

*Nacrite from Hirvivacra, northern Karelia, Finland.*

(With Plate XXVIII.)

By OLEG VON KNORRING, M.Sc.

Department of Geology

G. W. BRINDLEY, Ph.D., F.Inst.P., and K. HUNTER

Physics Laboratories

The University of Leeds.

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## I. OCCURRENCE AND GENERAL CHARACTERS (O. V. K.)

*Introduction.*

**N**ACRITE is the rarest member of the kaolin group of minerals. The name was first applied by Brongniart in 1807 to a mineral (talc granuleux of Haüy, 1801) the properties of which were not then adequately described. In 1832 Breithaupt recorded a mineral from an ore vein near Freiberg in Saxony, which has since been called nacrite. In the past, however, 'nacrite' has been applied quite frequently to different nacreous and micaceous minerals, not necessarily of kaolin composition, and the authenticity of the species was not definitely established until 1931 when Ross and Kerr,<sup>1</sup> on the basis of an X-ray study of nacrite from the locality Brand near Freiberg in Saxony, proved the mineral to be a distinct species of the kaolin group.

Apart from several occurrences in Saxony of which Brand is the type locality, nacrite has previously been recorded and confirmed only from St. Peter's Dome in the Pikes Peak district of Colorado, where it was originally described by Whitman Cross and W. F. Hillebrand<sup>2</sup> as a very pure kaolinite. In this latter occurrence the mineral is found as a well-crystallized alteration product of microcline in veins of obviously pegmatitic character, and is associated in the Eureka vein with the rare assemblage, fluorite, cryolite, columbite, zircon, astrophyllite, and mica. In the Freiberg localities, on the other hand, nacrite appears to be con-

<sup>1</sup> C. S. Ross and P. F. Kerr, The kaolin minerals. Prof. Paper U.S. Geol. Surv., 1931, no. 165-E, pp. 151-176. [M.A. 5-359.]

<sup>2</sup> W. Cross and W. F. Hillebrand, Minerals from the neighbourhood of Pikes Peak. Bull. U.S. Geol. Surv., 1885, no. 20, pp. 40-74.

fined to hydrothermal (quartz-galena) ore veins as one of the latest minerals to form.

The present find of nacrite was made by the writer in 1948, while mapping and prospecting Mount Hirvivaara in the area of Herajoki, Eno parish, northern Karelia, Finland. This region is occupied by pre-Cambrian rocks of the Karelian formation, which comprise quartzites, conglomerates, and intercalated andalusite-kyanite-chloritoid-sericite schists, penetrated in places by dolerite dikes. The quartzites, especially those of Hirvivaara, are strongly kyanite-bearing and locally, as on the hill Ilokallio, may contain patches of almost pure kyanite. On this hill nacrite occurs together with small perfect crystals of quartz and anatase, in cracks and cavities in an almost glassy, kyanite-bearing quartzite.

Attention was first attracted to the occurrence by the presence of small radial aggregates of an apple-green mineral of micaceous appearance, similar in general character to the pyrophyllite which is also found in the area. A preliminary chemical analysis, however, proved the mineral to have the composition of kaolinite. This first analysis (table I, anal. 1) showed an unusually high content of surface absorbed water, as determined at 110° C. on dry powdered material, and the coarsely crystalline habit of the kaolin mineral appeared moreover to indicate dickite or nacrite rather than kaolinite. X-ray powder photographs showed that the mineral was neither kaolinite nor dickite, but nacrite.

#### *Petrographical aspects.*

The nacrite, which is found in joints, cracks, and small pockets in the banded, kyanite-bearing quartzite, is coarsely crystalline in character and forms groups of radiating plates up to 5 mm. in diameter. When fresh and in compact masses, it is light green in colour, but otherwise appears colourless to yellow-brown. Usually quartz crystals line the walls of the cavities in which the nacrite occurs and in thin section are seen to be in optical continuity with the quartz grains in the surrounding quartzite. The nacrite occupies the central portion of the cavity and appears to have developed by outward growth from the cavity wall. Tiny excellent crystals of anatase are scattered sparingly amongst the nacrite, and a white, fine-grained, well-crystallized kaolinite (pl. XXVIII, figs. 1-3) fills the remainder of the cavity space.

The observed order of crystallization is quartz, nacrite, anatase, and kaolinite, but it is possible that some elongated low-temperature quartz crystals are of later formation than part of the nacrite. The first three minerals are primary, whereas the kaolinite has formed later and is

possibly of secondary origin. In the thin section the nacrite is colourless and non-pleochroic. Between crossed nicols (pl. XXVIII, fig. 1) it is seen to form fan-shaped or bunch-like twinned aggregates with low birefringence.

The bulk of the fine-grained crystalline kaolinite was lost in the preparation of the thin section, but some can still be observed enclosed in nacrite, where it forms excellent, minute, fan-shaped aggregates. The largest of these measures 0.2 mm. in diameter (pl. XXVIII, fig. 3).

The surrounding quartzite is a highly metamorphic kyanite-bearing type with a well-defined sutured texture (pl. XXVIII, fig. 4). A mineral separation showed the following accessory minerals: pyrite, rutile, monazite, apatite, zircon, and tourmaline.

It may be mentioned that in a patch of pure kyanite, almost in contact with the nacrite, the following minerals have been identified: diaspore, pyrophyllite, and kaolinite. Farther towards the NW., concentrations of pyrophyllite have been found in the quartzite and contain, in addition to corroded kyanite, relics of the rare mineral florencite, together with rutile, zircon, and tourmaline.

The entire complex of Hirvivaara thus appears to provide an interesting geological problem, as previously only a few localities with similar parageneses have been described from other parts of the world. In this connexion it may be pointed out that the minerals diaspore, florencite, pyrophyllite, and nacrite are new species for Finland.

#### *Chemical composition and physical properties.*

The kaolin minerals nacrite, dickite, and kaolinite are chemically identical and their composition corresponds closely to the chemical formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . A quantitative chemical analysis is consequently of limited value for the absolute identification of these minerals. So far three analyses of the Hirvivaara kaolin minerals have been carried out, two on the nacrite from Ilokallio and one on a kaolinite from a quartz-kyanite vein. The first analysis of nacrite (table I, anal. 1), a preliminary one, made in 1948 on hand-picked, ground material, showed a remarkably high content of hygroscopic water at 110° C. The second analysis, which was made later (1951) on hand-picked nacrite flakes, revealed, on the other hand, no surface absorbed water. A check on this matter was carried out. The nacrite flakes were ground and sieved through a 180-mesh silk sieve and the material thus obtained was exposed to the air for about 14 hours before  $\text{H}_2\text{O}$ - was determined. The water content was then found to be 2.70 %, or a value very similar to

that in anal. 1. It was further observed that the water could be driven off and reabsorbed reversibly.

Compared with earlier analyses of nacrite (table I, anal. 3-4) the present ones are very similar, especially anal. 2 which represents very pure material. The kaolinite analysis also corresponds very closely to the ideal formula. The Ti and Fe content is probably due to some traces of intermixed accessory minerals.

TABLE I. Chemical analyses of nacrite and kaolinite.

	1.	2.	3.	4.	5	6.
SiO <sub>2</sub>	... 44.36	46.32	44.75	46.06	46.40	46.54
TiO <sub>2</sub>		trace	—	—	0.18	—
Al <sub>2</sub> O <sub>3</sub>	... 38.60	{ 39.65	39.48	39.63	39.15	39.50
Fe <sub>2</sub> O <sub>3</sub>		{ 0.05	0.53	—	0.11	—
MnO	... —	trace	—	—	—	—
MgO	... —	trace	0.19	—	—	—
CaO	... —	0.08	0.13	0.68	—	—
H <sub>2</sub> O —	... 2.90	none	0.61	—	0.24	—
H <sub>2</sub> O +(ign.)	... 14.48	14.21	14.40	13.77	13.98	13.96
	100.34	100.31	100.09	100.14	100.06	100.00

1. Nacrite in kyanite-quartzite, Hirvivaara, Finland. Analyst, O. von Knorring.
2. Nacrite in kyanite-quartzite, Hirvivaara, Finland. Analyst, O. von Knorring.
3. Nacrite in galena-quartz vein, Brand, Saxony. Analyst, F. A. Gonyer (in Ross and Kerr, 1931).
4. Nacrite in granite pegmatite, St. Peter's Dome, Pikes Peak, Colorado. Analyst, W. F. Hillebrand, 1885.
5. Kaolinite in kyanite-quartz vein, Hirvivaara, Finland. Analyst, O. von Knorring.
6. Theoretical composition for Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.2H<sub>2</sub>O.

The refractive indices of the nacrite from Hirvivaara are shown in table II, together with the values determined for nacrites from other localities. The specific gravity determination was carried out with a Berman balance and the result represents the mean value of seven determinations.

TABLE II. Optical data of nacrite.

	$\alpha$	$\beta$ .	$\gamma$ .	Sign.	Sp. gr.
1.	1.560	1.566	1.568 $\pm$ 0.002	negative	2.60 $\pm$ 0.02
2.	1.557	1.562	1.563	negative	—
3.	1.560	1.563	1.566	positive, negative	—

1. Nacrite, Hirvivaara, Finland.
2. Nacrite, Brand, Saxony (Ross and Kerr, 1931).
3. Nacrite, St. Peter's Dome, Colorado (Ross and Kerr, 1931).

*Dehydration of nacrite.*

According to Richardson<sup>1</sup> it is generally misleading to regard the structural breakdown of the kaolin minerals as a function purely of temperature. The time of heating at various temperatures is an important factor. Samojlow<sup>2</sup> carried out some dehydration experiments on kaolinite (possibly dickite or nacrite) from cinnabar occurrences at Zaitsevo in Donets and found that the loss of total water in two hours at 525° C. was 7·63 %, and 12·99 % after 22 hours at the same temperature. It is very important, therefore, to know the exact conditions under which dehydration analyses have been carried out before comparisons of dehydration curves of kaolin minerals can be made. Ross and Kerr have shown that the kaolin minerals, kaolinite, dickite, and nacrite, have distinct dehydration curves, and that most of the water is lost between 400 and 525° C. in the case of kaolinite, between 500 and 600° C. in the case of dickite (1 sample only), and between 500 and 700° C. in the case of nacrite (2 specimens). Unfortunately the time of heating at different temperature intervals is not recorded by Ross and Kerr, nor is the state of the samples indicated (whether ground or unground). The two curves for nacrite given by these authors, although not identical, nevertheless show certain similarities. Thus the first break in the curve for nacrite from Brand is at about 460° C. and for nacrite from St. Peter's Dome at 550° C. The second break at about 675° C. is significant for both samples.

Two dehydration experiments were carried out on nacrite from the present occurrence, both ground and unground material being used. The specimens were heated in a platinum crucible in an electric furnace at 50° C. intervals over a range of temperatures for two hours each. The curves thus obtained are reproduced in text-fig. 1. In each determination 0·5 gram of material was used. The ground sample of nacrite was the same as that used in the determination of hygroscopic water. The dehydration curve obtained on this material was therefore made on a sample dried at 110° C. The coarse unground sample consisted of wedge-shaped nacrite flakes from 1 to 3 mm. in diameter. There is a considerable difference between these two curves although the major changes occur at approximately the same temperatures. In the range of 110–400° C

<sup>1</sup> H. M. Richardson, Phase changes which occur on heating kaolin clays. Chap. III in *X-ray identification and crystal structures of clay minerals*. Min. Soc., London, 1951.

<sup>2</sup> J. Samojlow, Über das Wasser des Kaolinitis. *Zeits. Kryst. Min.*, 1913, vol. 51, pp. 106–108.

the loss of water is almost nil for the coarse sample, whereas the fine one loses 2% at 400° C. From this point the curves rise fairly steeply and the ground sample is seen to lose the bulk of its water between 400 and 500° C. During the same temperature interval the loss of water for the coarse sample is only about 1%, the bulk of the water, that is 12%, being lost between 500 and 600° C. Two definite breaks are recorded at about 650° C. and 750° C. respectively in both samples.

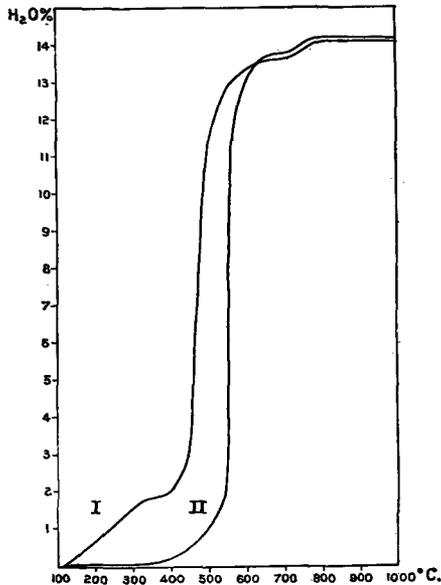


FIG. 1. Dehydration curves of nacrite (I, ground, II, unground) from Hirvivaara, Finland.

### Conclusions.

The nacrite described in this paper occurs in association with quartz, anatase, and kaolinite as a cavity mineral in a highly metamorphosed kyanite-quartzite. The association is very different from those previously described and in many ways resembles the deposits of the alpine mineral veins formed in cavities and on joint surfaces. Nacrite has in fact been reported, although the identification has not been confirmed by X-ray data, by Koenigsberger<sup>1</sup> from Monti Camperio near Olivone,

<sup>1</sup> P. Nigghi, J. Koenigsberger, and R. L. Parker, *Die Mineralien der Schweizeralpen*. Basel, 1940, p. 237. [M.A. 8-49.]

where it occurs as a filling in 'Anhydrit-Hohlprismen' in crystals of quartz.

As regards the origin of nacrite, Ross and Kerr believe that nacrite is probably formed by pneumatolytic or hydrothermal processes and that the temperature of formation is higher than in the case of kaolinite formed under similar conditions. The nacrite from Hirvivaara might well be of hydrothermal origin as there is evidence of widespread hydrothermal activity throughout the entire complex.

## II. X-RAY EXAMINATION (G. W. B. and K. H.).

### *Rotation diagrams.*

Several flakes, about 0.2 mm. in size, were carefully selected under a microscope and examined with Cu- $K\alpha$  radiation using a camera of 6 cm. diameter. Rotations were made about the  $a$ - and  $b$ -axes, and also about an axis normal to the cleavage plane, approximately the  $c$ -axis. The lattice parameters agreed with those previously given by Hendricks,<sup>1</sup> and in particular confirmed a  $c$ -axis spacing of about 43 Å. This corresponds to a unit cell containing six layers of the kind found in kaolinite. Rotation diagrams about the  $b$ - and  $c$ -axes are reproduced in pl. XXVIII.

All the rotation diagrams showed evidence of disorientation of the fragments composing the individual crystals. The disorientation, however, was not random but was similar to that observed with brucite and discussed by Brindley and Ogilvie.<sup>2</sup> On  $a$ - and  $b$ -axes rotation diagrams, some reflections are recorded as sharp spots, others are streaked along Debye-Scherrer arcs. The sharp spots correspond to reflections with the  $l$ -index zero (or small values). In  $c$ -axis rotation diagrams, all the reflections are extended along short arcs. As in the case of brucite, the results are consistent with some tilting of the  $a$ - and  $b$ -axes and with absence of rotation of these axes about  $c$ ; they agree also with the appearance of the nacrite crystals shown in pl. XXVIII.

### *Powder diagrams.*

Since relatively few occurrences of nacrite are recorded in the literature and since the X-ray data for this mineral are rather sparse, it was thought worth while to measure the powder diagram in detail. A 20 cm.

<sup>1</sup> S. B. Hendricks, The crystal structure of nacrite  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$  and the polymorphism of the kaolin minerals. Zeits. Krist., 1939, vol. 100, pp. 509-518. [M.A. 7-422.]

<sup>2</sup> G. W. Brindley and J. G. Ogilvie, The texture of single crystals of brucite. Acta Cryst. (to appear), 1952.

diameter camera employing glancing-angle technique was used with both filtered Ni- $K\alpha$  and filtered Co- $K\alpha$  radiations. An internal calibration was based on reflections from a trace of quartz impurity and the quartz spacings were calculated from the parameters given by Wilson and Lipson,<sup>1</sup> namely  $a$  4.9032,  $c$  5.3937 kX. The nacrite was crushed rather than ground in order to minimize lattice distortion. A diagram obtained with Co- $K\alpha$  radiation is reproduced in pl. XXVIII. The lattice spacings and the visually estimated intensities of the reflections are listed in table III, where they are compared with data previously published by Ross and Kerr (1931, loc. cit.), Gruner,<sup>2</sup> and Nagelschmidt.<sup>3</sup> Lines which have been recorded but are probably due to impurities are listed at the bottom of each column. Powder data for nacrite from Augustusburg, Saxony, recorded in Report no. 7 of the American Petroleum Institute's Project no. 49, are in very poor agreement with other data and are therefore omitted; the strong low-order reflections appear to be split by specimen absorption and the high-order spacings are consistently low.

A particular feature of the nacrite diagram is that it is much poorer than diagrams normally obtained with dickite and kaolinite. The occurrence of a number of broad lines which are still not resolved with a 20 cm. diameter camera may arise, as Gruner suggested, from the presence of groups of lattice planes of similar but not identical spacings, which is in accordance with the  $\beta$ -angle given by Hendricks, viz.  $90^\circ 20' + 10'$ . We have, however, resolved the very strong line previously recorded at about 2.416 kX ( $I = 10$ ) into a doublet 2.433 ( $I = 7$ ) and 2.392 ( $I = 7$ ), and the line at 4.40<sub>5</sub> ( $I = 7$ ) may also be a close doublet having a separation of about 0.04 kX. For the unresolved broad lines, we have measured the apparent spacings corresponding to their outer edges; these are indicated in column 1 of table III by the bracketed values and the letter B signifying 'band'.

The lattice constants given by Hendricks are  $a$  8.94,  $b$  5.14,  $c$  43.0 =  $6 \times 7.17$ ,  $\beta$   $90^\circ 20'$ . The  $a$  and  $b$  parameters of kaolinite and dickite,  $a$  5.14,  $b$  8.93, are interchanged in nacrite and the medium-strong line observed at 1.485 kX, usually indexed as (060), now becomes

<sup>1</sup> A. J. C. Wilson and H. Lipson, The calibration of Debye-Scherrer X-ray powder cameras. Proc. Physical Soc., 1941, vol. 53, pp. 245-250.

<sup>2</sup> J. W. Gruner, The crystal structure of nacrite and a comparison of certain optical properties of the kaolin group with its structures. Zeits. Krist., 1933, vol. 85, pp. 345-354. [M.A. 5 474.]

<sup>3</sup> G. Nagelschmidt, Röntgenographische Untersuchungen an Tonen. 1934, Zeits. Krist., vol. 87, pp. 120-145. [M.A. 6-136.]

TABLE III. X-ray powder data for nacrite.

1.		2.		3.		4.		5.	
<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>
7.16	10	7.15	vs	7.15	vs	7.078	10	—	—
4.405	7	4.42	s	4.40	s	4.404	8	4.471	8
4.115	3	4.16	m	4.15	w	4.126	3	4.201	5
3.570	10+	3.59	vs	3.57	vs	3.579	9	3.621	9
3.053	1	3.07	w	3.06	w	3.042	1b	3.101	3
2.911	$\frac{1}{2}$	—	—	—	—	—	—	—	—
2.573	3B	2.54	m	2.538	m	2.537	1b	2.541	5
2.497									
2.433	7	2.416	vs	2.413	vs	2.418	10	2.425	10
2.392									
2.325	2	2.305	vw	—	—	—	—	2.335	4
2.233	$\frac{1}{2}$	—	—	—	—	2.263	$\frac{1}{2}$ -1b	—	—
2.125	1B	2.100	m	2.095	w	2.069	1vb	2.095	4
2.065									
1.978	$\frac{1}{2}$	—	—	—	—	—	—	1.980	5
1.937	2B	1.922	m	1.918	m	1.902	2-3vb	1.920	5
1.897									
1.814	2	—	—	—	—	—	—	—	—
1.789	3	1.797	m	1.795	m	1.795	1	—	—
1.683	3B	1.676	w	1.672	vw	1.675	2i	1.671	5
1.648									
1.614	$\frac{1}{2}$	1.618	w	1.610	vw	1.616	2b	—	—
1.485	5	1.489	s	1.486	s	1.486	8	1.480	9
1.459	1	1.466	w	1.462	w	1.455	4b	1.450	3
1.432	$\frac{1}{2}$	—	—	—	—	1.434	$\frac{1}{2}$ -1	—	—
1.316	$\frac{1}{2}$	—	—	—	—	1.314	$\frac{1}{2}$	1.318	1
1.283	$\frac{1}{2}$	1.282	vw	—	—	1.284	1	1.273	4
1.264	$\frac{1}{2}$	1.270	w	1.272	w	1.263	3	—	—
1.226	$\frac{1}{2}$	—	—	—	—	1.230	2vb	1.230	2
						1.208	$\frac{1}{2}$ -1	1.209	5

Some additional lines which may arise from impurities:

4.24	quartz lines	—	—	—	—	3.928	2	—	—
3.336		3.38	w	3.38	w	3.442	1b	3.371	4
2.452		1.740	vw	—	—	1.744	$\frac{1}{2}$ -1	—	—
2.278		—	—	—	—	1.583	1	—	—
2.123		1.372	m	1.366	w	1.358	1-2	1.368	4
1.538		—	—	—	—	—	—	—	—
1.379	—	—	—	—	—	—	—	—	
1.285	—	—	—	—	—	—	—	—	

b = broad, vb = very broad, B = band, i = indistinct.

1. Present data. Nacrite from Hirvivaara, Finland. Filtered Ni- and Co- $K\alpha$  radiations; camera radius 10.0 cm. Spacings in kX.

2 and 3. Data by Nagelschmidt (1934). Nacrite from Freiberg, Saxony (2), and Kunnerstein, Augustusburg, Saxony (3). Filtered Cu- $K\alpha$  radiation; camera radius 2.88 cm. Spacings apparently in Å.

4. Data by Gruner (1933). Nacrite from Brand, Saxony. Unfiltered Fe- $K\alpha$  radiation; camera radius 5.73 cm. Spacings in Å.

5. Data by Ross and Kerr (1931). Nacrite from Brand, Saxony, and Pikes Peak, Colorado. Filtered Mo- $K\alpha$  radiation. Spacings in Å.

(600) and this gives  $a = 8.91$ . Assuming the following lines to be basal 00 $l$  reflections, the layer spacings given in parentheses are obtained: 7.16 (7.16); 3.570 (7.140); 2.392 (7.176); 1.789 (7.156); 1.432 (7.160). The mean layer-spacing is 7.158 kX. Since  $\beta$  is so near to  $90^\circ$ , the  $c$  parameter within the limits of experimental error is 7.16 kX. The  $b$  parameter is difficult to obtain accurately, but as in other similar layer minerals, it is probably closely equal to  $a/\sqrt{3} = 5.14$ , and this agrees exactly with the value obtained from the  $b$ -axis rotation diagram.

*Summary of X-ray results.*—Single-crystal and powder analyses prove conclusively that the kaolin mineral from Hirvivaara, Finland, is nacrite; the six-layer structure discovered by Hendricks is confirmed. The powder diagram is resolved in somewhat greater detail than has previously been recorded. The lattice parameters are  $a$  8.91,  $b$  5.14,  $c$  7.16 kX. Hendrick's value for  $\beta$  has not been modified.

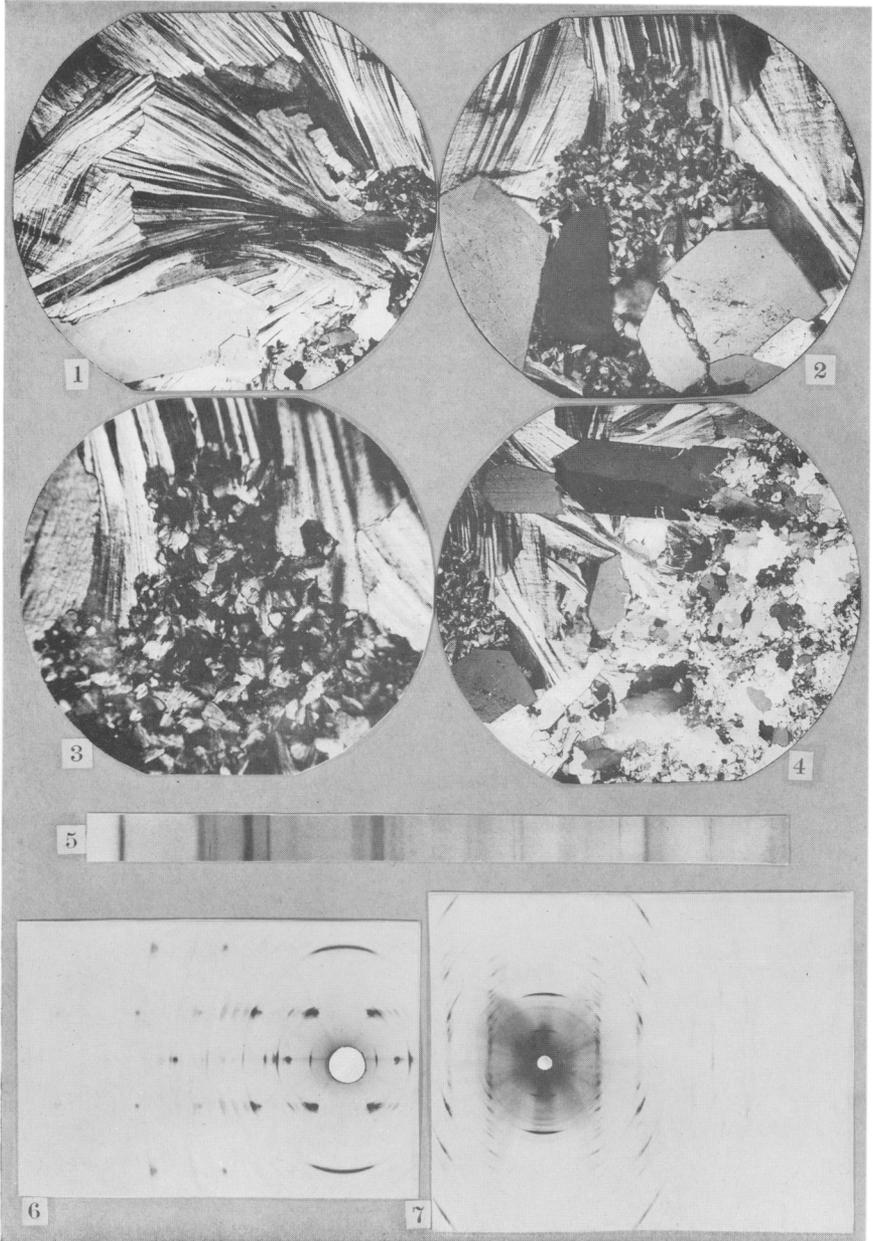
*Acknowledgement.*—One of us (K.H.) is indebted to the Durham Co. Education Committee for the award of a post-graduate scholarship.

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#### EXPLANATION OF PLATE XXVIII.

Photomicrographs and X-ray photographs of nacrite from Hirvivaara, Finland.

- FIG. 1. Bunch-like masses of nacrite and quartz crystals from a cavity in kyanite-quartzite. Crossed nicols.  $\times 17$ .  
FIG. 2. Kaolinite enclosed by nacrite and quartz. Crossed nicols.  $\times 27$ .  
FIG. 3. Kaolinite 'replacing' nacrite. Crossed nicols.  $\times 54$ .  
FIG. 4. Contact between the minerals in the cavity and the surrounding quartzite. Crossed nicols.  $\times 17$ .  
FIG. 5. X-ray powder photograph.  
FIG. 6. X-ray rotation photograph about the  $b$ -axis (vertical on the page).  
FIG. 7. X-ray rotation photograph about the  $c$ -axis (horizontal on the page).
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O. VON KNORRING, G. W. BRINDLEY, AND K. HUNTER: PHOTOMICROGRAPHS AND X-RAY PHOTOGRAPHS OF NACRITE FROM FINLAND.