

MINERALOGICAL STUDIES OF KAOLINITE-HALLOYSITE
CLAYS: PART III. A FIBROUS KAOLIN MINERAL
FROM PIEDADE, SÃO PAULO, BRAZIL

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ABSTRACT

An unusual form of kaolin mineral, filling cracks in weathered porphyritic granite in the county of Piedade, São Paulo, Brazil, consists of visibly fibrous material which, in the electron microscope, appears as thin tubular fibers of considerable length; platy particles are almost entirely absent. X-ray rotation diagrams of dried fiber bundles and selected area electron diffraction patterns of single fibers show an appreciable degree of structural regularity in the kaolin layer structure, with b as the fiber axis. The results show general agreement with previous data by Honjo, Kitamura and Mihama. Prior to drying, the material as collected can be described as consisting of $\frac{2}{3}$ endellite and $\frac{1}{3}$ halloysite. The endellite component has the swelling and shrinking behavior characteristic of this mineral with respect to ethylene glycol, water, and gentle heat treatments. This may be the first observation of a mineral of endellite-halloysite type existing in a directly visible fibrous form.

INTRODUCTION

An unusual form of kaolin clay has been found in the county of Piedade¹, São Paulo, Brazil. It is fibrous in character at all degrees of magnification and behaves with respect to water, ethylene glycol, and gentle heat treatments, as a mixture of endellite and halloysite in a roughly 2:1 ratio.²

The material occurs in layers, about 1–3 cm thick, within cracks of weathered porphyritic granite (for a general description of the geology of of the area, see Knecht, 1949) and is easily visible in road cuts as white layers running in various directions within the bulk material. Where the surface of the altered granite is eroded, the white layers protrude and eventually break off in fragments which on drying have a remarkable fibrous appearance. Samples were collected from below the exposed surface and were kept in water in closed containers. They were crushed, ground, or separated by hand in the wet state.

Chemical analysis of material dried at 110° C. gave the results listed

¹ The pronunciation is approximately as follows: The word has four syllables of equal emphasis, Pi (as 'pee' in peel), e (as 'ay' in say), da (as in dark), and de (as 'dir' in dirt).

² Endellite and halloysite are used to signify kaolin clay minerals having basal spacings of about 10.0 and 7.2 Å respectively.

TABLE 1. CHEMICAL ANALYSIS OF PIEDADE CLAY DRIED AT 110° C.

| | |
|--|--------|
| SiO ₂ | 45.0 |
| Al ₂ O ₃ | 40.1 |
| H ₂ O (+110°) | 15.4 |
| Iron as Fe ₂ O ₃ | 0.72 |
| CaO | trace |
| MgO | trace |
| Na ₂ O | trace |
| K ₂ O | 0.02 |
| Total | 10.124 |

in Table 1. Differential thermal analysis of dried material gave the usual endothermic and exothermic peaks of a halloysite or kaolinite mineral.

OPTICAL AND ELECTRON-OPTICAL EXAMINATION

The fibrous character of the clay material can be seen directly in fractured surfaces. With the optical microscope, at 80× magnification,

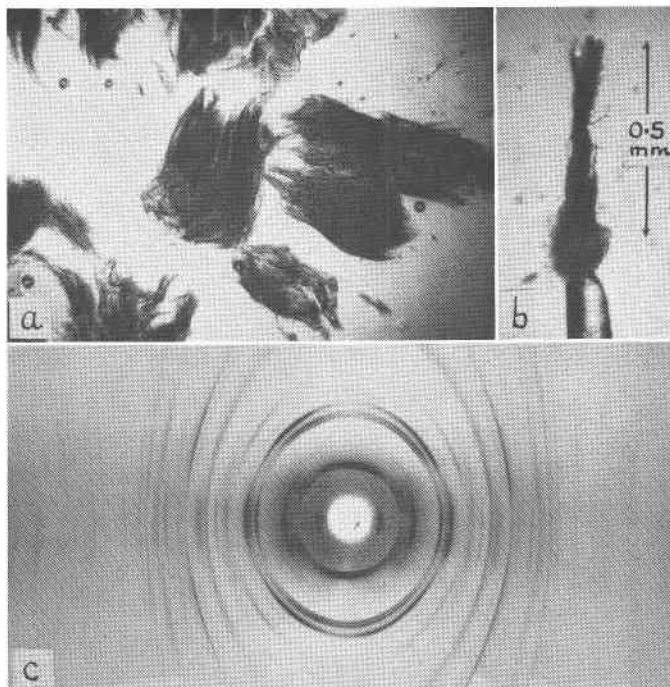


FIG. 1. (a) Fiber bundles, about 0.3 mm long, photographed at 80× magnification. (b) Thin fiber bundle mounted on glass fiber for α -ray study. (c) X-ray fiber diagram of bundle shown in (b).

the material appears as shown in Figs. 1, a,b. The fibers form thick bundles parallel to their length and have considerable coherence so that dry material is difficult to grind.

A lightly Pt-shadowed carbon replica of a fracture surface appears in the electron microscope as in Fig. 2a, where the individual fibers are about 0.05–0.1 micron wide and many microns long in nearly parallel

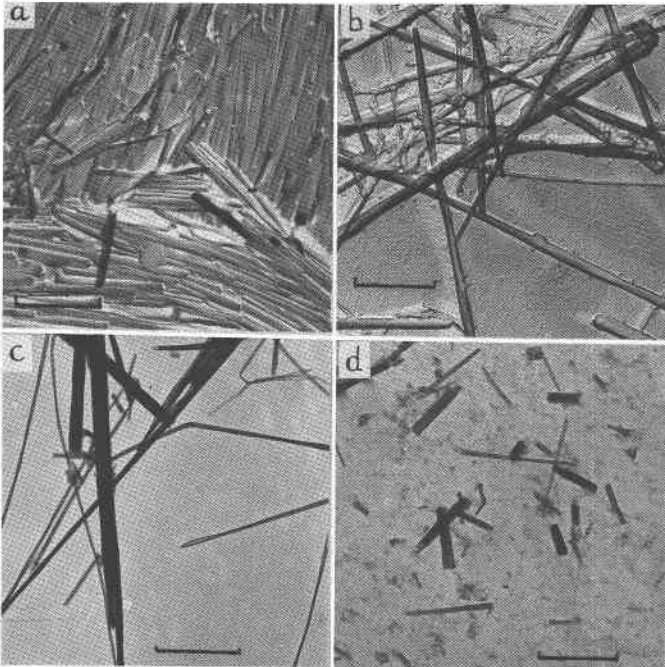


FIG. 2. (a) Lightly Pt-shadowed, carbon replica of a fracture surface of Piedade clay. (b) Carbon replica of dispersed fibers. (c) Dispersed material on a collodion film. (d) Dry-ground fragments of Piedade clay fibers.

aggregates. Individual fibers are seen more clearly in Fig. 2b, obtained from a carbon replica of wet material crushed and smeared between glass plates, and in Fig. 2c, obtained by placing a drop of water-dispersed material on a collodion film.

In Fig. 2a, the fibers have a flat, or flattened, lath-like appearance. In several places, they appear to open out into almost platy forms. In Fig. 2b, they appear as rolled tubes, sometimes only partially rolled; thin, fractured walls, with holes possibly formed by escaping water or vapor, can be seen. Some fibers are split lengthwise, and others are flattened and twisted into ribbon-like forms. Figure 2c shows fibers which

are thin and long, and others which are much thicker and have a fractured appearance.

Attempts have been made to obtain direct evidence for the cross-sectional form of the fibers by preparing thin transverse sections of methacrylate-embedded fibers with a Porter Blum glass-knife ultramicrotome, but the material 'smeared' under the cutting action and little direct evidence was obtained. However, longitudinal sections prepared in this way showed very clearly the hollow nature of the elongated fibers.

Figure 2d shows fragments of tubes obtained after dry grinding the material twelve times and each time setting it in "Lakeside" cement as described by Brindley and Kurtossy (1961). This was the only method by which the long fibers could be broken into short lengths which permitted *x*-ray powder diffraction data to be obtained without marked orientation effects.

DIFFRACTION STUDY

X-ray fiber diagram. The fiber bundle shown in Fig. 1b, about 0.5 mm long, was obtained by drawing out a thin wisp of material from the dry clay. It was attached to a glass fiber as shown in the figure, and was mounted in a rotation-type *x*-ray camera. The resulting diffraction diagram, taken with filtered $\text{CuK}\alpha$ radiation and a stationary fiber bundle, is reproduced in Fig. 1c. It has the appearance of a rotation diagram due to the large number of individual fibers within the bundle, but with considering 'arcing' of the reflections along powder lines. The repeat distance along the fiber axis, about 9 \AA , corresponds to the *b*-axis of the kaolinite and halloysite structures. Basal reflections along the zero level, up to 005, correspond to $d(001) = 7.10 \text{ \AA}$ in agreement with the values for kaolinite and halloysite within the accuracy of the measurement. On either side of the 003 reflection, are strong and sharp reflections which can be indexed 200 and $20\bar{2}$.

Single fiber electron diffraction. Electron diffraction patterns of single fibers taken by selected area diffraction yield results (Fig. 3) somewhat similar to the *x*-ray fiber pattern in that the fiber axis has a repeat distance of 8.93 \AA , measured on the 040, 060, and 080 reflections, and $d(001) = 7.14 \text{ \AA}$, measured on 001, 002, and 003 reflections. The material was lightly shadowed with Al metal to obtain the calibration rings seen in Fig. 3.

The diffraction pattern clearly does not correspond with a single net plane in reciprocal space. With b^* as the fiber axis and c^* perpendicular to the axis, such a net plane would contain reflections with indices $0kl$, and with k an even number since $(h+k)$ is even for the base-centered kaolin-

ite structure. In Fig. 3, many diffractions appear with k an odd number, and the diagram as a whole has the appearance of a rotation, or partial rotation diagram. This result is broadly consistent with the rolled form of the particles. Sharp reflections on either side of 003 appear to be the 200 and $20\bar{2}$ reflections, which were seen also in the x -ray diagram, and the close doublet with $k=1$ appears to be the 110, $1\bar{1}1$ pair.

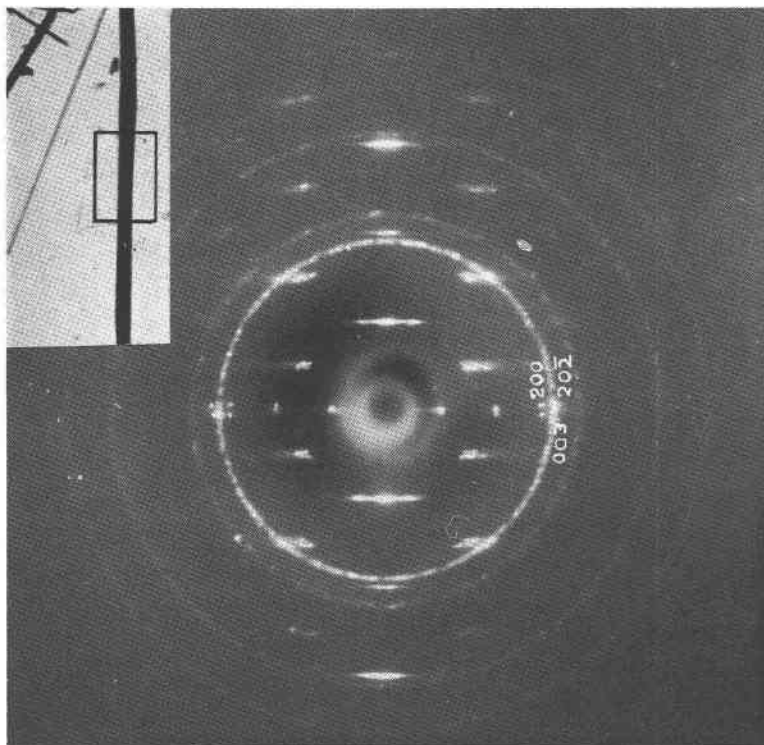


FIG. 3. Selected area, electron diffraction pattern of the single fiber shown in the inset.

The detailed interpretation of electron diffraction patterns of single halloysite particles has been considered already by Honjo and Mihama (1954), by Honjo *et al.* (1954), and by Waser (1955). The closely analogous problem of diffraction by chrysotile has been considered in considerable detail by Whittaker (1953–57) and by other investigators. In the case of halloysite, the discussions have by no means reached finality. The information contained in Fig. 3 appears to be very similar to the results obtained by Honjo and his collaborators and probably is similar to the diagram given by Waser so far as one can judge from a very poor reproduction. In particular, it is seen in Fig. 3 that the strong 020 reflection is

drawn out into a streak with broad maxima on either side which correspond in position with l indices $\pm \frac{1}{2}$. Honjo *et al.* indexed these maxima as 021 reflections from a two-layer unit cell with a doubled c -parameter, and some weaker spots also were given odd-numbered l indices with respect to the larger cell. Waser analysed, along much the same lines as Whitaker, the diffraction effects to be expected from a tubular halloysite particle, but made no detailed comparison between the analytical and the experimental results. However, he observed details in the diffraction patterns which required "that the layers making up a curved sheet have not become disordered through the curving" of the layers; such a model would seem to imply cracks or flaws in the overall tubular structure so that appreciable radial alignment of the layers could be maintained. Similar models have been shown schematically by Hofmann *et al.* (1962).

The evidence from these sources and from the present study points, therefore, to some degree of three dimensional structural order in halloysite greater than that which is normally assumed on the basis of x -ray powder diffraction data. It may be noted that in the supposedly analogous case of chrysotile, the diffuse scattering along layer lines¹ appears to be considerably more marked than one finds for halloysite, a result which points to greater order in the halloysite structure.

X-ray powder diffraction. Diffractometer data obtained from samples under a variety of conditions lead to the conclusion that the initial material consists of a mixture of endellite and halloysite in a ratio of about 2:1, see Fig. 4a. After gentle heating ($<100^\circ$ C.) or after a few hours in vacuo, the 10.0₅ Å reflection of the endellite component is largely lost and the 7.2 Å reflection of the halloysite considerably increased (Fig. 4b). No expansion of the 7.2 Å spacing occurs in water vapor, but when the material is wetted with water for an hour or more, the 7 Å reflection is greatly reduced without restoring the 10 Å reflection; a broad band of scattering indicates a partial but very irregular rehydration. With repeated vacuum and water treatments the previous history is repeated. Addition of ethylene glycol to vacuum dried material gives a clear 10.6 Å reflection which, however, is considerably less intense than the original 10.0 Å reflection (Fig. 4c); evidently the ethylene glycol re-expands only part of the vacuum collapsed material. Treatment with water does not restore a clear 10 Å spacing.

The most notable aspect of the diffractometer data is the high degree of

¹ See, for example, fiber diffraction patterns for chrysotile given by Warren and Bragg (1930, p. 209) and by Hey and Bannister (1948).

basal plane orientation achieved when the dispersed clay is allowed to dry in open air conditions on a glass slide or a porous tile (Fig. 4b). Ordinarily the tubular morphology of halloysite appears to eliminate such marked basal plane orientation (see, for example, Fig. 1, patterns C and D, given by Brindley and de Souza Santos, 1963, p. 899), but with the present material, the basal 001 and 002 reflections give intensities of the order of ten times that of the 02 band maximum. This behavior is consistent with the flattened appearance of the fibers seen in Fig. 2a. The

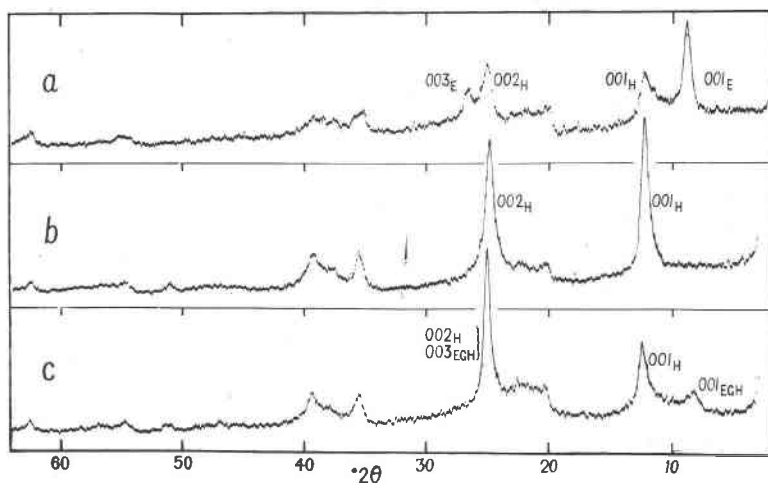


FIG. 4. Diffractometer traces of Piedade clay with filtered $\text{CuK}\alpha$ radiation; H=halloysite, E=endellite, EGH=ethylene glycol complex of halloysite. (a) Wet clay without prior drying in cavity-type holder; 001_E more intense than 001_H . (b) Air-dried material on glass slide; H reflections only. (c) Material of (b) saturated with ethylene glycol; 001_H approximately the same as in (a); 001_{EGH} is not to be confused with 001_E in (a).

marked orientation was eliminated only after grinding the dry material twelve times in "Lakeside" cement and drastically reducing the fiber length (Fig. 2d).

The 20, 13 band between $2\theta = 35^\circ$ and 40° in the powder diffraction pattern of halloysites previously called "type D" (Brindley and de Souza Santos, 1963) is a broad band of scattering with no marked maxima or minima. The halloysites previously called "type C," which showed a small enhancement of basal reflections with respect to the 02 band, also showed structural features within the 20, 13 band. The present material, with still more marked orientational ability, likewise yields a 20, 13 band with maxima and minima of the type C kind.

DISCUSSION AND CONCLUSIONS

The experimental data for the Piedade clay give rise to interesting questions of classification. Its fibrous and tubular morphology, the absence of platy particles, the existence of a 10 Å spacing in about $\frac{2}{3}$ of the material prior to dehydration, and the partial re-expansion in ethylene glycol, lead one to classify it as a mixture of endellite and halloysite. The marked tendency of the material to give basal plane orientation, and the evidence for some degree of structural regularity indicated by both *x*-ray and electron diffraction data lead one to consider whether kaolinite is a more appropriate name, at least for the material with the 7.2 Å basal spacing, with the 10 Å material as an expanded form.

If one admits that a mineral with tubular or rolled form can exhibit an appreciable degree of structural order, then the question arises whether it should be called a "tubular kaolinite." The present writers have discussed already (P. and H. de Souza Santos and Brindley, 1964) some of the materials previously called "tubular kaolins" and have shown that they consist of mixtures of platy and rolled forms. The Piedade clay, however, is not such a mixture and the observed structural characteristics must be attributed to the tubular particles. Therefore, there is a better justification for calling this clay a "tubular kaolinite," if by "kaolinite" one understands a material with some degree of three-dimensional structural order but not necessarily a platy morphology. The description of the material depends, therefore, on nomenclature. The present writers consider that the terms "kaolinite" and "halloysite" should apply primarily to platy, and rolled or tubular forms of composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ respectively; they also consider that both forms may possess varying degrees of structural order. The evidence presently available indicates that generally the platy forms tend to be structurally ordered and the rolled or tubular forms to be structurally disordered, so that classifications based on morphology or based on structural order lead generally to the same result. Nevertheless there are now indications that such classifications may not always lead to the same result, and it becomes necessary to define the basis on which the terms are used.

It may be argued that the presence of a 10 Å basal spacing or the ability to expand to a 10 Å spacing is clear evidence for the presence of endellite and halloysite. However, this view implies that a platy kaolin mineral cannot exist with a 10 Å spacing or be made to expand to a 10 Å spacing. Under appropriate conditions, however, kaolinites have been caused to expand (see for example Wada, 1961; Weiss *et al.*, 1963) though not simply by addition of water or ethylene glycol.

In conclusion, the Piedade clay can be described as a fibrous kaolin

mineral, exhibiting 10.0 and 7.2 Å basal spacings, having particles of tubular form many microns in length, with cross-sections of the order of 0.05–0.1 micron, which normally are aggregated to give a visibly fibrous character, and showing by x-ray and electron diffraction an appreciable degree of structural regularity. In the expanded 10 Å form, the material is an endellite and in the contracted 7 Å form it is a halloysite. The halloysite has an appreciable degree of structural regularity and can be placed in the type C category of kaolin minerals, as previously described. It is considered that the terms "kaolinite" and "halloysite" should be used primarily for materials with platy and tubular (or rolled) particles respectively, and that (for the present at least) one cannot exclude considerable variations in the extent of structural order, or disorder, in these different morphological forms.

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REFERENCES

- BRINDLEY, G. W. AND SARI S. KURTOSY (1961) Quantitative determination of kaolinite by x-ray diffraction. *Am. Mineral.* **46**, 1205–1215.
- P. DE SOUZA SANTOS AND H. DE SOUZA SANTOS (1963) Mineralogical studies of kaolinite-halloysite clays, I. Identification problems. *Am. Mineral.* **48**, 897–910.
- HEY, M. H. AND F. A. BANNISTER (1948) Thermal decomposition of chrysotile. *Mineral. Mag.* **28**, 333–337.
- HOFMANN, U., S. MORCOS AND F. W. SCHEMBRA (1962) Das sonderbarste Tonmineral, der Halloysit. *Ber. deutschen Keram. Gesell.* **39**, 474–482.
- HONJO, G., N. KITAMURA AND K. MIHAMA (1954) A study of clay minerals by means of single-crystal electron diffraction diagrams—the structure of tubular kaolin. *Clay Min. Bull.* **2**, 133–141.
- AND K. MIHAMA (1954) Study of clay minerals by electron-diffraction diagrams due to individual crystallites. *Acta Cryst.* **7**, 511–513.
- KNECHT, T. (1949) Ocorrências de minerais metálicos na Serra de São Francisco, São Paulo. *Mineração e Metalurgia*, **14**, 37–40.
- SOUZA SANTOS, P. DE, HELENA DE SOUZA SANTOS AND G. W. BRINDLEY (1964) Mineralogical studies of kaolinite-halloysite clays, II. Some Brazilian kaolins. *Am. Mineral.* **49**, 1543–1548.
- WADA, K. (1961) Lattice expansion of kaolin minerals by treatment with potassium acetate. *Am. Mineral.* **46**, 78–91.
- WARREN, B. E. AND W. L. BRAGG (1930) Structure of chrysotile, *Zeit. Krist.* **76**, 201–210.

- WASER, J. (1955) Fourier transforms and scattering intensities of tubular objects. *Acta Cryst.* **8**, 142-150.
- WEISS, A., W. THIELEPAPE, G. GÖRING, W. RITTER AND H. SCHÄFER (1963) Kaolinit-Einlagerungs-Verbindungen. *Inter. Clay. Conf.*, 1963, 287-305.
- WHITTAKER, E. J. W. (1953-1957) Structure of chrysotile, I-V. *Acta Cryst.* **6**, 747-748; **9**, 855-867; **10**, 145-156.
- (1954-1955) Diffraction of x -rays by a cylindrical lattice, I-IV. *Acta Cryst.* **7**, 827-832; **8**, 261-271; **8**, 726-729.

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