmatite formation and used the results to postulate a 'no oxide' stability field of narrow T–f_{O_2} limits (the upper boundary being the QMF buffer curve) for ænigmatite in trachytic and phonolitic rocks.

The Ægirine–Riebeckite Granite in which the Nigerian ænigmatite is found seems to fill the general requirements of a silicic host rock. It is more titaniferous than many similar granites reported from the Nigerian Province, containing 0·26 % TiO_2 as compared with a general range of between 0·04 to 0·16 % TiO_2 (Jacobson *et al.*, 1958). This concentration of 0·26 % TiO_2 in the parent granite is lower than for parent rocks of ænigmatite from other areas, e.g. 0·41 % for trachytes from the Nandewar volcanics (Abbott, 1967), and 0·35 to 0·60 % in the Pantelleria lavas (Carmichael, 1962), but it is very close to the range of TiO_2 contents for the pantellerites from Mayor Island, 0·14 % to 0·29 % (Ewart *et al.*, 1968). Additional relevant features of the Ægirine–Riebeckite granite from Liruei Complex are that it is peralkaline and from a consideration of the composition of its alkali amphibole Borley (1975) suggested that the granite crystallized at a low to moderately high oxygen fugacity, and probably near 800 °C. All these data suggest, therefore, that the Nigerian ænigmatite crystallized under similar conditions to ænigmatite from other peralkaline rocks.

Paragenetic relationship of ænigmatite and rhönite. Rhönite, like ænigmatite, occurs in a range of silica-poor rocks in which it may be associated with olivine, titanaugite, plagioclase, or feldspathoids. Its most interesting occurrence, in so far as its relationship to ænigmatite is concerned, is in the teschenite described by Tomita (1934), which contains crystals zoned from kaersutite→rhönite→ænigmatite. This occurrence of the two minerals may give a useful clue to their paragenetic relationship, which for the zoned crystals mentioned above could be:

> Basic liquid → subtract kaersutite → residual liquid depleted in Al, Ca, Fe, and K → rhönite subtracted → residual liquid depleted in Ca, Al, Fe, *becomes locally peralkaline* and enriched in Na → ænigmatite subtracted

This suggested relationship envisages that in a Ca, Al depleted basic liquid the role of rhönite is analogous to that of plagioclase in a more silicic liquid depleted in Ca and Al, when subtraction of the feldspar is believed to produce a peralkaline liquid (the 'Bowen' effect). If this relationship is valid then the paragenetic scheme for the two minerals would be:

1. Rhönite crystallizes from basic to intermediate liquids of high to moderate T, low f_{O_2}. Possibly, like ænigmatite, rhönite takes up excess Ti and Fe from the liquid in the absence of iron–titanium oxides.
2. Ænigmatite crystallizes in zoned crystals where subtraction of rhönite has created local peralkalinity in the residual liquid. Decreasing T and probably slightly increasing f_{O_2}.
3. Ænigmatite crystallizes by reaction with iron-titanium oxides or directly from silicic or silica-poor peralkaline magmas. Moderate to low T, moderate f_{O_2}.

With the kind of paragenetic relationship envisaged it would be most unlikely that rhönite and ænigmatite would show a high degree of miscibility with each other.

REFERENCES

Abbott (M. J.), 1967. *Amer. Min.* **52**, 1895.
Borley (G. D.), 1975. *Proc. First Conference on Nigerian Geology*. Centre for Advanced Studies, Ife University, Nigeria.
Cameron (K. L.), Carman (M. F.), and Butler (J. C.), 1970. *Amer. Min.* **55**, 864.
Cannillo (E.), Mazzi (F.), Fang (J. H.), Robinson (Paul D.), and Ohya (Y.), 1971. Ibid. **56**, 427.
Carmichael (I. S. E.), 1962. *Min. Mag.* **33**, 86.
Ernst (W. G.), 1962. *Journ. Geol.* **70**, 689.
Ewart (A.), Taylor (S. R.), and Capp (A. C.), 1968. *Contr. Min. Petr.* **17**, 116.
Fleischer (M.), 1936. *Amer. Journ. Sci.*, ser. 5, **32**, 343.
Gibson (I. L.), 1970. *Contr. Min. Petr.* **28**, 89.
Grunhagen (H.) and Seck (H. A.), 1972. *Tsch. Min. Petr. Mitt.* **18**, 17.
Hodges (F. N.) and Barker (D. S.), 1973. *Carnegie Inst. Washington Yearbook*, **72**, 578.
Jacobson (R. R. E.), MacLeod (W. N.), and Black (R.), 1958. *Memoir* No. 1, *Geol. Soc. London.*
Kelsey (C. H.) and McKie (D.), 1964. *Min. Mag.* **33**, 986.
Lindsley (D. H.), 1971. *Carnegie Inst. Washington Yearbook*, **69**, 190.
Marsh (J. S.), 1975. *Contr. Min. Petr.* **50**, 135.
Tomita (T.), 1934. *Journ. Shanghai Sci. Inst.* Sect. 2, **1**, 99.
Upton (B. G. J.), Thomas (J. E.), and MacDonald (R.), 1971. *Lithos*, **4**, 163.
Yagi (K.), 1953. *Bull. Geol. Soc. Amer.* **64**, 769.
—— and Souther (J. G.), 1974. *Amer. Min.* **59**, 820.

[*Manuscript received 27 May 1975, revised 30 August 1975*]