The unit-cell of aenigmatite

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Summary. Redetermination of the unit-cell dimensions as *a* 10·406 Å, *b* 10·813 Å, *c* 8·926 Å, α 104° 56′, β 96° 52′, γ 125° 19′, has shown that the hitherto accepted unit-cell of Gossner and Spielberger (1929) is in error. The morphological unit-cell of Palache (1933) is related to the new unit-cell, to a high degree of precision, by the transformation[1] Palache → Kelsey–McKie $[001/0\frac{1}{2}\frac{\bar{1}}{2}/\frac{1}{2}00]$. Fifteen published and two new analyses indicate that the unit-cell contents approach $Na^{+}_{4}[Fe^{2+}_{10}Ti^{4+}_{2}]Si^{4+}_{12}O^{2-}_{40}$. The common twin axis constitutes the diad of a pseudo-monoclinic cell, the (010) plane of which is dimensionally closely related to that of pyroxenes and amphiboles. It is suggested that the aenigmatite structure is based on silicate chains of pyroxene type cross-linked by Ti^{4+} and Fe^{2+} on distinct 6-fold sites, with Na^{+} on sites of higher coordination number. Aenigmatite from volcanic in contrast to that from plutonic parageneses is often submicroscopically twinned and may be inverted from a high temperature monoclinic polymorph.

AENIGMATITE has, since its discovery by Breithaupt in 1865, received a considerable amount of attention from mineralogists; it has been described from more than a score of widely scattered occurrences, but remained obscure alike in its systematic position and in its stability relations. Breithaupt (1865) described aenigmatite as pseudomorphous after kölbingite in a nepheline–syenite from the Julianehaab District of Greenland. Lorenzen (1882) described independent crystals of aenigmatite from the sodalite–syenite of the Tunugdliarfik and Kangerdluarsuk fjords in Greenland and disputed Breithaupt's observation of pseudomorphs. Groth (1883) suggested that cossyrite, described by Foerstner (1881) from the pantellerite lavas of Pantelleria, was closely related to, if not identical with aenigmatite and kölbingite. Foerstner's contention, based on chemical and goniometric data, that cossyrite was a triclinic member of the amphibole series was endorsed by Brögger (1890), who moreover confirmed the identity of aenigmatite with cossyrite and discredited kölbingite as an arfvedsonite–aenigmatite intergrowth. Titanium was not recorded in Foerstner's analysis and for a number of years cossyrite was reserved as a varietal name for the

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[1] In the convention used here *A* → *B* represents transformation from indices in terms of cell *A* to those for cell *B*.

apparently titanium-free aenigmatites of Pantelleria; Dittrich's analysis in Soellner (1909) eventually showed that cossyrite was titaniferous. The early study of its X-ray diffraction pattern by Gossner and Mussgnug (1929) and by Gossner and Spielberger (1929) appeared conclusively to invalidate the classification of aenigmatite as a triclinic amphibole; in the following pages it will be shown that their unit-cell parameters are wholly in error and that their structural argument is at least questionable.

Determination of lattice parameters. Approximate unit-cell dimensions were obtained from a crystal of aenigmatite from the Kola peninsula[1] by measurement of a-, b-, and c-axis oscillation photographs and a-, b-, and c-axis zero layer Weissenberg photographs. Reciprocal lattice parameters for Cu-$K\alpha$ radiation were found to be a^* 0·193, b^* 0·191, c^* 0·190, α^* 66·5°, β^* 70°, γ^* 51°, corresponding to direct lattice parameters,[2] a 10·37 Å, b 10·73 Å, c 8·92 Å, α 104·5°, β 97·5°, γ 125°. The similarity of the reciprocal axial lengths introduced the possibility of confusion, but by careful matching of intensities along axial row lines on the Weissenberg photographs and by observation of the offset on a first layer equi-inclination Weissenberg photograph the consistency of the reciprocal axial system was demonstrated.

Accurate reciprocal axial lengths were obtained from the same crystal from back-reflection oscillation photographs by modification of the methods described previously by Megaw and Kelsey (1955) and McKie (1962). The oscillation ranges, reduced to 5° to facilitate unambiguous indexing and to avoid overlapping of reflections, were selected to enable high θ zero layer reflections with two zero indices to be recorded on a flat film mounted in the back-reflection position. A rod of specpure silicon powder, mounted on the same goniometer head as the crystal and capable of being centred in the X-ray beam without disturbing the setting of the crystal merely by traverse on the slides, provided an internal standard of high accuracy. Each film was exposed three times, with 5° oscillation of the aenigmatite crystal such that the chosen reflection would appear first on one side then on the other side of the centre of the film and finally with the silicon rod in position for diffraction. The θ-values taken for the Si powder lines used were: for 444 θ(Cu-$K\alpha_1$) 79·314° and θ(Cu-$K\alpha_2$) 80·100°, for 533 θ(Cu-$K\alpha_1$) 68·446° and θ(Cu-$K\alpha_2$)

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[1] Department of Mineralogy and Petrology, Cambridge, specimen 38075: aenigmatite–aegirine–arfvedsonite–lamprophyllite rock, Khibinite quarry, east of Kirovsk.

[2] It was shown subsequently that the axes of the chosen *preliminary unit-cell* were coincident with those of the conventional Delaunay unit-cell.

68·811°, for 531 θ(Fe-$K\beta$) 73·094°, and for 511, 333 θ(Fe-$K\alpha_1$) 67·849° and θ(Fe-$K\alpha_2$) 68·137°. Wavelengths were taken as Cu-$K\alpha_1$ 1·54050 Å, Cu-$K\alpha_2$ 1·54434 Å, Fe-$K\alpha_1$ 1·93597 Å, Fe-$K\alpha_2$ 1·93991 Å, Fe-$K\beta$ 1·75654 Å. The parameter a^* was determined from the 10.0.0 reflections on two c-axis oscillation photographs (for the second the crystal was turned through 180° relative to its orientation for the first) taken with Cu-$K\alpha$ radiation with reference to Si (444) and Si (533), from the 10.0.0 reflections referred to Si (444) on a b-axis photograph taken with Cu-$K\alpha$ radiation, and from the 800 reflections referred to Si (531) and Si (511, 333) on a c-axis photograph taken with Fe-K radiation. The parameter b^* was determined from the 0.10.0 reflections referred to Si (444) on a c-axis photograph taken with Cu-$K\alpha$ radiation, and c^* was determined from the 0.0.10 reflections referred to Si (444) and Si (533) on a b-axis photograph also taken with Cu-$K\alpha$ radiation. Separate measurement of corresponding α_1 and α_2 aenigmatite reflections on each film gave eight determinations of a^*, two of b^*, and two of c^*. The small standard deviations calculated therefrom provide a crude estimate of observational error; in the case of a^*, which was determined on four films, the estimate is probably significant and the standard deviations of b^* and c^* are of the same order of magnitude as that of a^*. The reciprocal axial lengths and their standard deviations are shown in table I.

TABLE I. Reciprocal and direct lattice parameters for aenigmatite

a^*	0·125260 ± 0·000016 Å^{-1}	α^*	66° 12′ ± 5′
b^*	0·123868 ± 0·000008 Å^{-1}	β^*	70° 05′ ± 7′
c^*	0·123326 ± 0·000007 Å^{-1}	γ^*	50° 36′ ± 5′
a	10·406 ± 0·013 Å	α	104° 56′ ± 9′
b	10·813 ± 0·014 Å	β	96° 52′ ± 11′
c	8·926 ± 0·006 Å	γ	125° 19′ ± 6′
$a{:}b{:}c$	0·9624:1:0·8255	V	744·5 ± 1·0 Å^3

Accurate reciprocal lattice angles were obtained, again from the same crystal, from zero layer precession photographs taken with Cu-$K\alpha$ radiation. The crystal was mounted in turn about b^* and c^*; for each mounting photographs were taken at various values of μ with the X-ray beam precessing in turn about each of the two possible direct lattice axes. The angle α^* was measured on six, β^* on four, and γ^* on three photographs with a vernier arc measuring device reading to 1′. The mean values of α^*, β^*, and γ^*, together with their standard deviations are shown in table I, where the direct lattice parameters calculated from the observed reciprocal axial lengths and angles are also set down.

Choice of unit-cell. Two distinct sets of criteria for the selection of the unit-cell in the triclinic system are in current use. The Delaunay cell (Delaunay, 1933; Donnay and Nowacki, 1954, p. 138) has axes parallel to the three shortest non-coplanar translations that permit the interaxial angles to be all obtuse with the subsidiary condition that the direction cosines of [111] shall all be positive; the axes are labelled such that $c < a < b$. The reduced cell (Buerger, 1957) has axes parallel to the three shortest non-coplanar translations without further restriction except that the sense of the axes is chosen to give interaxial angles that are all acute (Type I crystals of Buerger, 1956) or all obtuse (Type II); for Type I crystals the reduced cell differs from the Delaunay cell, while for Type II the Delaunay cell is the reduced cell. Aenigmatite belongs to Type I and the Delaunay cell, which will be referred to below as the *KM*-cell, has been preferred, in part because of its accidental choice in the preliminary investigation and in part because the triclinic section of Crystal Data (Donnay and Nowacki, 1954) is based on the Delaunay cell. The dimensions of the reduced cell for aenigmatite are a 9·753 Å, b 10·406 Å, c 8·926 Å, α 83° 8′, β 55° 35′, γ 64° 47′. The matrix for the transformation $KM \rightarrow$ reduced is $[110/100/00\bar{1}]$ and that for reduced $\rightarrow$ KM is $[010/1\bar{1}0/00\bar{1}]$.

The crystal morphology of aenigmatite, studied imperfectly by Foerstner (1881) and more completely by Brögger (1890), Soellner (1909), Kostyleva (1930), and Palache (1933), has been described in terms of several sets of lattice constants, which have been correlated by Palache (1933) with a morphological unit-cell, referred to here as the *P*-cell, with constants: $a{:}b{:}c = 1{\cdot}0050{:}1{:}0{\cdot}5862$, α 96° 59·5′, β 96° 49·5′, γ 112° 28′. Examination of all axes of less than 25 Å in the *KM*-cell and the corresponding interaxial angles leads to two possible orientations of the *P*-cell relative to the *KM*-cell: orientation *A* with $a_P \parallel [120]_{KM}$, $b_P \parallel c_{KM}$, $c_P \parallel a_{KM}$ corresponding to $(d_{[120]}/2c)_{KM} = 0{\cdot}9955 \approx (a/b)_P$, $(a/2c)_{KM} = 0{\cdot}5829 \approx (c/b)_P$, $\beta_{KM} = 96° \, 52' \approx \alpha_P$, $[120]_{KM} \wedge a_{KM} = 96° \, 46' \approx \beta_P$, $[120]_{KM} \wedge c_{KM} = 112° \, 34' \approx \gamma_P$, and orientation *B* with $a_P \parallel c_{KM}$, $b_P \parallel [120]_{KM}$, $c_P \parallel a_{KM}$ corresponding to $(2c/d_{[120]})_{KM} = 1{\cdot}0046 \approx (a/b)_P$, $(a/d_{[120]})_{KM} = 0{\cdot}5856 \approx (c/b)_P$, $[120]_{KM} \wedge a_{KM} = 96° \, 46' \approx a_P$, $\beta_{KM} = 96° \, 52' \approx \beta_P$, $[120]_{KM} \wedge c_{KM} = 112° \, 34' \approx \gamma_P$. Thus the coincidence of c_P and a_{KM} is uniquely determined, with a_P and b_P each coincident with either c_{KM} or $[120]_{KM}$. The transformation matrices for face indices are for orientation *A*, $P \rightarrow KM[001/\tfrac{1}{2}0\bar{\tfrac{1}{2}}/0\tfrac{1}{2}0]$ and for orientation *B*, $P \rightarrow KM[001/0\tfrac{1}{2}\bar{\tfrac{1}{2}}/\tfrac{1}{2}00]$. A decision between the two possible orientations can be made, although not completely unambiguously, by examination of the estimated errors in the derived functions of the *KM*-cell, $d_{[120]}/2c$, $2c/d_{[120]}$, $a/2c$, $a/d_{[120]}$, $[120]\wedge a$, and $[120]\wedge c$; assuming that the measured reciprocal lattice parameters are independent variables, the standard deviations of the derived functions have been evaluated from the standard deviations of the six reciprocal lattice parameters. The calculation, although tedious, is straightforward enough not to require description; its result $\sigma(d_{[120]}/2c)$ 0·0006, $\sigma(2c/d_{[120]})$ 0·0006, $\sigma(a/2c)$ 0·0008, $\sigma(a/d_{[120]})$ 0·0008, $\sigma([120]\wedge a)$ 7′, and $\sigma([120]\wedge c)$ 6′, where σ denotes standard deviation, clearly indicates that orientation *B* is the more likely.

The X-ray unit-cells of Gossner and Mussgnug (1929) and Gossner and Spielberger (1929) were obtained by measurement of layer-line spacings on a number of rotation photographs of aenigmatite and cossyrite respectively, the measurements for the latter being the more precise. They concluded that the two diffraction patterns were identical in geometry and qualitatively in the intensities of equivalent reflections, and they proposed two alternative unit-cells, one pseudo-monoclinic with a 10·02 Å, b 14·73 Å, c 10·43 Å, $\alpha \approx 90°$, β 101° 58′, $\gamma \approx 90°$, and the other with a 17·99 Å, b 18·14 Å, c 10·43 Å, $\alpha \approx \beta \approx 96°$ 30′, γ 113° 30′. Their lattice translations are identifiable in terms of the *KM*-cell, but the corresponding interaxial angles that they record do not agree with those derived from the unambiguous observation of the diffraction pattern by moving film techniques. They had to identify each rotation axis by goniometric reference to the morphology of the crystal, and in changing from one rotation axis to another the crystal had to be remounted; in the course of this laborious procedure mistakes appear to have been made that led to the identification of a false unit-cell. The Gossner unit-cells cannot therefore be related to the *KM*-cell and must be rejected.

X-ray powder pattern. Data obtained with a Philips 114·6 mm diameter camera and Fe-$K\alpha$ radiation from the Kola specimen (table III, analysis 1) are presented in table II. The 38 lines of longest *d*-spacing are recorded there; at higher angles only an indistinct pattern of no diagnostic value is discernible. The shape and dimensions of the unit-cell are such that the pattern is unindexable except for the first three lines, which have been indexed, after consideration of relative intensities on single crystal photographs, as 8·11 Å 001 and 010, 7·43 Å $0\bar{1}1$, 6·38 Å $1\bar{1}1$. The three strongest lines are 8·11 Å vs, 3·144 Å vs, 2·705 Å s.

Direct comparison of photographs taken on the same camera with the same radiation has revealed no detectable variation in unit-cell dimensions over the range of composition of the analysed material from Kola,

TABLE II. X-ray powder data for aenigmatite. Fe-$K\alpha$ radiation, λ 1·93728 Å

d	I	d	I	d	I
8·11 Å	vs (1)	2·658Å	vvw	1·808 Å	vwB
7·43	vw	2·545	s	1·772	vvw
6·38	vw	2·462	vw	1·731	wB
4·82	w	2·413	m	1·680	w
4·40	w	2·347	vw	1·627	m
4·20	w	2·310	vw	1·610	w
3·704	mw	2·197	vvw	1·590	vvw
3·484	w	2·119	ms	1·560	vvw
3·144	vs (2)	2·073	w	1·514	w
2·939	ms	2·007	mw	1·498	mw
2·806	vw	1·973	vvw	1·484	mw
2·753	vw	1·947	vvw	1·468	mB
2·705	s (3)	1·912	vw		

Greenland, and Pantelleria, columns I, II, and 15 of table IV respectively.

Twinning. The X-ray diffraction pattern of a twinned crystal of aenigmatite from Pantelleria[1] has been examined on a-axis oscillation photographs and on a zero layer a-axis Weissenberg photograph. The oscillation photographs exhibit an abnormally large number of reflections situated exactly on each layer-line, consistent with a twin axis normal to a plane $(0kl)$. On the Weissenberg photograph are displayed corresponding reflections of approximately equal intensity from a pair of individuals in a twinned relationship; the relative orientation of the two reciprocal lattice nets is consistent with twinning by rotation about the normal to $(01\bar{1})$. Measurement of the separation of high angle reflections leads to the value 40′ for (011) $\wedge$ $(\underline{0\bar{1}\bar{1}})$ in good agreement with the angle 43′ calculated from the measured reciprocal lattice parameters.

Twin axes are characteristically nearly parallel to rows of fairly closely spaced lattice points, that is to zone axes of simple indices. Application of the perpendicularity condition shows that $[12\bar{2}]$ is nearly normal to $(01\bar{1})$ in aenigmatite; the angle between $[12\bar{2}]$ and the normal to $(01\bar{1})$ was evaluated as 17′ with a desk calculator by the method outlined in Kasper and Lonsdale (1959, p. 106) and checked by a direction cosine calculation on EDSAC II. Projection down $[12\bar{2}]$ reveals that the strictly triclinic aenigmatite lattice can be described in terms of a pseudo-monoclinic C-lattice, a_m 9·888 Å, b_m 14·814 Å, c_m 5·203 Å, α_m 89° 56′, β_m 102° 21′, γ_m 90° 17′, provided that an additional lattice point is

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[1] Specimen 3A of Carmichael (1962). A portion of the sample separated for analysis was most kindly furnished by Dr. Carmichael.

inserted midway along the *a*-axis of the *KM*-cell; the relative orientation of the pseudo-monoclinic cell is given by the matrix for the transformation *KM*-cell → pseudo-monoclinic cell $[\frac{1}{2}11/\frac{1}{2}1\bar{1}/\frac{1}{2}00]$, which includes the condition $b_m = \frac{1}{2}d[12\bar{2}]$. The triclinic aenigmatite structure may therefore in the nomenclature of Buerger (1960, p. 55) be derivative from a lattice corresponding closely to the pseudo-monclinic *C*-lattice described above. In this context it is noteworthy that aenigmatite from volcanic parageneses is characteristically polysynthetically twinned on a submicroscopic scale in contrast to the common occurrence of single individuals or simple twins in plutonic parageneses. The polysynthetic twinning therefore may well be transformation twinning indicative of the stability of a monoclinic polymorph at high temperatures and low pressures; this point will be reverted to later.

TABLE III. New analyses of aenigmatite

	1	2
SiO_2	39·62	41·41
TiO_2	9·66	8·30
Al_2O_3	0·64	nil
Fe_2O_3	4·64	4·46
FeO	33·92	35·87
MnO	2·46	1·78
MgO	1·65	1·35
CaO	0·44	nil
Na_2O	7·20	6·87
K_2O	0·04	0·04
H_2O^+	0·05	nil
H_2O^-	nil	n.d.
Cl	0·02	n.d.
F	nil	n.d.
	100·34	100·08

1. Aenigmatite from Khibinite quarry, east of Kirovsk, Kola. Dept. Min. and Pet., Cambridge 38075. Analyst: J. H. Scoon.
2. Aenigmatite from South Boswell Bay, Kangerdlugsuak, East Greenland. Specimen W. A. Deer 3584. Analysts: P. E. Brown and Mrs. A. Chadwick.

Unit-cell contents. A sample of aenigmatite was kindly separated for us by Dr. G. A. Chinner from the Kola specimen used in the single crystal X-ray study. The analysis of this aenigmatite by Mr. J. H. Scoon is set down in table III. The specific gravity of the analysed material was determined by Dr. Chinner by measurement of the density of Clerici's solution in which it remained suspended after centrifuging for five minutes as 3·81. The chemical analysis, measured specific gravity, and unit-cell volume lead to an anion content, Σ (O,OH,Cl), of $39{\cdot}8_6$, sufficiently close to permit the assumption that the unit-cell of aenigmatite contains 40 anions; only after determination of the unit-cell volume to a high degree of accuracy could the possibility of 39 anions per unit-cell be dismissed.

Unit-cell contents calculated to 40 anions from all the reputable analyses of aenigmatite in the literature and from two hitherto unpublished analyses are shown in table IV; cations are listed in order of increasing ionic radii according to the values of Ahrens (1952). The assumptions that Si^{4+} is confined to sites of 4-fold coordination and that Al^{3+} and Fe^{3+} may lie either on 4-fold or on 6-fold sites require the presence of twelve and no more than twelve 4-fold sites in the unit-cell. The assumption that Na^+ and K^+ lie on sites of 8-fold or higher coordination and that Ca^{2+} can accept 6-fold or 8-fold coordination requires the presence of twelve 6-fold sites and four sites of high coordination number in the unit-cell. The four recent analyses (14, 15, I, II) suggest that aenigmatite is effectively anhydrous, but some of the older analyses indicate, perhaps erroneously, contents of up to nearly three hydroxyl ions per unit-cell; F^-, where it has been determined, has shown no more than a trace and Cl^- is present in small amount in the new Kola analysis. The unit-cell contents of aenigmatite can therefore be expressed generally with some confidence as $X^{[8]}_{\leqslant 4}Y^{[6]}_{12}Z^{[4]}_{12}(O,OH)_{40}$ or as $4\{X_{\leqslant 1}Y_3Z_3(O,OH)_{10}\}$.

Earlier formulations of the composition of aenigmatite showed that it was not amphibole-like: Gossner and Spielberger (1929) and Kostyleva (1930) produced metasilicate formulae and Fleischer (1936) proposed $X_4Y_{13}(Si_2O_7)_6$, not unlike the present interpretation when allowance is made for the variation of the total anion content from 42 to 40.

In detail table IV shows that substitution for Si^{4+} on 4-fold sites must be small, that Fe^{2+} dominates the occupation of the 6-fold sites, with lesser amount of Fe^{3+} and Ti^{4+} and minor amounts of other cations, that Na^+ is clearly the principal occupant of the sites of high coordination, and that, as Fleischer (1936) maintained, OH^- content is not essential. The disposition of cations on the 6-fold sites, derived from the average of the four recent analyses, corresponds to $(Al^{3+},Fe^{3+},Mg^{2+})_{0\cdot 841}Ti^{4+}_{1\cdot 915}Fe^{2+}_{8\cdot 798}(Mn^{2+},Ca^{2+})_{0\cdot 458}$; approximation to $Fe^{2+}_{10}Ti^{4+}_2$, with the minor constituents grouped appropriately, is in conformity with Carmichael's (1962) suggestion of $Fe^{2+}_9Ti^{4+}_2$ for 37 anions and in contrast to the more oxidized distribution $Fe^{2+}_9Fe^{3+}_2Ti^{4+}_2$ for 42 anions proposed by Fleischer (1936). The range of variation in the older analyses (table IV, columns

TABLE IV. Unit-cell contents of aenigmatite

	1	2	3	4	5	6	7	8	9
[4]									
Si^{4+}	10·912	11·422	11·348	11·687	11·551	10·847	11·003	11·422	11·274
Al^{3+}	1·088	0·066	0·652	—	0·449	0·398	0·325	0·320	0·460
Fe^{3+}	—	0·512	—	0·313	—	0·755	0·332	0·258	0·266
Σ[4]	12·000	12·000	12·000	12·000	12·000	12·000	11·660	12·000	12·000
[6]									
Al^{3+}	0·008	—	0·239	—	0·307	—	—	—	—
Fe^{3+}	1·258	0·607	1·194	1·721	0·838	1·354	—	1·185	1·156
Mg^{2+}	0·142	0·238	0·551	0·580	0·253	0·934	0·583	0·650	1·151
Ti^{4+}	1·638	1·731	1·845	1·744	1·670	2·137	2·425	1·751	1·797
Fe^{2+}	8·635	8·122	6·694	6·799	8·257	6·893	7·735	7·428	7·186
Mn^{2+}	0·244	0·330	0·729	0·759	0·237	0·538	0·478	0·552	0·514
Ca^{2+}	0·075	0·231	0·151	0·158	0·372	0·144	0·106	0·300	0·120
Σ[6]	12·000	11·259	11·403	11·761	11·934	12·000	11·327	11·866	11·924
[8]									
Ca^{2+}	0·344	—	—	—	—	0·079	—	—	—
Na^{+}	3·671	3·588	3·783	2·556	3·424	3·308	3·657	4·102	4·100
K^{+}	0·187	—	0·201	0·153	0·220	0·057	0·028	0·058	0·029
Σ[8]	4·202	3·588	3·984	2·709	3·644	3·444	3·685	4·160	4·129
Anions									
Cl^{-}	—	—	—	—	—	—	—	—	—
OH^{-}	—	2·409	0·939	0·872	0·452	—	2·829	—	—
O^{2-}	40·000	37·591	39·061	39·128	39·548	40·000	37·171	40·000	40·000
O.R.	12·7	12·1	15·3	23·0	9·2	23·4	4·1	16·3	16·5

O.R. = oxidation ratio,

1. Naujakasik, Greenland (Brögger, 1890).
2. Pantelleria (Soellner, 1909).
3. Kola (Chernik, 1927).
4. Kola (Fersman, 1926).
5. Putelichorr, Kola (Kostyleva, 1930).
6. Chasnachorr, Kola (Kostyleva, 1930).
7. Partomchorr, Kola (Kostyleva, 1930).
8. Kola (Kostyleva, 1930).
9. Chernik vein, Kola (Kostyleva, 1930).

1–13) is considerably greater than in the four newer analyses and may be attributable to the difficulty that would have been experienced thirty or more years ago in separating a pure sample of aenigmatite rather than to analytical error; that the separation is nowadays not fraught with particular difficulty justifies extra weight being placed on the evidence of the newer analyses. On the basis of that evidence the unit-cell contents of aenigmatite tend towards the idealized formulation $Na^{+}_{4}[Fe^{2+}_{10}Ti^{4+}_{2}]Si^{4+}_{12}O^{2-}_{40}$.

Rhönite, described by Soellner (1907) from the basic lavas of the Rhön Mountains in Germany and by Lacroix (1909) from a nephelinite on the calculated to 40 anions (O, OH, Cl)

	10	11	12	13	14	15	I	II
Si^{4+}	11·475	11·112	11·128	12·037	11·735	11·729	11·263	11·786
Al^{3+}	0·275	0·888	0·872	—	0·265	0·271	0·214	—
Fe^{3+}	0·250	—	—	—	—	—	0·523	0·214
	12·000	12·000	12·000	12·037	12·000	12·000	12·000	12·000
Al^{3+}	—	0·506	0·460	0·371	0·052	0·029	—	—
Fe^{3+}	0·940	0·644	1·041	0·339	0·282	0·256	0·470	0·741
Mg^{2+}	0·565	0·080	0·314	0·211	0·030	0·230	0·699	0·573
Ti^{4+}	1·684	1·648	1·520	1·695	1·919	1·901	2·065	1·777
Fe^{2+}	7·526	9·242	8·011	9·081	9·293	9·304	8·064	8·538
Mn^{2+}	0·784	0·150	0·605	0·418	0·281	0·262	0·592	0·429
Ca^{2+}	0·293	—	0·049	—	0·138	0·018	0·110	—
	11·792	12·270	12·000	12·115	11·995	12·000	12·000	12·058
Ca^{2+}	—	0·730	0·644	0·756	—	0·151	0·024	—
Na^{+}	4·618	1·802	2·028	2·011	4·083	3·847	3·969	3·791
K^{+}	0·015	0·040	0·093	—	0·022	0·029	0·015	0·015
	4·633	2·572	2·765	2·767	4·105	4·027	4·008	3·806
Cl^{-}	—	—	—	—	—	—	0·010	—
OH^{-}	—	0·061	0·919	—	—	—	0·095	—
O^{2-}	40·000	39·399	39·081	40·000	40·000	40·000	39·895	40·000
O.R.	13·7	6·5	11·5	3·6	2·9	2·9	11·0	10·1

100 $Fe^{3+}/(Fe^{3+}+Fe^{2+})$.

10. Kola (Kostyleva, 1930).
11. Naujakasik, Greenland (Gossner and Spielberger, 1929).
12. Kola (Gossner and Spielberger, 1929).
13. Pantelleria (Gossner and Spielberger, 1929).
14. Pantelleria (Carmichael, 1962, analysis 2A).
15. Pantelleria (Carmichael, 1962, analysis 3A).

I. Kola. Analysis 1 of table III.
II. Kangerdlugsuak, east Greenland. Analysis 2 of table III.

Puy de Barneire, Saint-Sandoux, in the Massif Central of France, has been thought from the similarity of its optical properties and crystal morphology to be a calcian aenigmatite. Fleischer (1936) suggested that it was related to aenigmatite by the substitution of CaAl for NaSi. Ficke (1961) has found it to be widely distributed in the Rhön lavas and refers to other occurrences in the Swabian Alps. Comparison of compositions calculated to 40 anions from the two available rhönite analyses (Soellner, 1907; Lacroix, 1909) with the unit-cell contents of aenigmatite shows that rhönite differs in its high contents of Al[4], Ca, and Mg; Fe^{2+} is much lower and Ti remains much the same as in aenigmatite. Although the compositional and morphological data are suggestive, the identity of rhönite as calcian aenigmatite cannot be held to have been conclusively demonstrated and, in the absence of X-ray evidence, the mineral will not be discussed further here.

Structural speculations. The authors have the determination of the crystal structure of aenigmatite in hand, but already some tentative structural conclusions can be drawn from the data presented above.

The classification of aenigmatite as a triclinic amphibole was disputed on the evidence of the incorrect X-ray crystallographic data of Gossner and Mussgnug (1929) and shown conclusively by the goniometric study of Palache (1933) and the chemical study of Fleischer (1936) to be invalid. Neither these nor any subsequent authors have suggested relationship to any other mineral of known structure. The newly-determined *KM*-cell does not correspond to any Delaunay cell listed by Donnay and Nowacki (1954). The reduced cell, however, has its *a*-axis 9·753 Å, similar to the *a*-axis 9·75 Å of the soda-amphiboles, and, more significantly, the pseudo-monoclinic *C*-lattice has a unit-cell with dimensions a_m 9·888 Å, b_m 14·814 Å, c_m 5·203 Å, β_m 102° 21′, $\alpha_m \approx \gamma_m \approx 90°$, corresponding approximately to the common elements of the pyroxene (e.g. aegirine *a* 9·65 Å, *b* 8·79 Å, *c* 5·29 Å, *β* 107° 24′, *C*2/*c*; Yagi, 1958) and amphibole (e.g. riebeckite *a* 9·74 Å, *b* 17·95 Å, *c* 5·30 Å, *β* 103° 54′, *C*2/*m*; Zussman, 1959) unit-cells. The relative shortness of the b_m-axis makes the presence of amphibole bands unlikely and it therefore seems probable that aenigmatite has pyroxene chains running parallel to the *a*-axis of the *KM*-cell and cross-linked in a distinctive manner. With unit-cell contents $Na_4Fe_{10}Ti_2Si_{12}O_{40}$, the chains could accommodate at most only $Si_{12}O_{36}$ and four oxygen anions would be required to lie outside the chains. With a volume of 18·6 Å^3 per oxygen atom, the oxygen packing in aenigmatite is clearly too loose to approximate to close packing; sapphirine for instance, which has a monoclinic *b*-axis of much the same length as b_m, has an almost cubic-close-packed oxygen arrangement with a volume of 16·75 Å^3 per anion (McKie, 1963). Aegirine, however, has 17·8 Å^3 per oxygen atom and riebeckite is volumetrically very close to aenigmatite with 18·7 Å^3 per anion.

It is suggested, therefore, that the aenigmatite unit-cell contains $Si_{12}O_{36}$ in pyroxene-type chains running parallel to the *a*-axis, the oxygen atoms of the chains being cross-linked by 6-fold coordinated Fe^{2+} and Ti^{4+}, which are also bonded to the four oxygen anions lying outside the chains; Na^+ lies on sites of high coordination number between the chains. The contention that Ti^{4+} is ordered on a particular pair of 6-fold sites is based on the chemical data of table IV and is consistent with what is known of the structures of other titanosilicates; in perrierite for instance Ti and Fe occupy distinct 6-fold sites and Ti–O octahedral chains are distinguishable in the structure (Gottardi, 1960). Ernst (1962), however, in the course of his study of the riebeckite–arfvedsonite join in the system Na_2O–FeO–Fe_2O_3–SiO_2–H_2O has produced what appears from its optics and its X-ray diffractometer pattern to be a titanium-free aenigmatite, more highly oxidized than any natural analysed specimen of the mineral; the apparent conflict with the evidence of table IV, that aenigmatite from a variety of natural occurrences always contains significant and similar amounts of titanium and is strongly reduced, can be resolved if it is supposed that at the highly simplified bulk composition of the synthetic runs other cations were constrained to fit into the positions preferentially occupied by titanium when it is available, in a phase with the aenigmatite structure crystallizing stably, or perhaps, metastably.

Paragenesis. Aenigmatite has been described from alkaline volcanic parageneses such as the pantellerites, pantelleritic trachytes, and comendites of Pantelleria (Foerstner, 1881; Soellner, 1909; Washington, 1914; Gossner and Spielberger, 1929; Carmichael, 1962), the phonolites of Haute Loire and Cantal in France (Lacroix, 1910), the comendites of Mount Nimrud, Armenia (Prior, 1928), the trachytes, phonolites, comendites, and pantellerites of the Kenya Rift Valley (Campbell Smith, 1931; Bowen, 1937), the phonolites of the Lupata Gorge in Portuguese East Africa (Teale and Smith, 1923), the phonolites and trachytes of the Ahaggar, Sahara (Denaeyer, 1923; Boucart and Denaeyer, 1925), the pantellerites of Afar (Adel-Esa) in Ethiopia and French Somaliland (Arsandoux, 1906), the phonolites of north-west Madagascar (Lacroix, 1910), the comendites of Mayor Island, New Zealand (Marshall, 1932 and 1936), the alkalic lavas of the Oki Islands, Japan (Tomita, 1934), and the pantellerite of Santa Rosa, California (figured in Williams, Turner, and Gilbert, 1954). Where rock analyses are available aenigmatite-bearing rocks are seen to be characterized by rather high titanium contents and relatively low iron oxidation ratios (Washington, 1914; Carmichael, 1962).

The other group of aenigmatite parageneses is plutonic: the nepheline- and sodalite-syenites of Kangerdluarsuk (Julianehaab District), west Greenland (Breithaupt, 1865; Lorenzen, 1882; Brögger, 1890), a microsyrenite vein from South Boswell Bay, Kangerdlugsuak, east Greenland (table III, analysis 2), the foyaite and khibinite pegmatites and the apatite rocks of the Khibina and Lovozero tundras and Luyavrurt in the Kola peninsula (Fersman, 1923, 1926, and 1937; Kostyleva, 1930;

Gerasimovsky, 1936), in veins in Langesundsfjord, Norway (Brögger, 1890), in veins in the Languard Alp, Ober Engadin, Switzerland (Niggli, Koenigsberger, and Parker, 1940), in monzonites and syenites from the Morotu River, Sakhalin Island, Japan (Yagi, 1953) in the nepheline-syenite of Kassa in the Isles de Los (Lacroix, 1910), in the Monte Chamaco alkali-syenite, Angola (de Andrade, 1954), in the Mounio aegirine-microgranite in the Sudan (Lacroix, 1910), in the aegirine-syenite of Ambohitrosy and the aegirine–nepheline syenite of the Bezavona massif in Madagascar (Lacroix, 1910), in the Fourche Mountains pulaskite in Arkansas (Williams, 1891), and in a nordmarkite from York, Maine (Woodard, 1957). In these occurrences aenigmatite is commonly associated with high sodium, high titanium, and low silicon contents and is accompanied by conspicuously more highly oxidized aegirine or alkali amphiboles.

There would appear from table IV to be no distinction of aenigmatite composition between volcanic and plutonic parageneses. The observation of Hintze (1897, p. 1270) that aenigmatite from Pantelleria is invariably twinned has however been confirmed and extended; *a*-axis oscillation photographs of crystals[1] from Pantelleria (52969 and table IV, column 15) and from Kenya (30158) exhibit polysynthetic twinning on $(01\bar{1})$, suggestive of inversion during cooling from a high-temperature monoclinic polymorph that crystallized primarily from the lava, whereas crystals from Kola (table IV, column I) and Greenland (table IV, column II) appear on similar evidence commonly to be untwinned and may therefore be presumed to have crystallized from the plutonic melt as triclinic aenigmatite.

In only one instance is an aenigmatite analysis accompanied by the analysis of a coexisting ferromagnesian silicate and that is a porphyritic obsidian from Pantelleria from which Carmichael (1962) analysed aenigmatite phenocrysts (table IV, column 14) and sodian ferrohedenbergite phenocrysts. Aenigmatite exhibits marked enrichment in Ti, Fe^{2+}, and Na with impoverishment in Al, Fe^{3+}, Mg, and Ca relative to the pyroxenes; most striking is the contrast in oxidation ratio, 2·9 for aenigmatite and 18·7 for sodian ferrohedenbergite.

Ernst (1962) has located the stability field of titanium-free aenigmatite + acmite at low p_{O_2}, defined by magnetite–wüstite and wüstite–iron buffers, and $p_{H_2O} < 1000$ bars; the low temperature boundary of the field is the reaction curve fayalite + acmite $\rightarrow$ aenigmatite + quartz + O_2 and at its high temperature boundary aenigmatite (+ quartz + fluid)

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[1] Dept. of Mineralogy and Petrology, Cambridge specimen numbers.

melts incongruently to fayalite+melt+O_2. While Ernst's experimental work is clearly relevant, it may be expected from the invariable presence of high concentrations of Ti in natural aenigmatite that the addition of TiO_2 to the system will considerably enlarge and modify the position of the stability field. Compositional comparison of aenigmatite with sodic titaniferous pyroxenes and amphiboles reveals that the titanium content of aenigmatite is consistently high, while the combination, characteristic of aenigmatite, of high iron content with very low oxidation ratio is most unusual in alkali amphiboles and is not recorded in alkali pyroxenes. Aenigmatite cannot therefore be regarded simply as a phase that crystallizes instead of alkali amphibole or pyroxene at high titanium concentration; clearly high iron concentration and low p_{O_2} are also requisite. Carmichael (1962) has suggested tentatively that aenigmatite may be alternative to fayalite–ilmenite or fayalite–ulvöspinel assemblages in the presence of sodium-enriched liquids. Its coexistence with pyroxenes and amphiboles containing very much lower concentrations of titanium and its frequent occurrence as the sole significantly titaniferous mineral of an assemblage suggest that the aenigmatite structure provides an energetically favourable environment for Ti^{4+}. One of the consequences of aenigmatite crystallization must then be to produce a concomitant strong decrease in Ti concentration in the melt; aenigmatite acts as a titanium sink and is followed in the paragenetic sequence by relatively titanium-poor amphibole or pyroxene.

In conclusion it may be said that while the newly determined unit-cell constants throw some light on the structure of aenigmatite, complete understanding of its stability and petrogenetic function must await the completion of the structure analysis and the investigation of the relevant TiO_2-bearing systems.

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Note added in proof: After this paper had gone to press Dr. Michael Fleischer kindly drew our attention to three new analyses of aenigmatite from the Kola peninsula in I. V. Bussen and O. B. Dudkin (1962). Neither these nor two earlier analyses (one in V. I. Gerasimovsky, 1936, and the other in O. B. Bøggild, Medd. Grønland, 1953, vol. 149, no. 3, p. 308) that were excluded from Table IV materially affect the conclusions drawn from the examination of unit-cell contents. In another recent paper Z. V. Shlyukova (1963) cites X-ray powder data to demonstrate the identity of cossyrite with aenigmatite.

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