

## Short Communications

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### A study of clay minerals by electron-diffraction diagrams due to individual crystallites. By

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By means of recent electron microscopes, such as the three-stage electron microscope (le Poole, 1947; see also Haine, Page & Garfitt, 1950) and the shadow-microscope (Hillier & Baker, 1946), it is possible to observe a micrograph and a diffraction diagram from the same small object. This extends the structural study of substances consisting of submicroscopic crystallites by giving diffraction diagrams due to individual crystallites (Davidson & Hillier, 1946; Brown & Clark, 1952). The present authors have applied this method to the study of clay minerals. Preliminary results on kaolins from Hongkong, China, and from Spruce Pine, North Carolina, U.S.A., and chrysotile from Quebec, Canada, will be reported here.

Clay minerals of the kaolin group are known to be composed of silica-gibbsite layers (or kaolin layers),

$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$  ( $a = 5.14$ ,  $b = 8.93$  kX.), while chrysotile, a fibrous variety of serpentine, is composed of silica-brucite layers,  $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$  ( $a = 5.33$ ,  $b = 9.24$  kX.)\* (cf. Brindley, 1952). Hongkong and Spruce Pine kaolins have been considered to be (meta-)halloysite, the most poorly crystallized variety of the kaolin group. Elongated crystallites of the kaolins and the chrysotile observed under an electron microscope have been believed to possess a tubular form of rolled sheet crystal (Bates, Hildebrand & Swineford, 1950; Turkevich & Hillier, 1949; see also Davis, 1950).

\* Following Brindley, the parameters  $a$  and  $c$  for the structure of chrysotile, given by Warren & Hering (1941), are interchanged so as to harmonize the structure with that of kaolin.

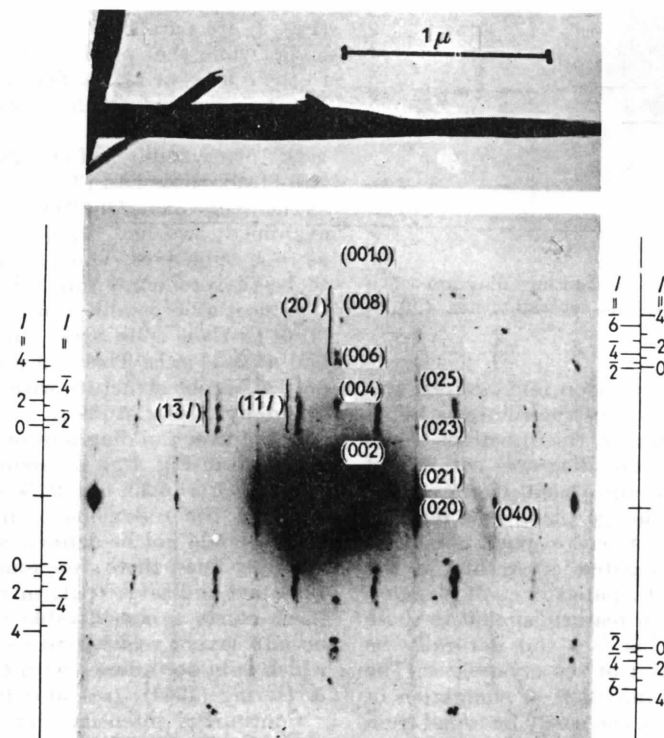


Fig. 1. Electron micrograph and diffraction diagram of a crystallite of Hongkong kaolin. The crystallite has a  $[0, 1]$  tube axis. The diagram was indexed by assuming a monoclinic unit cell with  $a = 5.14$ ,  $b = 8.93$ ,  $c = 14.7$  kX. and  $\beta = 104^\circ$ . The scale on the left of the diagram indicates the positions of the  $(h, 2k+1, l)$  reflexions along the layer lines and that on the right, the positions of  $(h, 2k, l)$  reflexions, where  $h \neq 0$ .

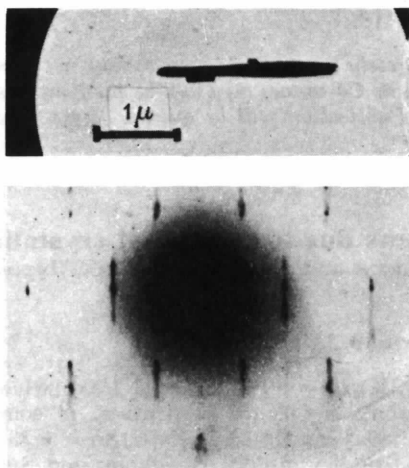


Fig. 2. Electron micrograph and diffraction diagram of a crystallite of Spruce Pine kaolin. The crystallite has a  $[0, 1]$  tube axis.

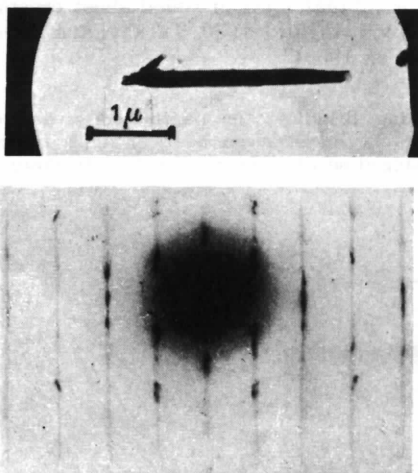


Fig. 3. Electron micrograph and diffraction diagram of a crystallite of Hongkong kaolin. The crystallite has a  $[1, 0]$  tube axis.

Figs. 1-4 reproduce pairs of electron micrographs and diffraction diagrams of crystallites of the minerals taken by le Poole's method.\* In each pair, the directions of the micrograph and the diffraction diagram correspond exactly to each other. For the diffraction diagrams, the aperture at the intermediate image plane was reduced to a limited area, so that only a central part, about  $1 \mu$  or less in length, of the elongated crystallite in the corresponding micrograph participated in each diagram.

The diffraction diagrams show features similar to those of rotating single crystals. This fact can naturally be understood by the tubular habit of the crystallites. The crystallographic index of the direction of elongation of the crystallites, or the tube-axis, can easily be found from the diffraction diagrams. The tube axes of the crystallites of Hongkong kaolin (Fig. 1) and Spruce Pine kaolin

\* The apparatus utilized is Type-4 E.M. of the Japan Electron Optics Laboratory Co., Ltd.

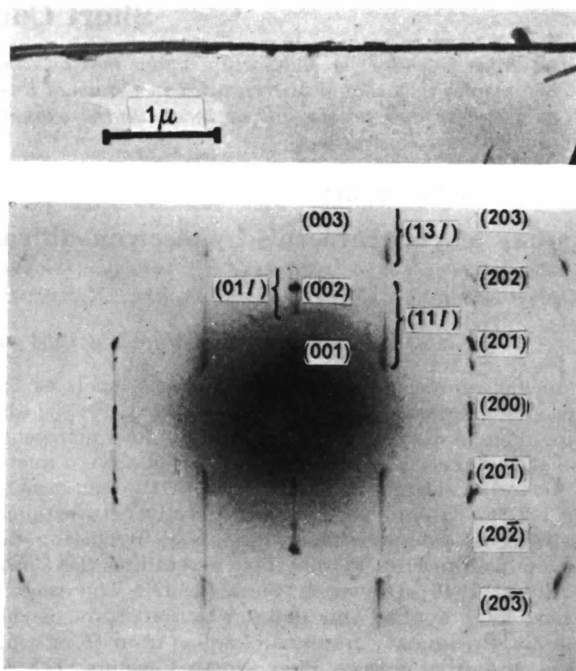


Fig. 4. Electron micrograph and diffraction diagram of a crystallite of chrysotile. The crystallite has a  $[1, 0]$  tube axis. The diagram was indexed by assuming a monoclinic unit cell with  $a = 5.33$ ,  $b = 9.24$ ,  $c = 7.33$  kX. and  $\beta = 93^\circ$ .

(Fig. 2) are parallel to the  $b$  axis, or  $[0, 1]$  of the kaolin layer, while that of Hongkong kaolin (Fig. 3) is parallel to the  $a$  axis, or  $[1, 0]$ . The tube axis of the chrysotile in Fig. 4 is parallel to the  $a$  axis, or  $[1, 0]$  of the silica-brucite layer.

Of 160 crystallites of Hongkong kaolin examined, eight had  $[1, 0]$ , three had  $[3, 1]$ , and the remainder had  $[0, 1]$  as their tube axes. Of 20 crystallites of Spruce Pine kaolin examined, two had  $[1, 0]$  and the remainder had  $[0, 1]$  as their tube axes. Thus, for tubular kaolin,  $[0, 1]$  seems to be the predominating tube axis.

Almost all crystallites of chrysotile were found to have  $[1, 0]$  as their tube axes, but one of 50 tubes examined had a  $[0, 1]$  axis. This fact seems to be of interest, since only a fibrous structure with a  $[1, 0]$  fibre axis has been found by X-ray studies.

The diffraction diagrams of chrysotile could be indexed as shown in Fig. 4(b), by assuming the known monoclinic unit cell ( $a = 5.33$ ,  $b = 9.24$ ,  $c = 7.33$  kX. and  $\beta = 93^\circ$ ). But, for the reflexions of non-vanishing  $k$  index, the  $l$  index could not be defined, since, along the corresponding layer lines, there were found only continuous streaks. This fact indicates that, in the structure of chrysotile, there exists a considerable displacement of the silica-brucite layers relative to each other along the  $b$  axis, which is in accordance with the X-ray study by Warren & Hering (1941); (see also Brindley, 1952).

Continuous intensity distributions along layer lines were also found, more or less, in the diffraction diagrams of Hongkong and Spruce Pine kaolins. But, for the kaolins, intensity peaks, which correspond to a well developed three-dimensional structure, were sometimes more predominant. The intensity peaks are due to a

structure having a period of about 14.4 kX. perpendicular to the kaolin layer, namely the stacking period of the layer (see Fig. 1(b)). Even when the continuous intensity distributions were considerable and the three-dimensional peaks were less defined, at least the existence of the (021) reflexion was always recognized.

This observation is of interest when contrasted with the current concepts of the kaolin group minerals as follows (Brindley, 1952; Davis, 1950). According to Bates's interpretation, the tubular habit is considered to be a criterion to identify a kaolin to the halloysite, which is characterized, according to X-ray studies, by such a poorly crystallized structure that it gives only a two-dimensional diffraction due to kaolin layers, except for (00 $l$ ) reflexions corresponding to the inter-layer spacing. The stacking period mentioned above, which is twice as long as that reported for the kaolinite-halloysite series of the group, is now accepted only for dickite, a highly crystallized variety of the group, though it was once assumed for kaolinite by Gruner.

The existence of the three-dimensional structure for Hongkong and Spruce Pine kaolins was confirmed also by high-resolution electron-diffraction diagrams taken by Hillier & Baker's method and by X-ray powder diagrams taken with monochromatic radiation. The results and a discussion on the structure will be reported shortly in this column.

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**A construction giving the projection of the point  $h00$  on to the  $0kl$  plane in reciprocal space, for non-orthogonal axes.** By E. W. RADOSLOVICH, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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In the course of a three-dimensional structure determination on a triclinic crystal one frequently wishes to find the projection of the point  $h00$  on the  $0kl$  plane in reciprocal space, in order to use the  $0kl$  reciprocal net as the  $hkl$  net. This point can be marked on the  $0kl$  net by calculating its displacement from the point  $000$  using well known formulae (Bunn, 1945). It is, however, interesting to note that there is a very simple geometrical construction which gives the same result, as can be shown trigonometrically.

For a net containing  $b^*$  and  $c^*$ , with angle  $\alpha^*$  between them the construction is as follows (see Fig. 1):

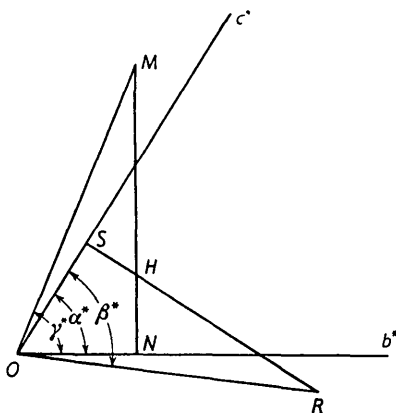


Fig. 1.

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(i) Draw  $OM$  at an angle  $\gamma^*$  to  $b^*$ ; make  $OM$  equal to  $ha^*$  in length, and draw  $MN$  normal to  $b^*$ .

(ii) Draw  $OR$  at an angle  $\beta^*$  to  $c^*$ ; make  $OR$  equal to  $ha^*$  in length, and draw  $RS$  normal to  $c^*$ .

Then the intersection,  $H$ , of  $MN$  and  $RS$  is the projection of  $h00$  on  $0kl$ . Usually one will put  $h = 10$ , say, and (having found the projection of  $10,0,0$ ) then divide the line  $OH$  into ten parts to give the projection of  $100, 200$ , etc.

The fact that this construction does give the correct projection can be appreciated as follows:

Imagine a cone constructed around  $b^*$  with apex  $O$ , vertical half-angle  $\gamma^*$ . Then  $a^*$  lies in the surface of this cone. Likewise  $a^*$  also lies in the surface of a cone constructed around  $c^*$ , apex  $O$ , vertical half-angle  $\beta^*$ . The two cones will in general intersect along two straight lines passing through  $O$ . These are both  $a^*$ ; they correspond to the two cases of right-handed or left-handed axes. The point  $h00$  lies at a distance  $ha^*$  from  $O$  along the intersection of the two cones; we require its projection on the plane of  $b^*$  and  $c^*$ . We obtain this projection by making the sloping sides of the cones of length  $ha^*$ , drawing the cones in projection on the plane of  $b^*$  and  $c^*$ , and noting the point  $H$  where the projections of their respective bases intersect.

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