

# THE STRUCTURE AND MORPHOLOGY OF A KAOLIN CLAY FROM LES EYZIES (FRANCE)<sup>1</sup>

*By*

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## ABSTRACT

It is shown by x-ray analysis and electron micrographs that the clay from Les Eyzies is composed of about equal amounts of platy material (kaolinite), and rolled or tubular material (halloysite). Detailed examination of the electron micrographs shows oriented tubes or rolled sheets which may have originated from well-aligned platy material which has fractured and subsequently curled into rolled forms. Hexagonal features on the surfaces of the rolled forms are described. The laboratory results are correlated with geological data on the formation of the clay.

## INTRODUCTION

X-ray and electron micrograph studies of the clay minerals kaolinite and halloysite have led to the conclusions that kaolinite has a platy morphology and a more or less well-ordered sequence of structural layers, whereas halloysite has a fibrous morphology with particles in the form of tubes or rolled sheets and a structure in which the layers are displaced in a largely random manner with respect to one another (Brindley, 1951). However, the general validity of these conclusions has recently been questioned. Although it is not difficult to visualize a platy mineral in which the structural layers are displaced in so random a manner that the resulting x-ray powder diagram is indistinguishable from that of halloysite, it is very difficult to see how a mineral with rolled sheets could give a diagram resembling that of kaolinite.

W. L. De Keyser and Deguedre (1954) reported that a kaolin clay from Les Eyzies, France, gave an x-ray diagram corresponding to a moderately well-organized kaolinite structure but which, in electron micrographs, appeared to consist of tubes. An independent investigation, not yet published, has arrived at similar conclusions for this same clay.

Through the kindness of Dr. W. Dekeyser of Ghent, Belgium, we have obtained a specimen of kaolin from Les Eyzies in order to study these anomalous results. Superficially our results confirm those previously published in that the dominant characteristics of the x-ray data suggest kaolinite, and the micrographs clearly show halloysite tubes. A closer examination of this material has therefore been made.

## X-RAY EXAMINATION

X-ray tests have been carried out with a Philips high-angle x-ray diffractometer using Cu *K* $\alpha$  radiation. Mixtures in various proportions have been made

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of a well-crystallized kaolinite from British Guiana and of a halloysite from Indiana, and their x-ray diagrams compared with that of the kaolin from Les Eyzies. Mixtures containing 40 percent kaolinite, 60 percent halloysite; and 50 percent kaolinite, 50 percent halloysite give almost exactly the same x-ray diagram as the material from Les Eyzies. Thus it appears that the latter contains about equal proportions of the two components, or a slight preponderance of halloysite.

Figure 1 shows the more significant parts of the x-ray diffractometer traces. Figures 1a and 1b show the diagrams of the British Guiana kaolinite and the Indiana halloysite. The relative heights of the 001, 020, and 002 peaks give the clearest indications. With halloysite the 020, or simply the 02, peak is higher than the 001 and 002 basal reflections. The reverse is always found for kaolinite, depending on the degree of preferential orientation, but the platy morphology of the mineral seems always sufficient to give enhanced basal reflections with normal methods of specimen preparation. The near equality of the 001, 002, and 020 reflections from the material from Les Eyzies (Fig. 1d) points to the presence of some halloysite along with kaolinite. Figure 1c shows the diagram for a 50/50 artificial mixture of kaolinite and halloysite which is practically indistinguishable from Figure 1d.

The reflections in the range  $2\theta=34^\circ$  to  $40^\circ$  are also important though their interpretation is less clear because the platy form of kaolin mineral with *b*-axis disorder, commonly found in fire clays, also shows a modified form of the kaolinite diagram in this region.

To obtain a more certain x-ray demonstration that halloysite is present in this clay, an attempt was made to expand the halloysite by treating the clay with ethylene glycol (MacEwan, 1946). The resulting diffractometer trace is shown in Figure 1e. The 001 peak at  $2\theta=12.5^\circ$  (i.e., the 7.2A spacing) is diminished to about half its original intensity, and a new broad peak is developed with a maximum at about 10.7A. This clearly demonstrates the presence of halloysite and confirms a mixture of kaolinite and halloysite in an approximately 1:1 ratio.

### ELECTRON MICROGRAPHS

Electron micrographs of dispersed fractions tend to show a predominance of halloysite tubes, which agrees therefore with the previous observations on this clay. With magnifications of 20,000  $\times$  or more, a considerable amount of fine platy material is visible. The largest plates are about 1 micron in size, but the average size is much less and may be about one-fourth micron from rough visual estimates. Using normal techniques it is difficult to obtain a clear separation of tubes and plates on the collodion substrate and frequently the thicker and more opaque tubes tend to be seen more easily than the fine plates which often appear to be entangled with the tubular material in aggregate masses.

The use of the preshadowed carbon replica technique on freshly fractured surfaces of the bulk clay, a method developed by Comer and Turley (1955), eliminates the necessity for dispersing the material and enables the minerals in the untreated clay to be studied directly. Stereoscopic pairs of photographs have been taken to obtain still clearer pictures of the material. Many unusual features are seen in the photographs which suggest that thin plates may be in the process of curling up into tubes.

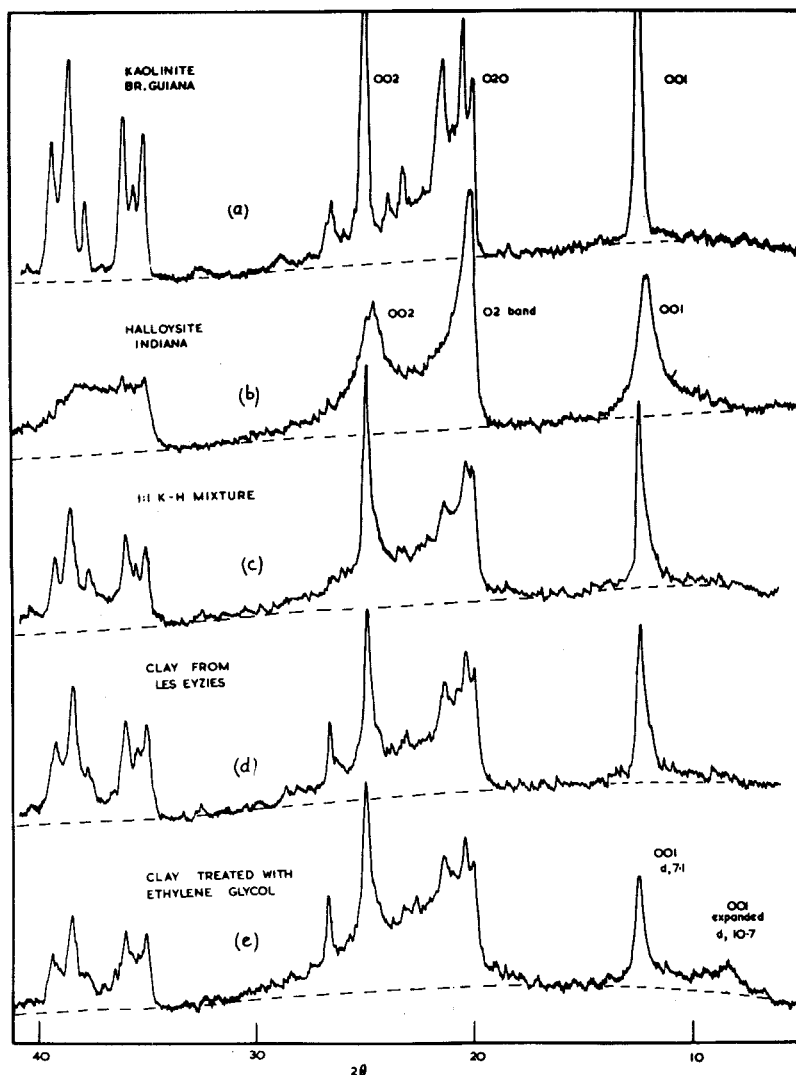


FIGURE 1. — X-ray diffractometer diagrams of (a) kaolinite, (b) halloysite, (c) 1:1 kaolinite-halloysite mixture, (d) kaolin clay from Les Eyzies. (e) the same clay after treatment with ethylene glycol.

A number of photographs taken at high magnification are reproduced in Figure 2. Figure 2a shows a field which is representative of most of the material. Both tubes and plates can be seen. The tubes show a marked preferential alignment which can be followed over considerable distances if the object is moved slowly in the field of view of the microscope. The surfaces of the tubes show unusual features which have not been described previously. They often appear to be fracturing into fragments having hexagonal outlines. Others appear to be rolled sheets rather than tubes, with the edges of the sheets showing hexagonal forms along the length of the roll. Figures 2b and 2c show some of these hexagonal features on the rolled surfaces. Another feature of this clay which has been seen in other materials is a considerable measure of alignment between adjacent hexagonal plates; Figure 2d shows an example. Occasionally a line of rupture can be seen between two such areas which suggests that an area of well-aligned flakes has been subject to stress and fractured more or less along a line. The fracture then exhibits hexagonal edges and angles. This flaky material is commonly very thin and it is easy to imagine that it will roll up giving a pattern of oriented tubes showing the hexagonally serrated edges. Figure 2d shows an area of oriented platy material which appears to be in the process of curling up into rolled fragments.

### GEOLOGY OF THE LES EYZIES CLAY

The following notes on the geology of this clay were kindly supplied by Dr. Georges L. Kulbicki.

The clay occurs between the valleys of the Dordogne and the Vézère. It lies in pockets which may be as deep as 50 m in a limestone plateau of Cretaceous age. The deposits are post-Cretaceous and pre-Stampian. Blocks of kaolin clay are mixed in a disorderly manner in quartz sands. Some blocks are bituminous and rich in pyrite, but for the most part they are formed of a very white, well-washed kaolin. Halloysite is found in cracks in the kaolinite or in nodules at the base of the deposit.

The formation developed at three periods: (i) deposition of argillaceous sand carried by torrents from the Massif Central; (ii) concentration of the clay by stream action within closed depressions; and (iii) cutting of valleys and the development of a karst-type topography on the limestone plateau. The sediments, trapped in holes in the limestone, were vigorously stirred and washed, and the pyrite oxidized, generating sulfuric acid which attacked and partially dissolved the kaolin. The alumina-silica gels subsequently recrystallized, usually to halloysite.

### DISCUSSION

It is of interest to attempt to correlate the laboratory observations with the large-scale geologic evidence. It is striking that both arguments point in the same general direction, namely a transformation of kaolinite to halloysite. Geologically this is seen as an acid attack on kaolinite leading to gel formation and subsequent recrystallization to halloysite. Prior to knowing the geological background, we had interpreted the electron micrographs as showing very thin kaolinite flakes which had fractured and rolled up into tubular halloysite.

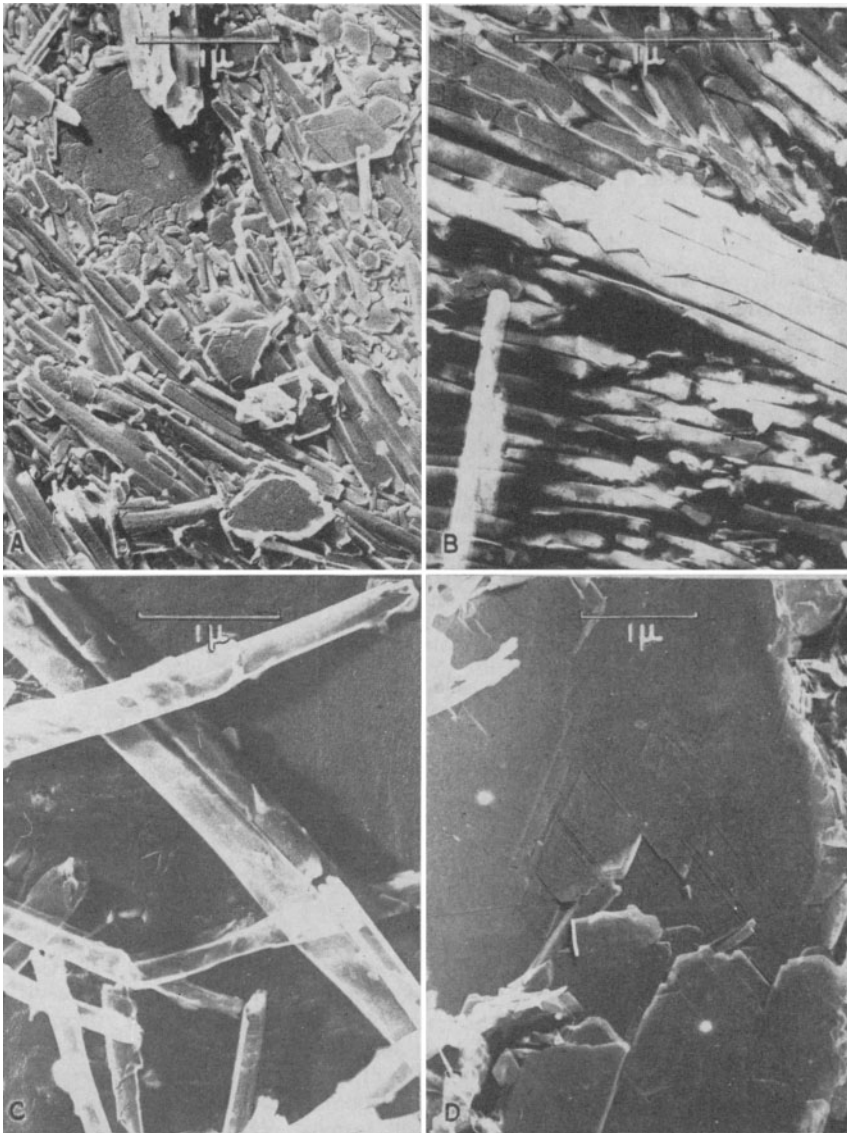


FIGURE 2.— Carbon replica electron micrographs of the clay from Les Eyzies. (a) A representative mixture of oriented tubes and small platy fragments, (b) Hexagonal features on edges of rolled material, (c) the rolled structure, (d) Well-aligned plates.

Combining the two points of view, we may perhaps visualize the kaolinite flakes being made thin by acid attack, then fracturing by internal lattice strain, and rolling up into tubular form.

The original point of the investigation, namely, to explain the apparent conflict between a kaolinite-type x-ray pattern from a material with halloysite-type morphology, has been clearly shown to arise from the intimate association of the two minerals in a roughly 1:1 mixture.

#### ACKNOWLEDGMENTS

Finally, we wish to express our thanks to Dr. W. Dekeyser for the specimen of clay and to Dr. G. L. Kulbicki for making available the geological data.

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