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Isokite, CaMgPO₄F, a new mineral from Northern Rhodesia.

(With Plate XVIII.)

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INTRODUCTION.

THE mineral, for which the name isokite is now proposed, occurs in the carbonatite plug which forms Nkumbwa Hill (lat. 10° 10' S. long. 32° 51' E.), 15 miles east of Isoka (pronounced Isōka) in Northern Rhodesia. A preliminary account of this interesting mineral locality has already been published (Reeve and Deans, 1954) and a more detailed account is now in preparation, so that only the main features of the occurrence need be mentioned here. The carbonatite plug or pipe, 0.6 by 1 mile across and rising to a height of 1000 feet above the surrounding country, pierces granitic and micaceous gneisses which are fenitized to a distance of 500 yards from the walls of the pipe, but, unlike the classic carbonatite complexes, no intrusive alkalic rocks are exposed. Near the margin of the intrusion the carbonatite contains abundant fragments of fine-grained phlogopite-rock, which can be shown to represent metasomatized fragments of brecciated gneiss.

The carbonatite consists of ankeritic dolomite (ω 1.680–1.695), usually coarsely crystalline and practically free from calcite, and contains only small percentages of silicates, chiefly phlogopite and alkali-amphiboles. In Brögger's terminology the rock is a rauhaugite. The principal accessory minerals are apatite (including strontian fluorapatite), isokite, pyrite, magnetite, ilmenite, baryte, monazite, pyrochlore,

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and rather rare sellaite. Hydrous minerals are conspicuously absent. Geochemically, the carbonatite is characterized by relatively high concentrations of Mg, Ca, P, F, Mn, Sr, Ba, La-Ce group, and Nb, while the surrounding metasomatic phlogopite-rocks and sodic fenites indicate outward migration of both K and Na. The Nkumbwa plug appears to be quite isolated, the nearest carbonatites yet recorded being Panda Hill in Tanganyika, 90 miles to the north, and Kangankunde Hill in Nyasaland, 380 miles to the south. Mineralogically, Nkumbwa is much more akin to Kangankunde than to Panda Hill.

Most of the specimens used in the present study were collected by Mr. K. A. Phillips of the Northern Rhodesia Geological Survey during his mapping of the hill in 1952, but additional material was obtained by one of the authors (Deans) during a brief visit in 1953 when it was already clear that the 'white phosphate' merited detailed study. When the optical properties and chemical composition of the mineral had been established, indicating a new mineral species, Mr. McConnell was invited to undertake the X-ray investigations.

PHYSICAL PROPERTIES.

Isokite is visible in a large minority of the carbonatite specimens from Nkumbwa as small white, buff or faintly pinkish spots or patches in the grey or brown (oxidized) ankeritic rocks, and with a hand-lens appears as fibrous spherulites with silky lustre, or less frequently as radiating aggregates of thin crystalline plates with slightly pearly lustre. In thin section the spherulites, commonly 0.5 to 1 mm. in diameter but sometimes as small as 0.05 mm., are usually finely fibrous (pl. XVIII, fig. 1) and characterized by moderate birefringence and negative elongation. Rarer specimens contain coarser spherulites up to 2 or even 3 mm. in diameter, built up of thin plates radiating from the centre (text-figs. 1 and 2). Those plates normal or steeply inclined to the plane of the section show straight extinction and negative elongation, but in one sector of each spherulite there are often two or three plates lying almost in the plane of the section and these show lower birefringence, a clear biaxial bisectrix interference figure which is positive, and oblique extinction. Consequently these coarser spherulites do not show between crossed nicols the symmetrical black cross characteristic of fibrous spherulites, but a distinctly distorted one.

The optical properties of the mineral have been measured from the thin plates split from these coarser spherulites, and are α 1.590, β 1.595, γ 1.615 (all ± 0.002), biaxial positive with Bx_a normal to the cleavage

plates, and $2V$ $51-51\frac{1}{2}^\circ$ ($\pm 2^\circ$) (universal-stage measurements by Dr. J. B. Allen), dispersion $r > v$. There is a single very good cleavage on which the plates separate, and only imperfect partings in other, sometimes divergent, directions. The plates attain a maximum width of

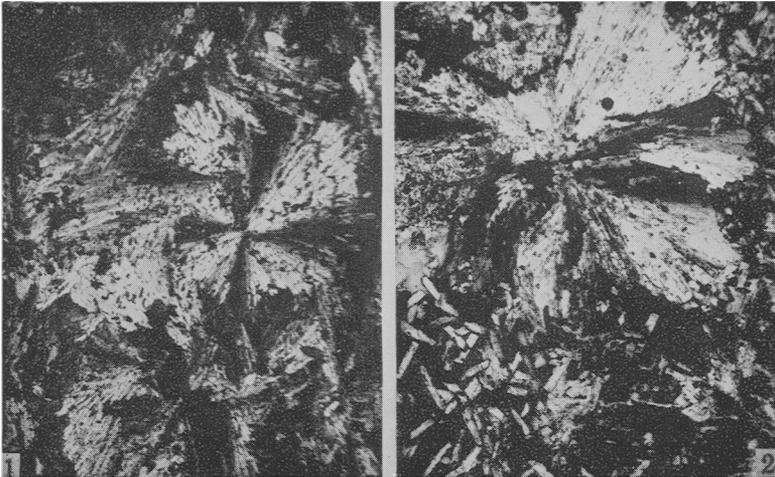


FIG. 1. Bladed spherulites of isokite. Crossed nicols. $\times 40$.

FIG. 2. Large bladed spherulite of isokite, and (lower half) basal plates of strontian fluorapatite with interstitial dolomite (dark). Crossed nicols. $\times 40$.

about 0.3 mm. and terminate obliquely in 3 or 4 edges. A typical selection of these terminated plates is illustrated in fig. 3, fig. 3c showing a complete individual with characteristic elongation, whereas the remainder are broken plates, as the great majority break at their widest part when the spherulites are split up. The peripheral angles have been measured with a Dick-Swift microscope, and the edges indexed from the X-ray crystallographic data (see below), measured and calculated angles being in good agreement as the following comparison shows:

		(001):(101).	(101):(100).	(100):(10 $\bar{1}$).	(10 $\bar{1}$):(10 $\bar{2}$).
Measured	150°	152-3°	126-7°	146-7°
Calculated	148 $\frac{1}{2}$	153	126 $\frac{1}{2}$	147

Very narrow prism and pyramid faces are visible bevelling terminal edges on some plates, but it was not possible to measure these. The plates are flattened parallel to (010) and elongated parallel to a , and the extinction angle between X and the edge (100), i.e. $\alpha:c$ is about 32° .

Extinction is frequently rather wavy, however, partly owing to superposition of thin plates. The optical orientation is shown in fig. 3D.

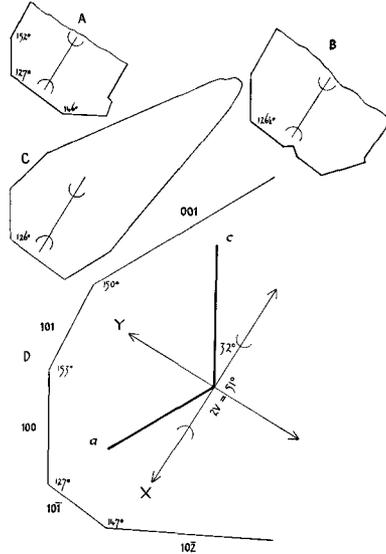


FIG. 3. Thin crystal plates of isokite split from spherulites, lying on (010) and showing measured angles between boundary edges, and the optical orientation.

The specific gravity of the isokite, determined by suspension in heavy liquids, ranges from about 3.15 to 3.27, with a mean value of about 3.22, the fibrous material being appreciably lighter than the crystalline plates, the specific gravity of which lies close to 3.27. Hardness is difficult to measure on such small thin crystals, but is certainly more than 4 and probably about 5 on Mohs's scale. In most specimens the isokite displays a blue fluorescence under long wave (3650 Å.) ultra-violet light. The sellaite from this locality shows a rather similar fluorescence, but is of much rarer occurrence. The mineral dissolves slowly in cold hydrochloric acid, and rapidly in warm acids. It is evidently more readily acid-soluble than the associated apatite, for whereas the fine red soils on Nkumbwa Hill contain abundant apatite liberated from the underlying carbonatite, only very small amounts of isokite occur in the soils, except among the coarser rubble.

CHEMICAL COMPOSITION.

For the separation of sufficient isokite for detailed chemical analysis, a specimen (DNR.5) from the north-eastern corner of the hill was

selected. This is a brown ankeritic dolomite-rock containing abundant white spherulites of isokite about 2 mm. in diameter, many of them coarsely crystalline, and only minor quantities of strontian fluorapatite, a little secondary calcite, and traces of monazite. In crushing the rock the isokite powders very readily, and when most of the material had passed a 60 British Standard mesh sieve, the finest fraction, — 240 mesh, was found to be very rich in isokite and was selected for further concentration. After washing off the finest dust the powder was centrifuged in methylene iodide–benzene mixtures and the fraction of density 3.16 to 3.30 was retained. A small amount of material contaminated with ankeritic and other ferruginous impurities was finally removed by means of a Cook magnetic separator, and left a product suitable for chemical analysis. This concentrate, weighing 4 gm., contained only a little ankeritic dolomite and apatite as impurities, and was analysed by Mr. Pickup with the results shown in table I.

TABLE I. Chemical composition of isokite.

	1.	2.	3.	4.	5.	6.
CaO	30.72	0.64	0.51	29.57	30.61	31.45
SrO	1.65	—	0.05	1.60	1.66	—
BaO	0.21	—	—	0.21	0.22	—
Rare-earths	0.16	—	—	0.16	0.16	—
MgO	21.58	0.40	—	21.18	21.93	22.60
FeO	0.49	0.08	—	0.41	0.42	—
MnO	0.13	—	—	0.13	0.13	—
P ₂ O ₅	37.76	—	0.40	37.36	38.68	39.79
F	9.55	—	0.03	9.52	9.86	10.65
H ₂ O + 300° C.	0.46	—	—	0.46	0.48	—
H ₂ O — 300° C.	0.26	—	—	—	—	—
CO ₂	1.02	1.02	—	—	—	—
Acid insol.	0.10	—	—	—	—	—
	<u>104.09</u>	<u>2.14</u>	<u>0.99</u>	<u>100.60</u>	<u>104.15</u>	<u>104.49</u>
Less O for F	4.02	—	—	4.01	4.15	4.49
	<u>100.07</u>			<u>96.59</u>	<u>100.00</u>	<u>100.00</u>

1. Analysis of concentrate from specimen DNR.5. Analyst, R. Pickup.
2. Constituents assigned to ankeritic dolomite.
3. Constituents assigned to strontian fluorapatite.
4. Composition of isokite.
5. Composition of isokite recalculated to 100 per cent.
6. Composition of CaMgPO₄F.

The principal impurity, ankeritic dolomite, has been corrected for by assuming that all the CO₂ can be assigned to this mineral. This is

certainly largely true, and the additional possibility that CO_3OH groups might replace PO_4 groups to a minor extent in isokite (as in carbonate-apatites), having no direct evidence in its favour, is not considered further. The apatite content appears to be very small, and although it cannot be estimated accurately, 1 % is assumed to be present. The constituents assigned to these impurities, based on previous analyses from this locality, are shown in table I, and after deducting these together with the water lost in 3 hours at 300°C . (regarded as adsorbed water) and the insoluble residue, the inferred composition of the isokite is as shown in columns 4 and 5. The analysis leaves no doubt that isokite is essentially CaMgPO_4F , with only minor substitution of calcium by strontium and of fluorine by hydroxyl. The strontium content is not to be regarded as essential, for it was to be anticipated in an environment such as Nkumbwa where strontium is relatively abundant, as in many carbonatites. The associated strontian fluorapatite contains even more of this element, an analysis by Mr. Pickup showing 4.72 % SrO. It may be mentioned here that some isokite specimens are somewhat stained with manganese to a pink or rhododendron tint, while others are speckled with green, owing to the presence of finely divided green monazite. Until this colour variegation was understood it led to the belief that rare-earths and manganese might be essential constituents of isokite, but this is clearly not the case.

A search of the literature reveals no mineral analysis sufficiently similar to that of isokite to warrant detailed comparison. Strunz (1938), however, has suggested that the mineral cryphiolite described by A. Scacchi (1888) from ejected blocks from Vesuvius was in fact CaMgPO_4F , and monoclinic, isostructural with tilasite ($\text{CaMgAsO}_4\text{F}$). This was contrary to the general belief that cryphiolite is a calcic variety of wagnerite, $\text{Mg}_2\text{PO}_4\text{F}$, but it was obviously desirable to investigate this point before naming the Rhodesian mineral. The fact that cryphiolite was found in close association with sellaite (belonesite of Scacchi), and that Vesuvius and Nkumbwa are the only localities from which sellaite is recorded in a volcanic environment, made this question appear even more important. Through the kindness of Professor A. Scherillo of Naples one of Scacchi's original cryphiolite crystals was obtained, and is at present being examined by X-ray methods in the British Museum, Department of Mineralogy. The X-ray evidence indicates that cryphiolite is related to neither wagnerite, tilasite, nor isokite, and so it need not be considered further in the present connexion, although it will be of interest to learn what it really is.

X-RAY INVESTIGATION.

The single crystals used for the X-ray study of isokite were selected from the crushed spherulites of specimen DNR.5. Preliminary examination, by single-crystal X-ray technique, of a number of the small flakes produced showed that most of these comprised several distinct individuals in parallel growth. Subsequently a small crystal was isolated which showed one main set of reflections with additional weaker reflections due to the presence of a second individual. This crystal was used for the single-crystal study described below.

Single-crystal photographs showed that the mineral is monoclinic and that the good cleavage is (010). The cell dimensions and space group were determined from a *b*-axis oscillation photograph and zero, first, and fourth layer-line Weissenberg photographs for the *b*-axis. The values obtained for the cell dimensions were, *a* 6.52, *b* 8.75, *c* 7.51 Å., all ± 0.05 Å., and β $121^\circ 28' \pm 12'$. The corresponding axial ratios are *a*:*b*:*c* = 0.745:1:0.858. Among the general reflections (*hkl*) only those with (*h*+*k*) even were observed. Examination of the (*h*0*l*) reflections showed that additional absences occurred when *l* was odd. The mineral gave negative results when tested for pyroelectricity; consequently the space group is *C2/c*.

TABLE II. Unit-cell contents of isokite.

Analysis.			Atomic ratios.		Unit-cell contents.	
CaO	29.57	Ca ... 0.5272	3.929	} 4.061
SrO	1.60	Sr ... 0.0154	0.115	
BaO	0.21	Ba ... 0.0014	0.010	} 3.969
(Ce,La) ₂ O ₃	0.16	Ce,La 0.0010	0.007	
MgO	21.18	Mg ... 0.5253	3.914	} 3.921
FeO	0.41	Fe ... 0.0057	0.042	
MnO	0.13	Mn ... 0.0018	0.013	} 4.115
P ₂ O ₅	37.36	P ... 0.5262	3.921	
F	9.52	F ... 0.5011	3.734	} 4.115
OH	0.87	OH ... 0.0511	0.381	
			101.01	O ... 2.1176	15.780	15.780
Less O for F,OH			4.42		31.846	
			96.59			

In table II the cell contents of isokite have been calculated from the observed density, 3.27, and the chemical analysis corrected for impurities. The formula unit is CaMgPO₄F, with minor partial substitutions, and the unit cell contains four formula units. The calculated

density of isokite is 3.29. X-ray powder data for isokite have been tabulated in table III.

TABLE III. X-ray powder data for isokite.

4.38	w	1.962	w	1.522	vw	1.202	vvw
3.62	vw	1.946	vw	1.510	vw	1.171	vw
3.45	vw	1.886	vw	1.495	vw	1.115	w
3.185	vvs	1.872	w	1.479	m	1.084	vw
3.023	vvs	1.837	vw	1.453	vw	1.078	vw
2.887	vw	1.807	m	1.428	w	1.052	w
2.784	m	1.740	vw	1.392	w	1.049	w
2.630	vvs	1.720	s	1.388	w	1.046	w
2.586	m	1.705	m	1.344	w	1.034	vw
2.487	vw	1.684	vw	1.313	w	1.017	vw
2.301	s	1.671	vw	1.303	vw	1.006	vw
2.222	mb	1.656	m	1.276	w	0.959	w
2.105	m	1.602	vw	1.234	w	0.875	w
2.069	m	1.557	m	1.225	vw	0.828	vw
2.041	m	1.539	vw	1.211	vw	0.811	vw

X-ray powder data for the analysed sample of isokite (DNR. 5A). The d spacings are given in Å. units and the relative intensities were estimated visually on the decreasing scale vvs, vs, s, m, w, vw, vvw, b = broad and diffuse. The X-ray powder photograph was taken on a 19-cm. camera using Cu- $K\alpha$ radiation.

To ensure that the X-ray and optical data should relate to the same material the single crystal used for the X-ray work was examined optically. The refractive indices obtained were α 1.590, β 1.594, and γ 1.614, all ± 0.002 , with γ parallel to b and $\alpha:c + 32^\circ$.

Isokite is homologous with the minerals of the tilasite group (Richmond, 1940, p. 464). The cell dimensions and chemical composition of the minerals of this group are compared in table IV.

TABLE IV. Comparison of members of the tilasite group.

	Durangite*	Tilasite†	Sphene‡	Isokite
	NaAlAsO ₄ F.	CaMgAsO ₄ F.	CaTiSiO ₄ (O,OH,F).	CaMgPO ₄ F.
a	... 6.53	6.66	6.55	6.52 Å.
b	... 8.46	8.95	8.70	8.75
c	... 7.30	7.56	7.43	7.51
β	... 119° 22'	121° 0'	119° 43'	121° 28'
Cell contents	4	4	4	4
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$

* Kokkoros (1938, p. 39) with transformation of axes.

† Strunz (1937, p. 10).

‡ Zachariassen (1930, p. 7), with formula as modified by Sahama (1946, p. 106).

Strunz (1949, p. 112) also includes in this group scholzite, Ca₃Zn(PO₄)₂(OH)₂.H₂O, which has comparable cell dimensions but is pseudo-orthorhombic ($\beta \sim 90^\circ$), so that its position in the group is rather anomalous.

PARAGENESIS.

In the Nkumbwa rocks isokite has so far been found in intimate association with dolomite, strontian fluorapatite, monazite, phlogopite, and pyrochlore. Sellaite and isokite have not as yet been found in the same thin section, although they occur together in the same bulk samples, but as sellaite has been seen in only a few sections this point may not be very significant. In the main, isokite appears to belong to a late stage of metasomatic activity which enriched the intrusive dolomite plug with fluophosphates, strontium, rare-earths, and niobium. Often isokite and monazite are intimately associated, both minerals occurring as spherulites which replace coarsely crystalline dolomite along the rhombohedral cleavage planes (pl. XVIII, fig. 1). The conversion of dolomite to isokite by replacement of carbonate by fluophosphate groups would involve a shrinkage in volume of about 15 % and occasionally there are signs that this may have taken place, in that the spherulites sometimes project into small cavities. Generally, however, this late metasomatism was complex, and the details of the process are not yet fully understood. In the xenolithic inclusions of phlogopite-rock (metasomatized gneiss) apatite is common but isokite is rather infrequent, although it may be plentiful in the immediately adjacent dolomite. The weathering of the Nkumbwa carbonatite has been accompanied in places by extensive silicification, and this has sometimes left isokite spherulites completely enveloped in secondary quartz with colloform textures.

Sahama (1945) has called attention to the rarity of the magnesium minerals sellaite MgF_2 and wagnerite Mg_2PO_4F in contrast to the abundance of their calcium equivalents, fluorite and apatite, and has discussed some of the reasons for this. Similar considerations may account for the rarity of isokite, and prompted inquiry as to what special circumstances have favoured its occurrence at Nkumbwa. One obvious condition for its formation is an abundance of fluorine, for isokite contains about three times as much fluorine as fluorapatite. This was clearly present at Nkumbwa where in addition to the large amount of fluorine contained in isokite, the phlogopite-rocks (containing 5 % F) and apatite (3.4 % F) must together contain a similar major quantity, with lesser amounts present as sellaite (61 % F), pyrochlore, &c. A second factor is the high magnesium/calcium ratio which was apparently maintained throughout all the intrusive and metasomatic stages represented at the present erosion level of the plug, indicating circumstances quite different from the general trend at Alnö where, according to Eckermann

(1948), the carbonatites underwent progressive dedolomitization with consequent later enrichment in calcium. At Nkumbwa there are no calcitic carbonatites (sövites), dolomite, usually ankeritic, being practically the only carbonate present, and what little calcite does occur appears to be largely of supergene origin. The only evidence of dedolomitization recognized so far is in the form of local enrichments of apatite in the carbonatite immediately surrounding the phlogopite-rock inclusions. This relative paucity of calcium and abundance of phosphate probably also account for the absence of fluorite at Nkumbwa, despite the abundance of fluorine.

Acknowledgements.—This work forms part of a joint investigation of the Nkumbwa Hill pyrochlore deposits undertaken by the Northern Rhodesia Geological Survey Department and the Mineral Resources Division of Colonial Geological Surveys, London. Thanks are due to the Department of Mineralogy, University of Cambridge, for arranging for Mr. McConnell to undertake the X-ray examination of this new mineral, and to the Department of Mineralogy, British Museum, for assistance at various stages of the work. The authors are indebted to several colleagues for help and advice.

References.

- ECKERMAN (H. von), 1948. The alkaline district of Alnö island. *Sveriges Geol. Undersök., Ser. Ca., no. 36*, 176 pp. [M.A. 11-27.]
- KOKKOROS (P.), 1938. Über die Struktur des Durangit $\text{NaAlF(AsO}_4\text{)}$. *Zeits. Krist., vol. 99*, pp. 38-49. [M.A. 7-237.]
- REEVE (W. H.) and DEANS (T.), 1954. An occurrence of carbonatite in the Isoka district of Northern Rhodesia. *Colonial Geol. Min. Res. London, vol. 4*, pp. 271-281. [M.A. 12-537.]
- RICHMOND (W. E.), 1940. Crystal chemistry of the phosphates, arsenates and vanadates of the type $\text{A}_2\text{XO}_4(\text{Z})$. *Amer. Min., vol. 25*, pp. 441-479. [M.A. 8-11.]
- SAHAMA (Th. G.), 1945. Abundance relation of fluorite and sellaite in rocks. *Ann. Acad. Sci. Fennicae, ser. A, III, no. 9*, 20 pp. [M.A. 9-258.]
- 1946. On the chemistry of the mineral titanite. *Compt. Rend. Soc. Géol. Finlande, no. 19 (Bull. Comm. Géol. Finlande, no. 138)*, pp. 88-120. [M.A. 10-302.]
- SCACCHI (A.), 1888. Sopra un frammento di antica roccia vulcanica involupato nella lava Vesuviana del 1872. *Atti Accad. Sci. Napoli, ser. 2, vol. 1, no. 5*.
- STRUNZ (H.), 1937. Titanit und Tilasit. Über die Verwandtschaft der Silikate mit den Phosphaten und Arsenaten. *Zeits. Krist., vol. 96*, pp. 7-14. [M.A. 7-92.]
- 1938. Isomorphie zwischen Tilasit, Durangit und Cryphiolith. *Centr. Min., pp. 59-60*.
- 1949. *Mineralogische Tabellen*. 2nd edit., p. 168. [M.A. 11-2.]
- ZACHARIASEN (W. H.), 1930. The crystal structure of titanite. *Zeits. Krist., vol. 73*, pp. 7-16. [M.A. 4-281.]

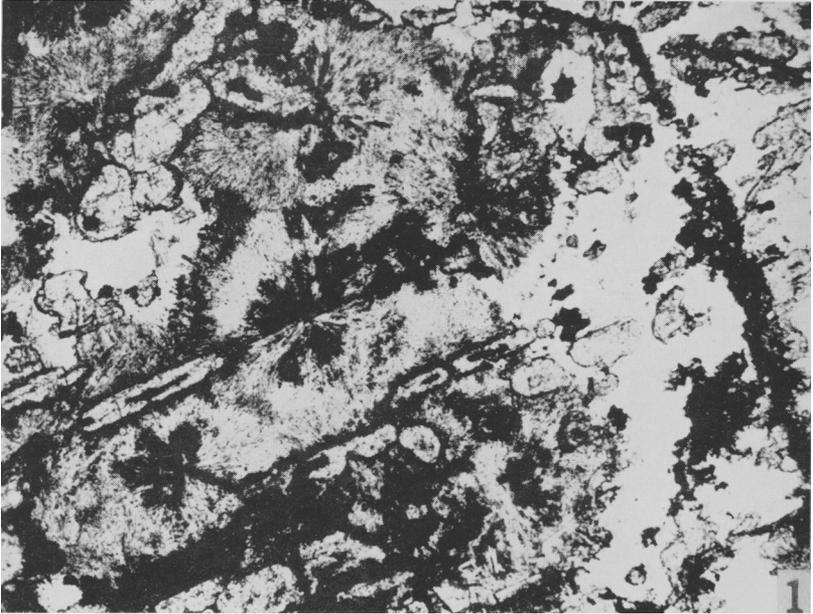


FIG. 1. Large fibrous spherulites of isokite, darkened by inclusions, and smaller elongated spherulites of monazite along dolomite cleavages



FIG. 2. Spherulites of isokite (top left and bottom right), and smaller spherulites of monazite showing black cross and concentric extinction bands.