

*Dickite and collophane in the Magnesian Limestone
of Durham.*

(With Plate XX.)

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With a chemical analysis by C. O. HARVEY, B.Sc.¹

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IN the course of examining the cores of a boring for water at Hesleden Dene, near Castle Eden, Co. Durham (no. 2 borehole), Mr. A. Fowler noticed a cream-coloured flaky mineral of talcose aspect coating joints in the Magnesian Limestone (Permian), at depths below surface of 246 to 250 feet. The rock at these depths is an impure dolomite mudstone (Geological Survey Slice, no. E. 21304) resembling the Marl Slate, and carrying ostracods, foraminifera, and sponge spicules. Investigation of the coatings in specimens sent in by Mr. Fowler and by Mr. W. Anderson has shown that the flaky mineral is dickite, and that it is associated with fluorite, baryte, galena, zinc-blende, pyrite, and collophane. Dr. J. Phemister had previously concluded on optical evidence that dickite might be present among the minerals of metalliferous affinities discovered in the Magnesium Limestone by Mr. Fowler.²

The coating, scraped from the joint surfaces, was centrifuged in a bromoform-benzene mixture of specific gravity 2.75. The light crop carried the flaky mineral, with a little dolomite which was removed by treatment overnight with cold N/10 hydrochloric acid. The heavy crop was centrifuged in bromoform of specific gravity 2.89, a light fraction consisting of dolomite and a heavy fraction with colourless or faintly purple cubes of fluorite averaging about 0.1 mm., yellow zinc-blende, and euhedra of galena and baryte being obtained.

DICKITE.

The dickite occurs as plates up to 0.5 mm. diameter, some of which show well-marked hexagonal outlines. These are aggregated into sheaf-

¹ By permission of the Director of H.M. Geological Survey.

² A. Fowler, *Geol. Mag.*, 1943, vol. 80, p. 44. [M.A. 9-258.]

like or radial clusters, and it was not found possible to isolate a single sheet. Interference-figures obtained were thus poor, but a high optic axial angle was indicated, and the mineral is probably optically positive. Extinction angles with the strong basal cleavage up to 16° were observed. The maximum and minimum refractive indices, measured by the immersion method, are 1.566 and 1.560, respectively.

Some 0.6 gram of pure concentrate was obtained and on this Mr. C. O. Harvey carried out a semi-micro analysis with the following results (Geological Survey, Lab. no. 1472, 1947):

					Atoms on basis 9(O,OH)		
SiO ₂	45.4	1.99	Si,Al	... 2.00
Al ₂ O ₃	39.2	2.03	Al	... 2.02
Fe calculated as Fe ₂ O ₃	0.2	0.01	(OH)	... 3.91
MgO	0.3	0.02		
CaO	trace	—		
Na ₂ O	trace	—		
K ₂ O	0.2	0.01		
H ₂ O > 105° C.	13.4	3.91		
H ₂ O < 105° C.	0.4			
TiO ₂	nil			
P ₂ O ₅	nil			
MnO	nil			
CO ₂	trace			
F	n.d.			
Carbonaceous matter*	1.0			
100.1							

* Loss on ignition, other than H₂O.

This yields the formula (Si,Al)_{2.00}(Al)_{2.02}(OH)_{3.91}O_{5.09}, which may be compared with the ideal formula for the minerals of the kaolin group, Si₂Al₂(OH)₄O₅.

C. S. Ross and P. F. Kerr,¹ who established dickite as a species distinct from kaolinite, state that dickite most commonly occurs in association with metallic minerals; and recently Ross² has gone farther and suggested that where hydrothermal processes are clearly indicated, dickite forms rather than kaolinite. W. A. Tarr³ and V. T. Allen⁴ have accepted a hydrothermal origin for the mineral at localities far removed from proved igneous activity, while W. D. Keller⁵ accepts an origin from warm

¹ C. S. Ross and P. F. Kerr, Amer. Min., 1930, vol. 15, p. 34; Prof. Paper U.S. Geol. Surv., 1931, no. 165 E, p. 158. [M.A. 4-247, 5-359.]

² C. S. Ross, Journ. Amer. Ceramic Soc., 1945, vol. 28, p. 182.

³ W. A. Tarr, Econ. Geol., 1936, vol. 31, p. 749.

⁴ V. T. Allen, Amer. Min., 1936, vol. 21, p. 457. [M.A. 6-373.]

⁵ W. D. Keller, Amer. Min., 1947, vol. 32, p. 468.

solutions while doubting a necessary connexion with a magma. Dickite has, however, been recorded in a normal clay-ironstone of Coal Measure age,¹ and its presence, while suggestive, cannot be regarded as proving a hydrothermal origin for the metallic minerals in the Durham Permian.

An X-ray examination of the mineral was carried out in the Mineral Department of the British Museum of Natural History. A few flakes of the white mineral forming a thin veneer on magnesian limestone from Durham were powdered and a rotation photograph of the preparation taken. The powder pattern obtained (pl. XX, fig. 2) is identical in spacings and relative intensities with that of powdered dickite from Red Mountain, Colorado (fig. 3). A rotation photograph (fig. 1) of a single flake shows that it is polycrystalline with preferred orientation yielding enhanced low-order basal diffractions. The dickite from Durham does not, however, yield photographs with well-defined high-order lines as do powdered samples of well-crystallized dickite from Colorado and Anglesey. Minute hexagonal flakes from both latter localities yield single-crystal photographs and when powdered high-order lines are easily visible and resolved into $\alpha_1\alpha_2$ doublets. The rather poor optic pictures and relatively weak powder lines of the dickite from Durham are probably due to the extreme thinness of the individual flakes making up the oriented aggregates. This does not, however, prevent a satisfactory identification of the mineral. All the dickite photographs are clearly distinguished from those of kaolinite from Cornwall and nacrite from Saxony (figs. 4, 5). The reproductions of the X-ray photographs of these three minerals illustrate the diagnostic value of sharply defined powder patterns obtained with minute samples in a small-diameter camera.

COLLOPHANE.

One of the specimens from which dickite was obtained was found to have in it a concretion or filled gash carrying an intergrowth of zinc-blende with a brown phosphate mineral which in thin section (E. 22285) appeared mainly isotropic but passing into small birefringent areas. Immersed in oils, some birefringent grains yielded an apparently positive biaxial interference-figure with $2V$ approximately 20° , and refractive indices α 1.608, γ 1.614. Brown patches resembling glue and, therefore, entirely characteristic of collophane are adjacent on the hand-specimen to a golden-brown transparent variety, specific gravity 3.00, also showing marked anisotropism.

¹ P. G. H. Boswell, *Mineralogy of sedimentary rocks*. London, 1933, p. 115.

X-ray photographs, with filtered copper radiation, of fragments of the glue-like and transparent collophane (pl. XX, fig. 6) were taken. Both photographs proved to be powder patterns identical with each other and closely resembling that of powdered apatite (var. asparagus-stone) from Murcia, Spain (fig. 7). A fragment of the anisotropic transparent 'collophane' was then oriented with the negative extinction direction normal to the incident X-ray beam. The fragment was not rotated during exposure so that the optimum conditions existed for the determination of a 'fibre axis' in the fragment. The powder photograph obtained revealed no preferred orientation and the powder lines are smooth and sharp. Hence typical collophane and also the transparent variety from Durham are identical and belong to the apatite family. Moreover, the average size of the crystallites must lie between 0.5 and 5 μ . It is interesting to record that during the X-ray exposures the brown transparent fragments of 'collophane' lose their transparency and become glue-like. This is possibly due to the removal of moisture locked between the minute crystallites by the heating of the fragments when exposed to X-rays. When the fragments are immersed in water or a refractive index oil they become transparent again and also birefringent.

We have not succeeded in finding any completely satisfactory explanation of the positive anisotropy of the collophane. Although J. D. H. Donnay¹ has applied with success O. Wiener's² theory of form-birefringence to vaterite, chalcedony, and nemalite, it is difficult by this theory to reconcile the low water-content³ of collophane with its optical sign. Strain-birefringence may account, however, quite satisfactorily for anomalous birefringence, and the low value of refractive index of collophane, as for all fine-grained aggregates, must then be attributed to porosity.

No accurate chemical analysis of collophane from Durham has been carried out, but fragments of the Durham mineral when treated with dilute hydrochloric or nitric acids effervesce quietly and continuously until solution is complete, thus showing that this collophane is a carbonate-apatite. It is indeed probable that the composition of the Durham mineral is similar to that of collophane from other localities and is essentially fine-grained francolite.

¹ J. D. H. Donnay, *Ann. (Bull.) Soc. Géol. Belgique*, 1936, vol. 59, pp. B 215, B 289 [M.A. 6-460]; *Univ. Toronto Studies, Geol. Ser.*, 1945, no. 49, p. 5 [M.A. 10-160].

² O. Wiener, *Abh. math.-phys. Kl. sächs. Gesell. Wiss.*, 1912, vol. 32, p. 507.

³ $H_2O < 105^\circ C$. 1.0 %, $H_2O > 105^\circ C$. 1.1 %, determined by C. O. Harvey.

This would agree with C. Frondel's conclusions, which were based upon collophane specimens from many localities.¹ Frondel rightly identified collophane with a member of the apatite series by means of X-ray powder photographs and concluded that most collophanes, so far studied by modern techniques, are undoubtedly finely crystalline francolites containing varying amounts of adsorbed water and, therefore, exhibiting variable specific gravities and refractive indices. In his opinion and ours, F. Sandberger's original analysis² corresponds to a carbonate-hydroxyl-apatite (dahllite). Sandberger wrongly deduced the CO₂ content and may have overlooked a probable fluorine content.

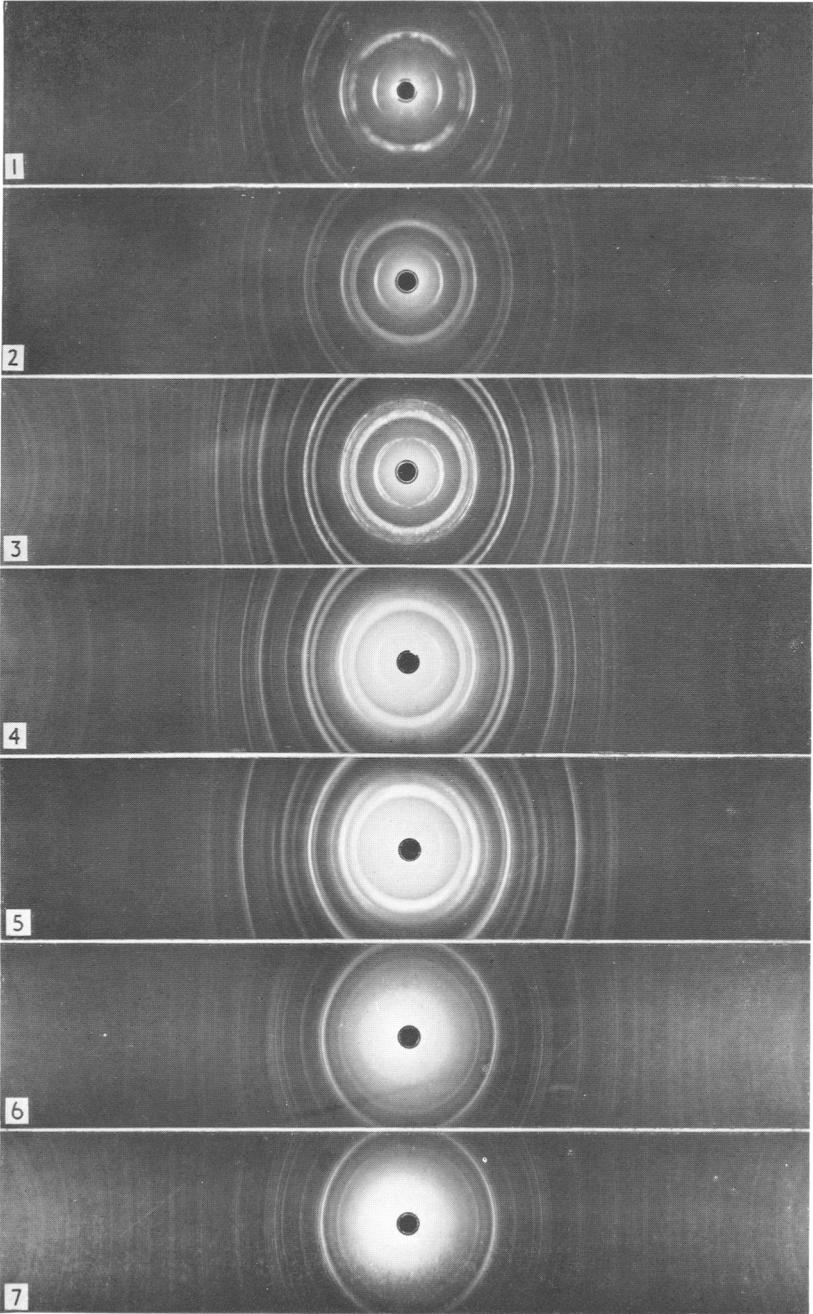
EXPLANATION OF PLATE XX.

X-ray diffraction photographs taken in a 6 cm. diameter camera with filtered copper radiation. A length of 14.72 cm. on the original films is equivalent to 10 cm. on the reproduced figures.

- FIG. 1. Flake aggregate of dickite from a core in the Magnesian Limestone, Hesledene Dene, Co. Durham, rotating about a direction in the plane of the flake. Geol. Survey, E. 21304.
- FIG. 2. Powdered flake aggregates of dickite from a core in the Magnesian Limestone, Hesledene Dene, Co. Durham. Geol. Survey, E. 21304.
- FIG. 3. Powdered crystals of dickite from Red Mountain, San Juan Co., Colorado. B.M. 1923, 393.
- FIG. 4. Kaolinite from Cornwall; portion of a washed sample of china-clay studied by G. W. Brindley and K. Robinson, *Min. Mag.*, 1946, vol. 27, p. 244, no. 1 of table I.
- FIG. 5. Powdered stellate aggregates of nacrite from Freiberg, Saxony. B.M. 31086.
- FIG. 6. Fragment of anisotropic collophane from a core in the Magnesian Limestone, Hesledene Dene, Co. Durham. Geol. Survey, E. 22285.
- FIG. 7. Powdered crystals of fluor-apatite from Jumilla, Murcia, Spain. B.M. 60729.

¹ C. Frondel, *Amer. Min.*, 1943, vol. 28, p. 215. [M.A. 9-33.]

² F. Sandberger, *Neues Jahrb. Min.*, 1870, p. 308.



K. C. DUNHAM, G. F. CLARINGBULL, AND F. A. BANNISTER: X-RAY PHOTOGRAPHS OF DICKITE AND COLLOPHANE.