On collophane in Thames gravel.

(With Plate XVII.)

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IN mid-1949 the London Natural History Society set up a committee to investigate and record temporary geological sections in the London area. Among the earliest to be dealt with was the excavation in flood-plain gravel for the foundations of the Concert Hall for the Festival of Britain (1951).[1] Samples of 100–200 grams were taken from two sand-lenticles for heavy mineral investigation, and material from one of these, passing 60 mesh and washed by laevigation, yielded, on separation by means of a bromoform-benzene mixture of density about 2·73, an assemblage with abundant garnet, tourmaline, zircon, and kyanite, very occasional staurolite, cassiterite, and fluorite, and moderately abundant collophane. The last-named has subsequently been found as isolated grains in the heavy or semi-heavy residues from other sand samples (including the second sample from the Concert Hall site) from the City and Westminster area. In only one other case, a sand from gravel of the same age in Bridewell Place, on the opposite bank and about half a mile down the river, has it been found in comparable abundance.

The material is extremely variable in character. It is of resinous appearance; the prevailing colour is cinnamon-brown, but it ranges to brownish-green and from deep to pale coloured. The brown colour tends to be associated with transparency and the green with opacity; some of the green grains from the Concert Hall site are translucent only on the edges. There are many inclusions, generally of deeper colour than the body of the grain and often opaque (pl. XVII, fig. 3). They may be of irregular form; some are linear, with curving branches radiating from a main axis, and seem to be due to the deposition of darker material in shrinkage cracks (fig. 2). Some semi-opaque grains show broad shrinkage

[1] B. Ainsley and S. E. Ellis, The London Naturalist, 1950, no. 29 for 1949, pp. 39, 42.

cracks filled with lighter coloured and more translucent material (fig. 3). Minute spherical or ovoidal inclusions, of darker colour and higher refractive index than the body of the grain, are common in the cinnamon-brown material. Spherulitic or pseudo-spherulitic structures (fig. 4), and a layered structure which gives rise to a tabular habit are also seen. The present boundaries of the grains cut across all such structures, so that they must have been produced by the breaking up of more massive material. Most of the grains are rounded, and such angular fragments as are found are probably (often obviously) due to the recent fracture of rounded grains. In the Bridewell Place heavy residue, colourless to very pale blue material of similar refractive index (in this case near that of crystalline apatite) is seen, which shows the relatively large Haversian canals and lacunae of mammalian bone; such material is always in unworn fragments and contrasts sharply with the rounded grains of brown or green collophane. All the forms seen (excepting the spherulitic or pseudo-spherulitic) may be either isotropic or birefringent. The latter gives vague, apparently biaxial interference figures, on one of which a negative sign was obtained. Birefringence varies from nil to about 0·005. Extinction is often irregular, but in many elongated grains it is sharp and parallel to the elongation (which is negative). Such grains are often curved and occasionally branched, the extinction direction being tangential. A submicroscopic fibrous structure is presumed from this and from the X-ray data given below.

The refractive index is extremely variable. Twenty grains were picked out of the residue from the Concert Hall site, and their range of refractive indices determined by immersion in eugenol-cinnamic aldehyde mixtures, which were measured on a Bellingham-Stanley refractometer. Nineteen grains gave values ranging 1·614–1·626 (Na-light at about 20° C.), and one (indistinguishable in general character from the others) gave a value of 1·583. Five grains from the Bridewell Place residue gave a range 1·622–1·638, while a single grain was as low as 1·585. The maximum refactive index observed is within the range of crystalline apatite and above the maximum (1·63) found by Rogers[1] for 250 determinations on fossil bone. In most cases there are perceptible variations in refractive index within the grains.

Density is also variable; of the Concert Hall material, a dozen grains (determined by suspension in methylene iodide-benzene mixtures) gave values ranging 2·78–2·90. There is no close relationship between density and refractive index; the grain of maximum refractive index (1·626)

[1] A. F. Rogers, Bull. Geol. Soc. Amer. 1924, vol. 35, pp. 535–556.

from the Concert Hall site had a density near the minimum, and that of 1·583 lay near the middle of the density range.

That the grains are minutely porous is indicated by their opacity in air (hand-picking had to be done under xylol) and by the fact that when mounted in canada balsam they are at first opaque and only become transparent or translucent after some hours. They dissolve with extreme slowness in acids (hydrochloric or nitric) with the evolution of gas bubbles, from which it is presumed that carbonate is present. The quantity of material available did not permit of a chemical test, but its identity was proved by a composite X-ray powder photograph of six grains (X4791) which indicated a fluor-apatite structure and was identical with photographs of the collophane described by Dunham, Claringbull, and Bannister[1] from the Magnesian Limestone of Durham, of the apatite (var. asparagus-stone) from Murcia, Spain, with which it was compared, and of an Iguanodon bone and shark's tooth referred to below. A single elongated grain, rotated about its long axis, gave a photograph (X4787, pl. XVII, fig. 5) indicating aggregate orientation parallel to the *c*-axis. A specimen of enamel from a mammoth tooth (referred to below) which shows a parallel fibrous structure, gave an identical photograph X5081,) fig. 6) when rotated about the axis of elongation of the fibres.

The detrital collophane was compared with a variety of forms, both of organic and inorganic origin, in the hope of throwing light on its source. Much of the material resembles in appearance (excepting in the rounded form of the grains) that produced by powdering portions of a phosphatic nodule from the Gault clay at Sevenoaks, Kent. The latter has a similar range of densities (2·78–2·94) but a much lower refractive index (mean 1·6055). Reptilian bones yielded fragments similar to the grains giving extinction parallel to length. Among these, two turtle plates from the Purbeck Beds of Durlstone Bay, Dorset, have mean refractive indices (1·614 and 1·615 respectively) falling within the range of the material from the Concert Hall site, while Iguanodon bone from the Smokejacks brick pit, Ockley, Surrey, shows a lower range (1·601–1·611). These, however, are all distinctly heavier than the detrital material (density ranging up to 3·02). Some grains show a resemblance to fragments of shark's teeth, but here again there is no correspondence in refractive index and in specific gravity; dentine from the roots of two teeth of *Odontaspis macrota* (London Clay, Harefield) has a mean refractive index of 1·610 (range 1·608–1·612) and specific gravities

[1] K. C. Dunham, G. F. Claringbull, and F. A. Bannister, Min. Mag. 1942, vol. 28, pp. 338–343 and pl. xx, figs. 6 and 7.

ranging 2·90–3·01 and 2·96–2·99. Mammalian bones and teeth have yielded no comparable material. None of Rogers's numerous figures of thin sections of collophane shows a close likeness to the detrital material.

The failure to discover comparable material of the same refractive index does not necessarily show that the detrital collophane could not have been derived from the material it most resembles (phosphatic nodules and reptilian remains of Mesozoic age). A number of refractive index determinations on different forms of fossil bone and nodular phosphate indicate great variability, not only as between one species or occurrence and another, but within material from the same species, within a single bone or tooth and even within a single tissue of a tooth. For example, enamel from a mammoth tooth from the Doniford river gravels (late Pleistocene) of Watchet, Somerset, from which the X-ray photograph (X5081) already mentioned was taken, has a mean refractive index of 1·611 (1·606–1·616) and a specific gravity of 2·896 (solid material) at 20° C. Dentine from three different points in the same tooth has refractive index ranges of 1·583–1·586, 1·576–1·582, and 1·562–1·576 respectively, and the specific gravity does not rise above 2·60. A horn of *Bos primigenius* from the Upper Pleistocene at Gomshall, Surrey, also gave two refractive index ranges. The structure is minutely cellular and the bulk of the material is colourless with a refractive index range 1·575–1·591, but brown compact material forming cores to the cell-walls ranges 1·604–1·610. The same applies to the Gault phosphatic nodule, with a mean refractive index of 1·605, but with inclusions giving values 1·56–1·57. The existence of material of two distinct ranges has already been mentioned as characteristic of both detrital occurrences described.

Because the degree of variation is about the same, but the actual range different, in both major samples of detrital collophane, and because they are similar in other respects, the possibility has been considered that local conditions (physical and chemical) may give rise to variations in the refractive index, and in particular, that the presence of ultramicroscopic goethite in the pores may be responsible for the unusually high range of both samples, which occurred in a highly ferruginous environment. According to Rogers (loc. cit., p. 544), who admittedly bases his contention on no more than three analyses, the refractive index of fossil bones varies with the Fe_2O_3 content. It had already been observed that certain grains of collophane in the residue from the Concert Hall site, which survived digestion with hydrochloric acid (1 : 1), became very pale and suffered a reduction in the refractive index, in one case to below that of canada balsam. A few grains from the

Bridewell Place residue, with refractive indices ranging 1·622–1·634, were accordingly treated with a 10 % solution of sulphosalicylic acid, which dissolves ferric oxide readily yielding a coloured solution which can be used colorimetrically. The solution stained a filter paper faintly reddish-brown and the refractive index range of the grains was reduced to 1·605–1·615. This cannot, however, be regarded as proving that the high refractive index is due to goethite, since a specimen of mammoth dentine, which certainly contains no appreciable Fe_2O_3, had its refractive index reduced from about 1·57 to about 1·56 by the same treatment. It is, however, clear that the action of acids can lower the refractive index of collophane, though whether by the enlargement of the pores, by removal of material of high refractive index from within them, or by actual structural change is uncertain.

Since the refractive index of collophane is such a variable quantity, it can be presumed that the high values characteristic of the material described do not preclude its derivation from the phosphatic nodule beds of the Gault and from reptilian bones in the Gault and Weald Clay of the Wealden area.

In conclusion it should be mentioned that if the heavy mineral separations had been done with pure bromoform (density 2·90), instead of with a bromoform-benzene mixture of lower density, this detrital collophane would probably have passed unobserved. It is suggested, therefore, that all heavy mineral separations, at any rate of fluviatile sands, should be performed with a mixture of density of about 2·7–2·75, and that if this is done detrital collophane may prove to be much commoner than has hitherto been supposed.

Explanation of Plate XVII.

Figs. 1–4. Grains of detrital collophane from the Concert Hall site, south bank of the Thames west of Waterloo Bridge, London. Ordinary light, immersed in canada balsam. $\times 200$.

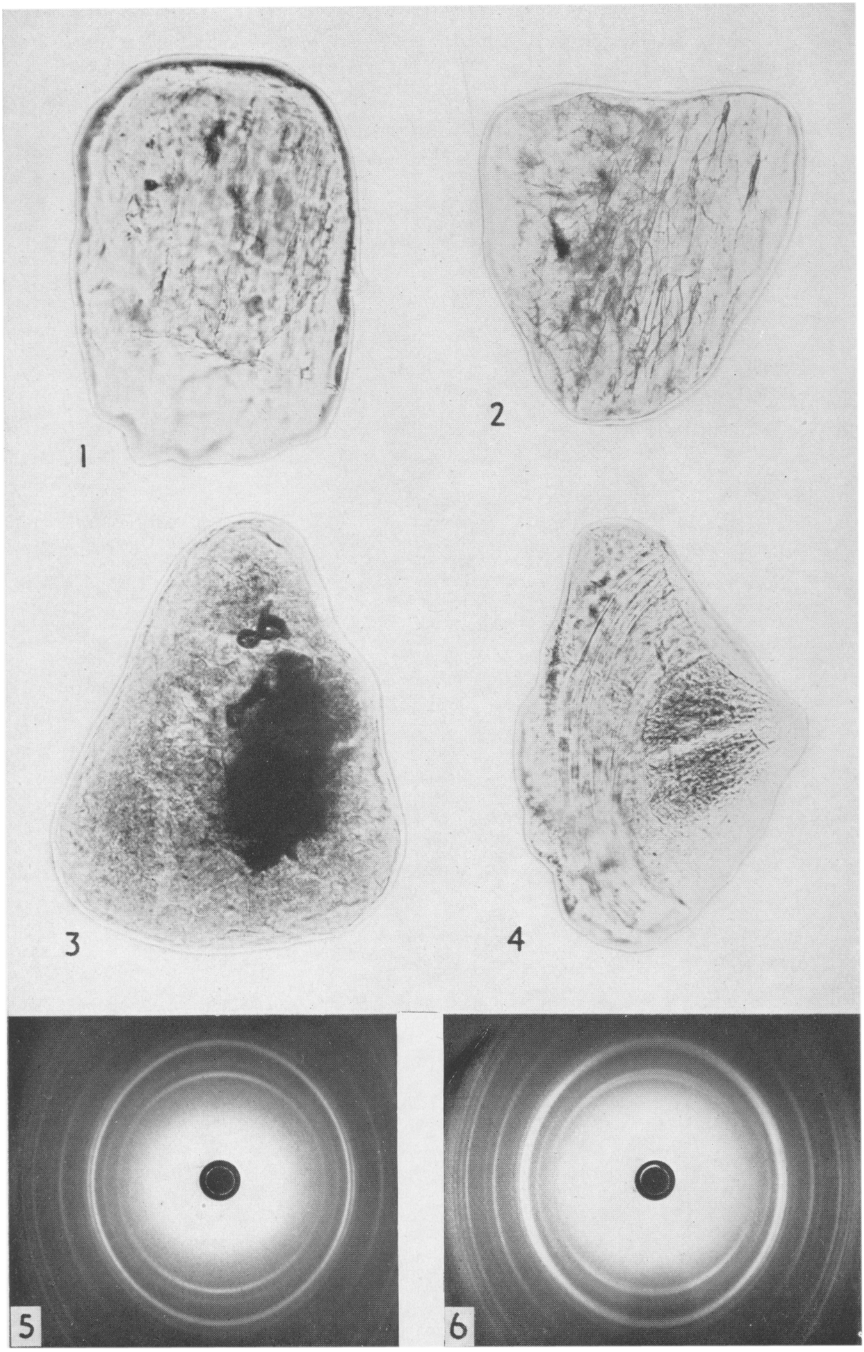
1–3. Refractive index about 1·62; the extinction direction in fig. 1 is parallel to the longest axis of the grain.

4. Refractive index about 1·54, after reduction by digestion in HCl.

Figs. 5, 6. X-ray rotation photographs; 6 cm.-diameter camera, Cu-$K\alpha$ radiation.

5. Single grain of collophane with rotation axis parallel to extinction direction.

6. Fragment of mammoth tooth enamel with rotation axis parallel to fibrous structure.



G. F. CLARINGBULL & S. E. ELLIS: COLLOPHANE