

*Kalsilite, a polymorph of  $KAlSiO_4$ , from Uganda.*

(With Plate VII.)

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PROFESSOR ARTHUR HOLMES has described in the preceding paper a suite of rocks from Mafuru, Uganda. During his study he observed in thin section a mineral which in optical properties is indistinguishable from nepheline. He gives chemical evidence, however, for the presumption that a potassium aluminosilicate is present in mafurite which would suggest either that the nepheline-like mineral is kaliophilite or a polymorphous form of  $KAlSiO_4$ . Kaliophilite is not isomorphous with nepheline, but has similar optical properties, and the two minerals could be easily confused in thin section. They may, however, be rapidly distinguished by X-ray methods.<sup>1</sup> Even minute grains insufficient for chemical analysis can be determined with certainty; so it seemed probable that an X-ray study of the nepheline-like mineral from Uganda would give additional information and decide whether or no a separation and chemical analysis of the mineral should be attempted. Professor Holmes accordingly invited me to examine his specimens and rock-sections.

A complete petrographic description of these specimens has already been given. Briefly, they are composed of a dark-coloured, fine-grained matrix enclosing abundant and large crystals of magnesium-rich olivine. Some of the hand-specimens show greenish-yellow patches which Professor Holmes terms 'pegmatitoid segregations'. In thin section these segregations reveal transparent colourless grains of low birefringence rarely more than 0.1 mm. across, abundant pale green diopside crystals up to 0.2 mm. across, and granular calcite. The colourless grains are the nepheline-like mineral and they are intergrown with pale brown phlogopite and with a nearly isotropic material of lower refractive index. Phlogopite also is concentrated in the rim of the 'pegmatitoid segregation'.

The first X-ray photographs of the nepheline-like mineral were taken of fragments detached from the edge of a thin section of mafurite which had been prepared without a cover glass. These showed conclusively that the mineral is neither nepheline nor kaliophilite. It was therefore desirable to isolate sufficient for chemical study. Only one hand-specimen (C.6073) of mafurite was available with a 'pegmatitoid segregation' large enough to be detached from the matrix. The segregation was roughly spherical, about 1 cm. in diameter, and detached fragments showed the presence of numerous grains of the mineral to be isolated. By chiselling and the use of dental tools  $\frac{1}{2}$  gram of the segregation was freed from matrix. This was powdered coarsely and then treated with bromoform to separate

<sup>1</sup> F. A. Bannister and M. H. Hey, *Min. Mag.*, 1931, vol. 22, p. 569.

the diopside which weighed 0.20 g. On diluting the bromoform the specific gravity of the remaining grains was found to vary between wide limits owing to their composite nature. They were separated into two approximately equal fractions: I, sp. gr. 2.62–2.67; and II, sp. gr. 2.45–2.62. Fraction I contained a little calcite which was removed by hand-picking. Microscopic and X-ray examination showed that the remainder of this fraction was composed chiefly of the nepheline-like mineral and its micro-chemical analysis is given in table I. Separate single crystal grains of the mineral visibly free from inclusions and quite colourless yield specific gravity values  $2.59 \pm 0.03$ .

TABLE I. Micro-chemical analysis of kalsilite.

Fraction of sp. gr. 2.62–2.67.		Atomic contents per 8 oxygen atoms.	
SiO <sub>2</sub> *	... 39.6	Si	... 2.13
Al <sub>2</sub> O <sub>3</sub>	... 21.3	Al	... 1.35
Fe <sub>2</sub> O <sub>3</sub>	... 5.9	Fe	... 0.24
MgO	... 3.7	Mg	... 0.30
CaO	... 5.0	Ca	... 0.29
K <sub>2</sub> O	... 20.1	K	... 1.38
Na <sub>2</sub> O	... 1.6	Na	... 0.17
	97.2		

\* 45 mg. of the fraction were used for analysis and yielded SiO<sub>2</sub> 39.2%. 12 mg. were used for the alkali determination; this gave a second value for SiO<sub>2</sub> 40.5%. The figure 39.6 is the weighted mean of 39.2 and 40.5.

0.308 mg. of picked grains of kalsilite was ignited at 800° C. for one hour. The ignition loss is less than 1%.

The composition of fraction I is approximately KAlSiO<sub>4</sub>; the iron, calcium, and particularly magnesium figures obtained may be due partly to inclusions of phlogopite and perhaps diopside. Many grains of the mineral possess a yellow tint which is due to internal films. These grains turn brown on heating, suggesting inclusions of an iron mineral. Not all the iron content given by analysis is accounted for by inclusions or admixture with other minerals, however, for quite colourless grains are readily attacked by dilute hydrochloric acid giving a gelatinous liquid coloured yellow by the presence of ferric chloride.

Optical examination of grains of the mineral revealed some oriented to give a sharp, nearly uniaxial negative picture. The refractive indices determined by the Becke line method are  $\omega$  1.542,  $\epsilon$  1.537  $\pm$  0.002. No grains with hexagonal outline have been found and no trace of a cleavage was discovered. Grains for single-crystal X-ray photographs were set up approximately by optical methods and then finally adjusted along zone axes by Laue and oscillation photographs. The mineral is truly hexagonal and possesses unit-cell dimensions  $a$  5.17,  $c$  8.67 Å. Assuming the unit-cell content is 2KAlSiO<sub>4</sub>, the specific gravity is calculated to be 2.60. From the composition given by analysis the specific gravity is calculated to be 2.57, in fair agreement with the observed value 2.59.

By indexing oscillation photographs of the mineral about the  $a$ - and  $c$ -axes no systematic halvings were discovered for any spectra save those from the basal plane. All odd orders of  $c(0001)$  are missing. The space-group is thus determined unequivocally as  $D_6^6 = C6_32$  which possesses no planes of symmetry. Since an X-ray photograph adds a centre of symmetry to the diffraction pattern, which

in this instance is not present in the lattice, planes of symmetry are added perpendicular to the two-fold axes. Hence a Laue photograph along the *c*-axis of the mineral (pl. VII, fig. 1) shows not only hexagonal symmetry but also lines of symmetry parallel to  $(10\bar{1}0)$  and  $(11\bar{2}0)$ .

The unit-cell dimensions of nepheline vary between the limits  $a$  9.93–10.05 and  $c$  8.33–8.43 Å., so that structurally the new mineral is more closely related to nepheline than to kaliophilite with dimensions  $a$  26.7–27.0 and  $c$  8.49–8.51 Å. Kaliophilite has a complicated structure which may be viewed as built up from nepheline-like cells having the dimensions  $a$   $27.0/3 \times 2/\sqrt{3} = 10.4$  Å. and  $c$  8.5 Å. The slightly larger dimensions for the nepheline-like cell are of the order to be expected in the replacement of sodium by potassium. The interesting point now reached is that the new mineral, which may undoubtedly be regarded as a polymorphous form of  $\text{KAlSiO}_4$ , is not isomorphous with nepheline and yet the *a*-axes are related more simply (i.e. by a factor of two,  $2 \times 5.17 = 10.34$  Å.) than are the *a*-axes of the new mineral and kaliophilite. An analogy is the break in the plagioclase series somewhere near the composition of labradorite where the *c*-axis is doubled. Plagioclases richer in soda are isomorphous with each other ( $c$  7.17 Å.) and plagioclases above the break containing less soda ( $c$  14.16 Å.) are also isomorphous with each other, but the series albite to anorthite is a broken one.<sup>1</sup> The difference between the new mineral and nepheline is marked not only by a doubling of the cell-side *a*, but also by change of space-group. It is not possible without X-ray examination of the hexagonal form of artificial  $\text{KAlSiO}_4$  which various workers have made, to decide whether G. Friedel<sup>2</sup> and N. L. Bowen<sup>3</sup> are correct in contending that it is truly isomorphous with nepheline.

Dr. M. H. Hey has succeeded in preparing the orthorhombic form<sup>4</sup> of  $\text{KAlSiO}_4$  twinned like aragonite, but so far has not synthesized the new mineral nor yet a potassium-nepheline. It is probable that a polymorph of  $\text{KAlSiO}_4$  truly isomorphous with nepheline does not exist and that the hexagonal form of  $\text{KAlSiO}_4$  reported by Friedel, Bowen, and Trömel<sup>5</sup> is closely related to, if not identical with, the new mineral. Bowen states that both the hexagonal and orthorhombic forms of artificial  $\text{KAlSiO}_4$  can be obtained at low temperatures, 500–600° C., but that the hexagonal form inverts to the orthorhombic form in the neighbourhood of 1540°; hence the latter is the stable form at high temperatures. An artificial preparation of kaliophilite has also been prepared at 208–211° C. which gives the same X-ray powder pattern as kaliophilite from Monte Somma.<sup>6</sup> In view of the lack of accurate thermal data on the three known polymorphous forms of  $\text{KAlSiO}_4$  it would be unwise at the present time to use

<sup>1</sup> W. H. Taylor, J. A. Darbyshire, and H. Strunz. *Zeits. Krist.*, 1934, vol. 87, p. 464. [M.A. 6–177.] S. H. Chao and W. H. Taylor, *Proc. Roy. Soc. London, Ser. A*, 1940, vol. 176, p. 76. [M.A. 8–13.]

<sup>2</sup> G. Friedel, *Bull. Soc. Franç. Min.*, 1912, vol. 35, p. 471.

<sup>3</sup> N. L. Bowen, *Amer. Journ. Sci.*, 1917, ser. 4, vol. 43, p. 115. [M.A. 1–167.]

<sup>4</sup> A. Duboin, *Compt. Rend. Acad. Sci. Paris*, 1892, vol. 115, p. 56. *Bull. Soc. Franç. Min.*, 1892, vol. 15, p. 191.

<sup>5</sup> G. Trömel, *Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikatforschung in Berlin-Dahlem*, 1930, vol. 3, p. 103. W. Eitel and G. Trömel, *Fort. Min. Krist. Petr.*, 1929, vol. 14, p. 28. [M.A. 6–60.]

<sup>6</sup> S. J. Thuggitt, *Arch. Min. Tow. Nauk. Warszaw. (Arch. Min. Soc. Sci. Varsovie)*, 1937, vol. 13, p. 112. [M.A. 7–146.]

the  $\alpha$ ,  $\beta$ ,  $\gamma$  nomenclature, although Trömel and Winchell<sup>1</sup> have already called the orthorhombic form  $\alpha$ -KAlSiO<sub>4</sub>. There is no evidence that there is an analogy with the  $\alpha$ - $\beta$  transition of quartz which takes place reversibly at a definite temperature and involves a distortion of a silicon-oxygen lattice with relatively small changes in unit-cell dimensions. The transition from the highly complex kaliophilite with a large unit cell to the new mineral with a much smaller unit cell and more simple crystal-structure may not necessarily be effected without passing through an intermediate phase. Naming the new mineral parakaliophilite would also be open to the same objection. Parakalinepheline correctly conveys the sense of a simple crystallographic relationship to nepheline, but such a name is unduly cumbersome. In the circumstances, it is proposed to name the new mineral kalsilite after its chemical composition KAlSiO<sub>4</sub>.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	$\omega$ .	$\epsilon$ .	Sp. gr.
Kalsilite ... ..	5.17	8.96	8.67 Å.	1.542	1.537	2.59
Kaliophilite ... ..	27.0	46.8	8.51	1.530	1.526	2.606
Orthorhombic KAlSiO <sub>4</sub>	9.00	15.68	8.53	$\gamma$ 1.536	$\alpha$ 1.528	2.60

Above are tabulated the known forms of KAlSiO<sub>4</sub>, together with their X-ray and optical data. A more detailed description of further X-ray data on the orthorhombic form and on yet another polymorph of KAlSiO<sub>4</sub> of unknown symmetry, recently prepared as a powder by Dr. Hey, must await X-ray examination of the hexagonal form described by Friedel and Bowen. Since the new mineral possesses a smaller unit cell than any other member of the nepheline family, a knowledge of its crystal-structure will assist in working out the more complex crystal-structures of nepheline, kaliophilite, and the orthorhombic form of KAlSiO<sub>4</sub>.

Powder photographs of kalsilite, kaliophilite, and nepheline are reproduced (pl. VII, figs. 2, 3, and 4) to show how readily the three minerals may be distinguished. The photograph of kalsilite has been indexed and the spacings and intensities of the lines are tabulated in table II. These photographs were taken with iron radiation to obtain greater resolution than is possible with a copper target. Yet the kaliophilite pattern contains a large number of weak lines very close to each other and is in contrast to the much less line-rich pattern of kalsilite.

It would obviously be an advantage to petrographers not equipped with X-ray apparatus to distinguish between kalsilite and nepheline in thin section. This can be done successfully with a straightforward chemical test.<sup>2</sup> A drop of *N* HCl is placed on the uncovered thin section or polished rock surface, and after  $\frac{1}{2}$  minute a drop of strong sodium cobaltinitrite solution is added; after a further 1-2 minutes the surface is washed gently. Kalsilite, but not nepheline, gives a yellow stain specific for the presence of potassium.

It will be recalled that the chemical composition of the new mineral kalsilite was obtained from the heavier of two fractions from which the diopside had already been removed. Fraction II contained grains varying in specific gravity from 2.45 to 2.62 and most of them were composite. Many indeed were kalsilite

<sup>1</sup> A. N. Winchell. The microscopic characters of artificial inorganic solid substances or artificial minerals. 2nd edit., New York, 1931, p. 308. [M.A. 5-2.]

<sup>2</sup> A. Gabriel and E. P. Cox, Amer. Min., 1929, vol. 14, p. 290. [M.A. 4-219.] M. L. Keith, Amer. Min., 1939, vol. 24, p. 561. [M.A. 8-17.]

grains, but they were generally attached to, or sometimes surrounded by, a transparent, colourless, nearly isotropic material of refractive index 1.500. Thin sections of the 'pegmatitoid segregation' also reveal this interstitial material, which at first was thought to be glass. Fraction II was more finely powdered and eventually separated into two components by centrifuging in a mixture of bromoform and benzene with sp. gr. 2.45. The heavier component yielded a powder photograph of kalsilite, but the minute amount of mineral sp. gr. < 2.45 yielded a powder pattern at first attributed to phillipsite. This pattern agrees exactly with extra lines and spots found on some of the preliminary powder and particle photographs of the 'pegmatitoid segregation' before crushing and treatment with heavy liquids. So little of this lighter mineral was separated that its specific gravity could not be determined with accuracy; its probable value is  $2.35 \pm 0.05$ . Certain differences in optical properties and the powder patterns of the mineral and phillipsite suggested further tests. Dr. Hey found that 0.738 mg. of fraction II on ignition at  $800^\circ \text{C}$ . lost  $5 \pm \frac{1}{2} \%$ . After ignition these grains showed adherent milky material which disintegrated readily.

TABLE II. X-ray powder data for kalsilite.

Spacing:					Spacing:				
2r.	Inten-	Ob-	Cal-	Index.	2r.	Inten-	Ob-	Cal-	Index.
cm.	sity.	served.	culated.		cm.	sity.	served.	culated.	
		Å.	Å.				Å.	Å.	
2.71	m	4.35	4.335	(0002)	9.43	w	1.375	1.375	(10 $\bar{1}$ 6)
3.00	s	3.97	3.979	(10 $\bar{1}$ 1)	9.79	w	1.335	1.334	(21 $\bar{3}$ 4)
3.49	m	3.12	3.115	(10 $\bar{1}$ 2) $\beta$	10.19	w	1.294	1.293	(2240)
3.85	s	3.11	3.115	(10 $\bar{1}$ 2)	10.52	m	1.264	1.261	(11 $\bar{2}$ 6)
4.20	w	2.572	2.585	(11 $\bar{2}$ 0) $\beta$	10.91	m	1.231	1.229	(31 $\bar{4}$ 1)
4.65	s	2.590	2.585	(11 $\bar{2}$ 0)				1.229	(30 $\bar{3}$ 4)
4.86	m	2.470	2.477	(11 $\bar{2}$ 1)	11.15	m	1.212	1.212	(20 $\bar{2}$ 6)
4.95	m	2.428	2.428	(10 $\bar{1}$ 3)				1.214	(21 $\bar{3}$ 5)
5.45	w	2.218	2.220	(11 $\bar{2}$ 2)	11.40	m	1.194	1.193	(31 $\bar{4}$ 2)
5.60	m	2.163	2.168	(0004)	12.20	w	1.141	1.142	(3143)
			2.168	(20 $\bar{2}$ 1)	12.75	vw	1.111	1.110	(4041)
6.15	w	1.984	1.989	(2022)				1.110	(2244)
6.25	w	1.955	1.951	(10 $\bar{1}$ 4)	13.29	w	1.085	1.084	(20 $\bar{2}$ 7)
6.36	w	1.926	1.927	(11 $\bar{2}$ 3)				1.083	(4042)
7.00	w	1.770	1.770	(20 $\bar{2}$ 3)	13.44	vw	1.078	1.077	(3144)
7.51	m	1.660	1.661	(11 $\bar{2}$ 4)	14.00	w	1.055	1.053	(10 $\bar{1}$ 8)
			1.661	(21 $\bar{3}$ 1)	14.28	w	1.045	1.043	(4043)
7.75	m	1.620	1.618	(10 $\bar{1}$ 5)	14.55	w	1.036	1.036	(2245)
7.98	m	1.576	1.576	(21 $\bar{3}$ 2)	15.42	m	1.011	1.009	(3145)
8.10	vw	1.556	1.557	(20 $\bar{2}$ 4)	15.85	m	1.000	1.000	(32 $\bar{5}$ 2)
8.51	m	1.490	1.492	(3030)				1.000	(11 $\bar{2}$ 8)
8.76	w	1.460	1.460	(2133)					

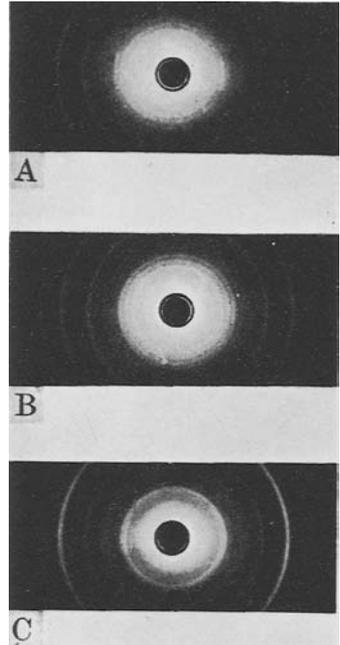
This and the powder photographs of nepheline and kaliophilite reproduced in pl. VII were taken with unfiltered iron radiation  $\lambda$  1.934 Å. in a cylindrical camera, 6.04 cm. diameter.

Thus far the weakly birefringent mineral interstitial to kalsilite would appear to be a zeolite, and a member of the phillipsite family. It is distinguished from phillipsite by lower birefringence, higher specific gravity, and easily detected differences in the spacings and intensities of the lines on powder photographs (text-fig. 1). A comparison with a powder photograph of another well-known

member of the phillipsite family, harmotome, reveals similarities, especially in the lines of high spacing at the centres of the photographs. The spacings and intensities of the powder lines tabulated in table III, however, show that the mineral under discussion is neither phillipsite nor harmotome. A positive test for barium was obtained by Dr. Hey on a small sample of fraction II which together with the X-ray evidence points to barium content of the zeolitic mineral. We have not, however, excluded the possibility of kalsilite itself containing barium. Although the zeolite associated with kalsilite is undoubtedly a member of the phillipsite family a satisfactory identification with a known mineral has not been achieved. There is a possibility that the mineral is identical with wellsite,<sup>1</sup> a member of the phillipsite family containing 5 % BaO with sp. gr. 2.278-2.366, but no specimens were available for comparison.

It may be significant that the *c* dimensions of the unit cells of harmotome<sup>2</sup> and phillipsite<sup>3</sup> are 8.60 and 8.62 Å. respectively, both fairly close to the *c* dimension of kalsilite 8.67 Å. The *c* dimension of the undetermined zeolite which rims many of the kalsilite grains is likely to be sufficiently close to that of kalsilite to suggest parallel growth. This idea can be tested more rigorously when the crystal-structure of kalsilite has been worked out.

Thin sections of the 'pegmatitoid segregation' show calcite filling cracks and flaws in the kalsilite-diopside matrix. The calcite sometimes encloses fan-shaped crystal groups reminiscent of stilbite and it was possible by dissolving some of the calcite grains picked from fraction I before analysis, in dilute HCl, to obtain small particles of a mineral with low birefringence and refractive index about 1.48. Needles of another mineral, possibly zeolitic, were also obtained in this way, but were too small for identification. It was possible, however, to obtain an X-ray photograph of a few particles of the chief mineral enclosed in the calcite. This proved to be identical with the pattern of the undetermined zeolite with refractive index 1.500 associated with kalsilite. It is not unlikely that a member of the phillipsite family might vary considerably in chemical composition and in refractive index, but chemical work on the minute amounts just sufficient for X-ray and optical data is out of the question.



TEXT-FIG. 1. Powder photographs of zeolite (A) associated with kalsilite, harmotome (B), and phillipsite (C), reproduced from films taken with unfiltered copper radiation,  $\lambda$  1.539 Å., in the same cylindrical camera, diameter 6.04 cm., to show the lines of longest spacing nearest the centre. Actual size. .

<sup>1</sup> J. H. Pratt and H. W. Foote. Amer. Journ. Sci., 1897, ser. 4, vol. 3, p. 443.

<sup>2</sup> J. Sekanina and J. Wyart. Bull. Soc. Franç. Min., 1937, vol. 60, p. 139. [M.A. 7-346.]

<sup>3</sup> J. Wyart and P. Chatelain. Bull. Soc. Franç. Min., 1938, vol. 61, p. 121. [M.A. 7-347.]

The X-ray, chemical, and optical studies have led to a more exact knowledge of the mineral composition of the 'pegmatitoid segregation', which contains approximately 50 % by weight of kalsilite, 40 % of diopside, and not more than 10 % of calcite, zeolite, biotite, &c. By centrifuging powdered mafurite surrounding the 'pegmatitoid segregation' a minute quantity of kalsilite was obtained which gave a powder photograph free from additional lines. It is unlikely that the separation of kalsilite from the fine-grained matrix was complete however, and no quantitative estimate of the percentage of the new mineral in samples of mafurite free from segregations has been attempted.

TABLE III. Spacings in Ångström units and the estimated intensities of the principal lines of X-ray powder photographs of the zeolite associated with kalsilite and of harmotome and phillipsite.

Zeolite (text-fig. 1A).	Harmotome (text-fig. 1B).	Phillipsite (text-fig. 1C).	Zeolite (text-fig. 1A).	Harmotome (text-fig. 1B).	Phillipsite (text-fig. 1C).
8.18 s	8.11 s	7.64 s	1.97 vw	1.95 m	2.16 vw
7.16 s	7.16 s	6.91 s	1.78 w	1.91 vw	2.07 vw
6.43 m	6.25 s	6.34 vw	1.72 w	1.84 w	1.97 w
4.96 vw	4.96 m	5.24 w	1.65 vw	1.80 w	1.91 vw
4.07 m	4.07 s	4.91 w	1.55 vw	1.74 w	1.84 vw
3.51 w	3.50 m	4.56 vw	1.49 vw	1.72 ms	1.78 w
3.18 s	3.18 s	4.25 m	1.37 vw	1.68 w	1.72 w
2.95 w	2.93 w	4.07 m	1.33 vw	1.54 m	1.67* vw
2.70 m	2.69 s	3.54 w	1.27 vw	1.48 m	1.61 vw
2.55 w	2.52 m	3.18 s		1.37 w	1.55 vw
2.34 vw	2.34* m	2.94 w		1.33 w	1.49 vw
2.25 vw	2.25 w	2.71 m		1.26 w	1.38 w
2.16 vw	2.16 m	2.52 w		1.17 vw	1.34 w
2.06 vw	2.03* w	2.40* w			1.28* w

\* Unresolved doublets.

#### EXPLANATION OF PLATE VII.

The Laue photograph was taken with unfiltered copper radiation,  $\lambda$  1.539 Å., the crystal-film distance being 3.5 cm. Actual size.

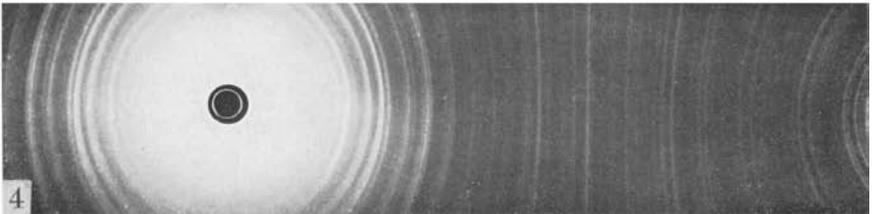
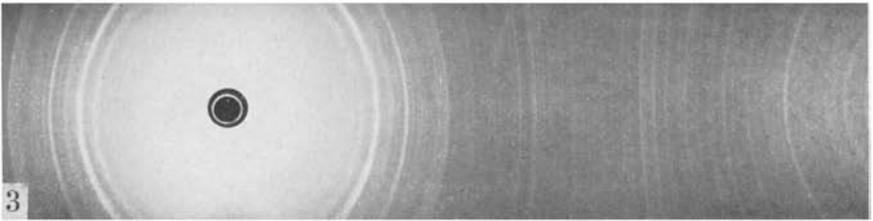
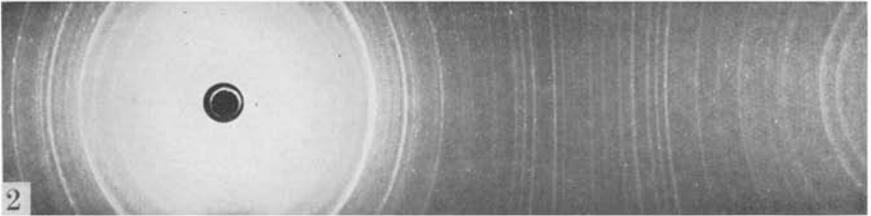
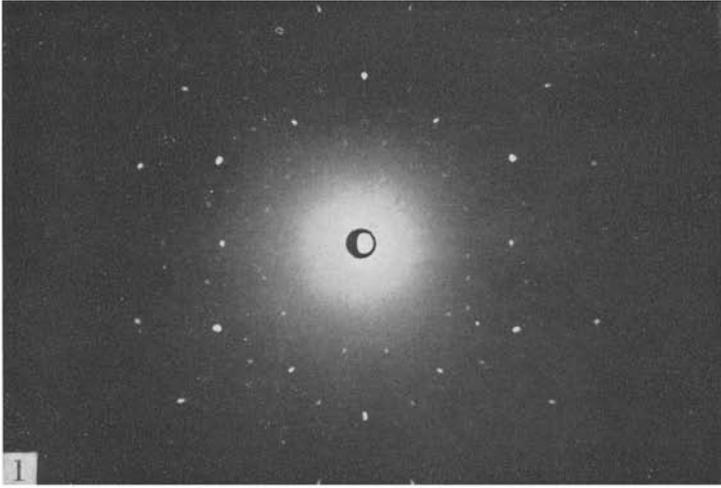
The powder photographs were taken with unfiltered iron radiation,  $\lambda$  1.934 Å., in the same cylindrical camera, 6.04 cm. diameter. All actual size.

FIG. 1. Laue photograph along the *c*-axis of a kalsilite grain from a 'pegmatitoid segregation' in mafurite, Mafuru, Uganda.

FIG. 2. Powder photograph of kalsilite from fraction I, micro-chemical analysis by M. H. Hey, table I.

FIG. 3. Powder photograph of kaliophilite from an ejected biotite-augite block, Monte Somma, Mt. Vesuvius, Italy. B.M. 68764.

FIG. 4. Powder photograph of nepheline from leucitite, Capo di Bove, Rome, Italy. B.M. 1926,1538.



F. A. BANNISTER: X-RAY PHOTOGRAPHS OF KALSILITE, ETC.