

Collophane from the chalk.

(With Plate XII.)

By GEORGE BROWN, B.Sc., and C. D. OLLIER, M.Sc., F.G.S.
 Pedology Department, Rothamsted Experimental Station, Harpenden.

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Summary.—Sixteen samples of Middle and Upper Chalk from the Chilterns yielded what appear to be fragments of fish scales, spines, and bones, which consist of collophane. X-ray examination by the powder method shows that the material has an apatite-type structure with cell dimensions close to those previously reported for francolite. Examination of single grains shows that the optical anisotropy is due to preferred orientation of the *c*-axes of the crystallites and this direction corresponds to the faster vibration direction. Such grains are found to be pseudo-uniaxial negative. Preferred orientation could not be detected in isotropic grains.

IN the course of an investigation of the soils of the Chiltern plateau it was necessary to examine the non-carbonate residue of the Upper Chalk, and a sample was taken from the upper pit on Whiteleaf Hill near Princes Risborough. Dissolution of the chalk was carried out with an ammonium acetate solution buffered at pH 3 in order to minimize alteration of the clay minerals. On microscopic examination it was found that collophane made up over 50 % of the sand fraction ($> 60 \mu$), and X-ray patterns show an apatite-like mineral to be present in the clay ($< 2 \mu$) and silt (2–60 μ) fractions.

As collophane is soluble in hydrochloric acid, chalk residues obtained by its use (for example by Double, 1927) do not contain collophane. The use of ammonium acetate at pH 3 to dissolve carbonate instead of the more usual hydrochloric acid treatment may eventually show that collophane is more abundant in limestones generally than has usually been supposed.

General appearance.

The grains show considerable variation in general appearance. The majority are thin platy grains up to 1 mm. in diameter and 0.1 mm. thick, and are usually slightly curved. Many are irregular in outline but others are tabular, lath-shaped, or approximate to rods and tubes. In air the grains may be white and opaque, brown and transparent, or

milky white and translucent. Thin plates tend to be translucent, the rods and tubes brown and transparent, and only the largest, thick grains are opaque. In immersion liquids many grains appear opaque at first but oil gradually diffuses into cracks and channels and after several minutes all grains become transparent and light brown in colour (see pl. XII, figs. 4, 5, 6, and 7). The thin platy grains appear from surface ornament and internal structure to be fragments of fish scales, and one flake (pl. XII, fig. 3) is an almost perfect ctenoid fish scale. The rods and tubes are apparently fragments of small fish spines, and some large irregular grains are possibly fragments of fish bones. A small number of fish teeth and vertebrae found in some of the samples referred to later also consist of collophane. Cretaceous fish scales kindly given to us for comparison by the Geology Department, University of Bristol, proved to be collophane. Several invertebrate fossils from the chalk samples have been examined and none of these consisted of collophane.

Optical examination.

There is considerable variation in the optical properties of the grains, which reflects the degree of ordering of the crystallites in the grains. Some are completely isotropic, some are mainly isotropic but contain irregular birefringent patches, and others, from their optical properties, would appear to approach single crystals. The refractive index of the majority of the grains is 1.61 but the total range of variation is from 1.60 to 1.62, and the birefringence is always less than 0.005. In lath-shaped grains the mineral has a somewhat fibrous appearance, length fast, and with straight though usually shadowy extinction. When the flaky grains are lying flat an interference figure is obtained that is similar to the flash figure obtained on sections parallel to the optic axis of uniaxial minerals. When the grains are set on end the interference figure is very nearly uniaxial negative, but a very slight parting of the isogyres shows that it is biaxial with a very small $2V$. In the literature collophane has been reported as biaxial negative (Ellis and Claringbull, 1951) and biaxial positive with a $2V$ of 20° (Dunham, Claringbull, and Bannister, 1948). Our optical results are not anomalous but are those to be expected from the arrangement of apatite crystallites in the grains as determined by X-rays. There is no need in this case to invoke form-birefringence or strain-birefringence, as was found necessary by Dunham, Claringbull, and Bannister (1948).

X-ray examination.

Powders. From the sand fraction grains of collophane mainly of the large opaque variety were separated by hand-picking and gently crushed. The resultant powder was mounted on a glass fibre and an X-ray pattern was obtained in a 9.0-cm. diameter camera with filtered Co-K α radiation. The specimen, which was 0.2 mm. diameter, was rotated during the exposure. The pattern closely resembled that of apatite. All the reflections are slightly broadened, probably due to small crystallite size.

Fron del (1943) and Dunham, Claringbull, and Bannister (1948) have concluded that most collophanes are finely crystalline francolites.

There is still some controversy on the nature of the carbonate in carbonate apatites (see McConnell, 1954) but the evidence of Thewlis, Glock, and Murray (1939) suggests that carbonate apatites have cell constants $a = 9.32 \text{ \AA.}$, $c = 6.87 \text{ \AA.}$, fluorapatites $a = 9.36 \text{ \AA.}$, $c = 6.87 \text{ \AA.}$, and hydroxyapatites $a = 9.41 \text{ \AA.}$, $c = 6.87 \text{ \AA.}$ Altschuler, Cisney, and Barlow (1953) have published cell constants which differ in detail but show the same relationships to each other.

The pattern of collophane from the Chalk treated with ammonium acetate solution at pH 3 can be completely indexed on the basis of an apatite unit cell. The best agreement between calculated and observed spacings is given by a cell with $a = 9.32 \pm 0.02 \text{ \AA.}$ and $c = 6.87 \pm 0.02 \text{ \AA.}$ Thus the material has an apatite structure and the cell constants appear to be close to those of carbonate apatites although much of the carbonate may have been removed by pre-treatment before examination.

Single grains. One optically isotropic grain and several anisotropic grains were examined for preferred orientation. All the grains tested were either flakes or tabular grains. The isotropic flake was mounted with the plane of the flake vertical, i.e. parallel to the rotation axis of the goniometer, and irradiated with the X-ray beam first normal to the flake and then parallel to the flake. The grain was kept stationary for each exposure, and the patterns were recorded on a cylindrical film. The photographs of the grain in the two orientations were identical; complete rings were obtained in both and the relative intensities of the reflections, which were the same as those obtained for the unoriented powder, did not vary round the rings. Anisotropic grains were mounted with the faster vibration direction normal to the axis of rotation, i.e. horizontal, and irradiated (i) with the X-ray beam normal to the faster vibration direction, and (ii) with the X-ray beam along the faster

vibration direction. Figs. 1 and 2 are a typical pair of photographs. Several weak reflections are visible on the original negatives which are not shown on the reproductions. With the grains in orientation (i) $000l$ arcs, and arcs for reflections from planes nearly parallel to (0001) appear on the equator and $h0\bar{h}0$ and $hki0$ arcs appear on the meridian.

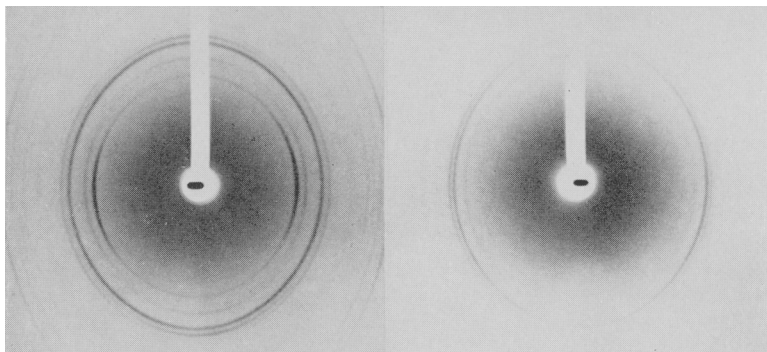


FIG. 1.

FIG. 2.

FIGS. 1 and 2. X-ray photographs with stationary grains. 6 cm.-diameter camera, Cu- $K\alpha$ radiation. FIG. 1. Single grain with faster vibration direction horizontal and normal to the X-ray beam. FIG. 2. Single grain with faster vibration direction horizontal and parallel to the X-ray beam.

In orientation (ii) complete rings are obtained for each reflection but their relative intensities differ from those for a random powder— $000l$ reflections, for example, are much weaker. These effects show that the faster vibration direction is the preferred direction of the c -axes of the crystallites and that no marked preferred orientation exists about the c -axes direction.

Other occurrences.

After the detailed work reported above on the sample from Whiteleaf Hill, fifteen further specimens from the Upper and Middle Chalk of the Chilterns, from Princes Risborough to Hitchin, were examined. Collophane identical in appearance and optical properties with that from Whiteleaf Hill was found in all the insoluble sand fractions, although generally in smaller amounts than in the original sample.

Many descriptions of the Phosphatic Chalk are available and are summarized by Willcox (1953), who has reported collophane (*op. cit.*, p. 125). We believe, however, that the present paper contains the first minera-

logical description of collophane from normal chalk. Ellis and Claringbull (1951) have described collophane from Thames gravels and had difficulty in finding its source. Although the properties they determined differ in some respects from those given here, the Chalk must be considered a possible source.

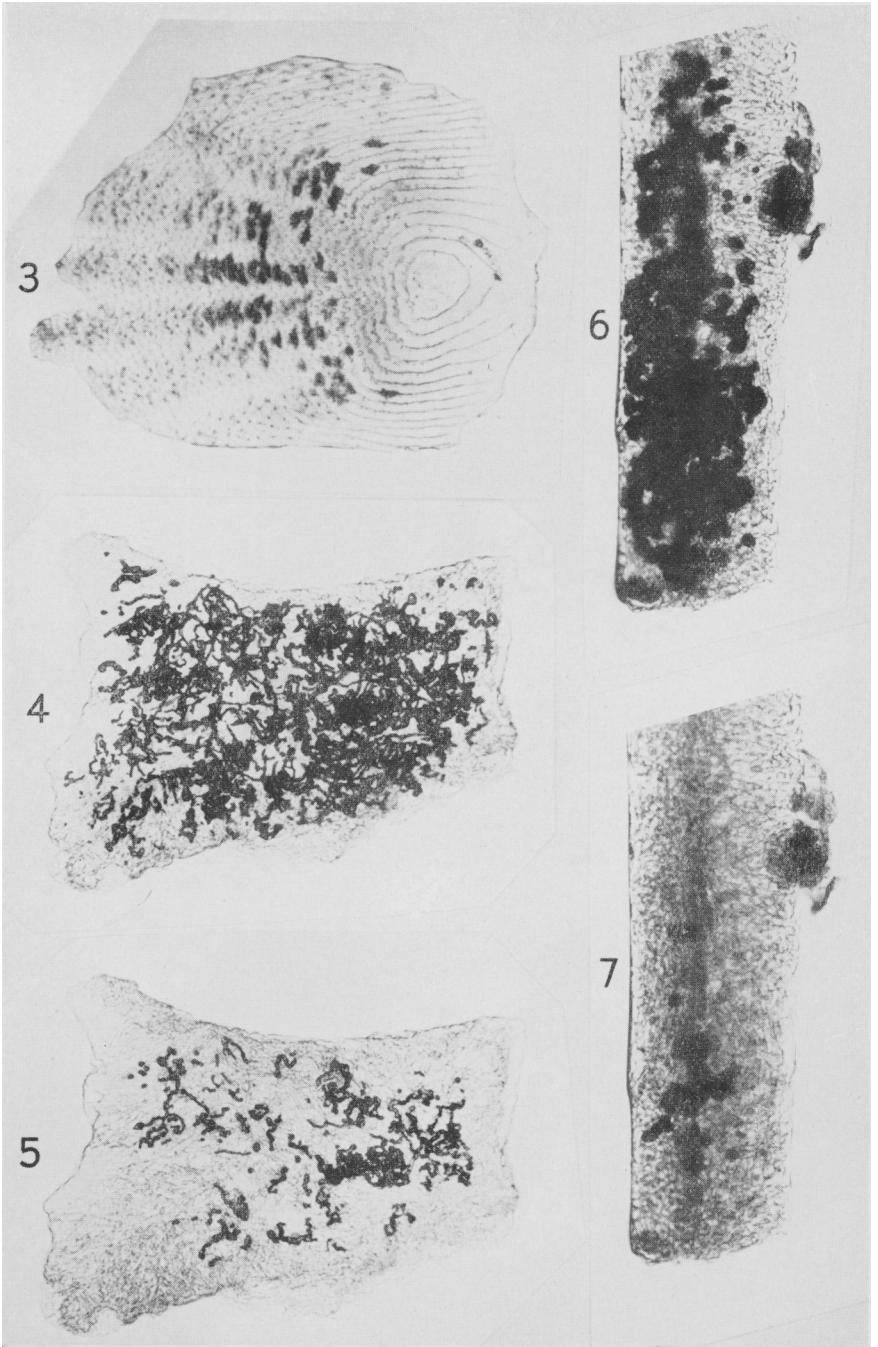
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EXPLANATION OF PLATE XII.

- FIG. 3. Collophane fish scale in xylol. $\times 35$.
FIG. 4. Collophane flake in immersion oil of refractive index 1.54, one minute after immersion. $\times 350$.
FIG. 5. As fig. 4, five minutes after immersion. $\times 350$.
FIG. 6. Collophane rod in immersion oil of refractive index 1.54, one minute after immersion. $\times 350$.
FIG. 7. As fig. 6, ten minutes after immersion. $\times 350$.

Photographs by V. Stansfield.



GEORGE BROWN AND C. D. OLLIER: COLLOPHANE