MINERALOGICAL STUDIES OF KAOLINITE-HALLOYSITE CLAYS: PART IV. A PLATY MINERAL WITH STRUCTURAL SWELLING AND SHRINKING CHARACTERISTICS

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Abstract

A mineral belonging to the kaolinite group from Poços de Caldas, M.R., Brazil, is described which, in its naturally humid state, has a basal spacing of 10.05 Å. Exposed to open air conditions, or placed in boiling water, it collapses to 7.3–7.2 Å, and in ethylene glycol it expands to 10.90 Å. Electron micrographs of freshly collected material show very thin, platy forms ranging in size from 0.5 micron downwards. The platy morphology deteriorates when the material is aged; the plates appear to aggregate and to curl, producing cabbage-like forms. The classification of minerals resembling kaolinite and halloysite, in terms of their x-ray diffraction and electron-optical characteristics, is discussed. It is shown that a divariant rather than univariant classification scheme is required.

Introduction

In previous papers, the writers have called attention to difficulties arising in the identification of kaolinites and halloysites, particularly when both are present (Brindley *et al.*, 1963). It was suggested that a sequence of platy, rolled and tubular forms exists with possibly related variations in the degree of crystal structure perfection (stacking order). The apparent anomalies presented by the so-called "tubular kaolinites" of Brazil (Visconti *et al.*, 1956) seemed to be resolved when these were shown to be intimate mixtures of platy and tubular forms, *i.e.*, of kaolinite and halloysite (Souza Santos *et al.*, 1964.) Subsequently, a macroscopically-fibrous, kaolinite-group mineral was found (Souza Santos *et al.*, 1965) which exhibits an appreciable degree of structural regularity, yet consists of very thin tubular fibers of considerable length, which, prior to drying, show the swelling characteristics of endellite. Platy particles are almost entirely absent from this material.

The present paper reports a kaolinite-group mineral which in electron micrographs is seen to consist of fine platy particles in which no tubular particles can be detected. This material exhibits the diffraction characteristics of a highly disordered layer sequence and shows the swelling and shrinking behavior of endellite. Kunze and Bradley (1964) have described a "tabular halloysite" which appears somewhat similar to the

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present material. However, the mineral to be described exhibits more strikingly the behavior of endellite, so that the term "tabular endellite" would seem more appropriate for the mineral in its initial state.

It is evident that problems of classification and nomenclature arise because there does not appear to be invariably a univariant relationship between degree of crystal structure order (or layer-stacking order), the gross structure of the particles as shown by their morphology, and the swelling and shrinking characteristics of the layer structure (Brindley and Souza Santos, 1966).

Occurrence

The mineral under consideration occurs as vein fillings between gibbsite-rich bauxite derived from weathered boulders of phonolite and is observable in road cuts near the city of Poços de Caldas, M.R., Brazil. The probable origin of the clay is either by deposition of solids from solutions containing silica and alumina, or by silicification of weathered bauxite by downward waters containing silicic acids. A description of these bauxite deposits has been given by Harder (1952). The mineral is closely associated with gibbsite and samples contaminated with gibbsite are cream-colored. Ochre-colored material also is found containing easily detectable goethite as well as gibbsite.

Properties

Chemical analysis. Analysis of a 2.5 gm sample hand picked to contain mainly the white material and dried to constant weight at 110° C. yielded the data listed in Table 1. The composition is close to that of kaolinite or of halloysite dried at this temperature, with some free gibbsite estimated as about 4% (Table 1).

Differential thermal analysis. A prominent endothermic peak at about 580° C. and a sharp exothermic peak at 960° C. (Fig. 1) are consistent with a kaolinite-group mineral as the principle component, and the small peak at about 300° C. could arise from a small amount of gibbsite.

X-ray powder diffraction data. Wet material packed in shallow cavities and x-rayed under humid conditions using filtered CuKα radiation and a Norelco diffractometer, gave diffraction patterns consistent with the mineral endellite. The basal spacing measured on 001 and 003 reflections from many samples gave d(001) = 10.05 ± 0.02 Å. These basal reflections were sharp and symmetrical; all other diffraction characteristics (positions, profiles and intensities of diffraction bands) agreed with those from the minerals halloysite and endellite. When the surface of the sample was repeatedly smoothed, the 001 peak intensity increased to about $2\frac{1}{2}$ times

TABLE 1. CHEMICAL ANALYSIS OF A KAOLINITE-GROUP MINERAL FROM POÇOS
DE CALDAS, MINAS GERAIS, BRAZIL

(Analyst, P. Santini)

	wt. per cent	calculated[2]
SiO_2	44.3	44.8
Al_2O_3	39.1	40.5
Fe_2O_3	1.42	—
CaO	tr	—
MgO	tr	—
K_2O	0.21	—
Na_2O	0.05	—
TiO_2	0.18	—
Loss on ignition[1]	14.6	14.7_5
Total	99.86	

[1] Referred to material dried at 110°C.
[2] Calculated for 96.3% kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and 3.7% gibbsite ($Al_2O_3 \cdot 3H_2O$).

that of the 02,11 diffraction band, indicating appreciable basal plane orientation.

Expansion and collapse of the structure with various treatments. Exposed to open air conditions for a few hours the material shows partial collapse
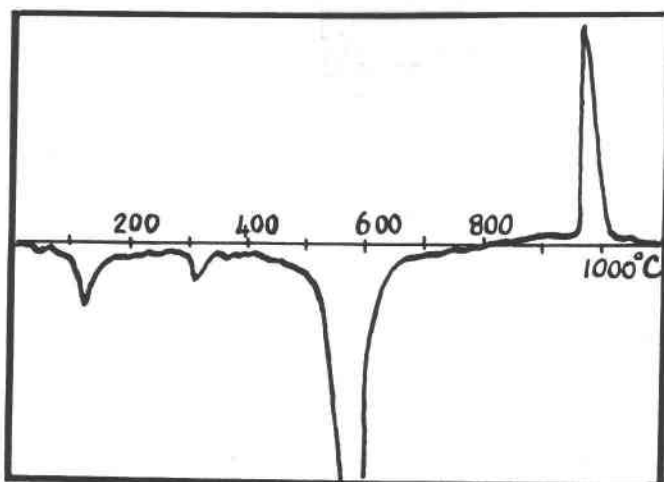

FIG. 1. Differential thermal analysis curve of a kaolinite-group mineral
from Poços de Caldas, M.R., Brazil.

to a spacing of about 7.3 Å, with diffuse scattering over the range 2θ $= 8.8 - 12.2°$ $(10.0 - 7.2$ Å$)$. This collapse takes place more readily than for most endellites. Placed in water, the partially collapsed material shows very little or exceedingly slow return to the initial state. Placed in boiling water overnight, the material shows considerable collapse towards a 7.2 Å spacing which is not reversed by immersion in water at normal temperatures.

Material held at 110° C. in a dry state overnight gives sharp symmetrical 001 and 002 reflections from a spacing $d(001) = 7.28$ Å. From $d(060)$ $= 1.485$ Å, b is calculated to be 8.91 Å. The resulting diffraction pattern agrees with that of halloysite, and in particular with the type of pattern previously called "type D" (Brindley *et al.*, 1963). The 001 peak intensity exceeds only slightly that of the 02,11 band; possibly the ability to orient is impaired by the 'blocky' texture seen in the electron micrographs.

Addition of ethylene glycol to the initial clay and also to air-dry material results in an expansion to $d(001) = 10.90 \pm 0.03$ Å. The diffraction pattern shows sharp 001 and 003 reflections, and diffuse bands characteristic of halloysite and endellite. Glycolated samples heated at 110° C. or higher temperatures collapse to a spacing $d(001) = 7.26$ Å and the diffraction diagram is that of halloysite. Ethylene glycol added to these or to other heated samples does not cause re-expansion.

Samples heated overnight at 300° C. showed the same diffraction pattern as those heated at 110° C. with $d(001) = 7.22$ Å. No evidence was found for any three-dimensional structural ordering.

Electron microscope examination. Materials collected in a wet state in sealed containers and dispersed in water without prior drying in the laboratory, show very thin platy particles with sizes ranging downwards from about 0.5 micron, (Fig. 2a). Material allowed to dry in open air conditions prior to dispersion never yielded such well-dispersed particles; the thin plates appeared to aggregate so that re-dispersion was difficult or impossible. Retention of the platy forms under laboratory conditions in the dispersed state seems, however, to be short-lived. Figure 2b shows a dispersed sample aged for 8 months; many of the larger particles have curled into lettuce- or cabbage-like forms and smaller particles appear to have rolled into tube-like forms. Takahashi (1958) described a similar clay from Japan with rounded grains "composed entirely of polyhedral crust like a cabbage". Even after a few days in the dispersed state, the flatness of the particles deteriorates appreciably so that their initial flatness appears to be related to the constraints present in the natural environment; when these are removed, then curling and rolling set in.
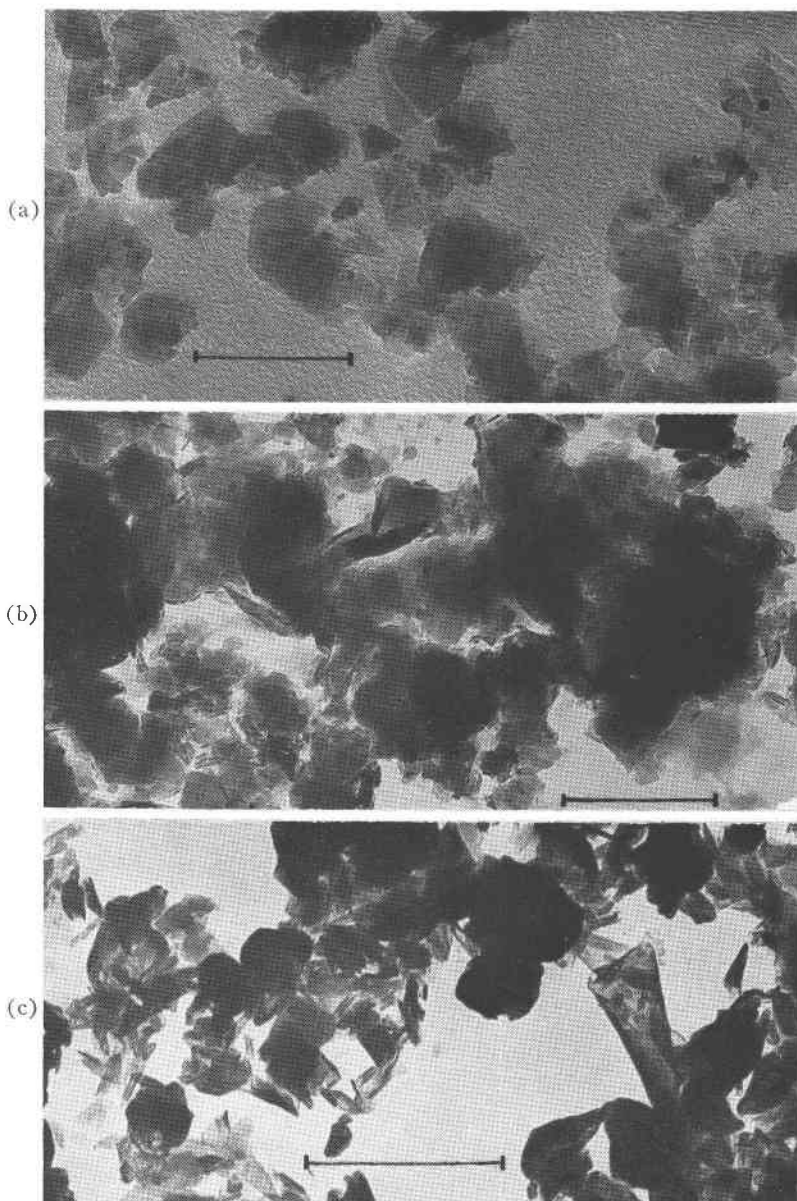
FIG. 2. Electron micrographs of a kaolinite-group mineral from Poços de Caldas, Brazil. A 1-micron length is shown on each micrograph. (a) Freshly collected material, dispersed without prior drying; chromium-shadowed. Note very thin, flaky forms, without 120° angles, often showing fractures. (b) Same material as (a), but aged for several weeks in water. Note poorer dispersion and tendency for curling of flakes or flaky aggregates. (c) Material aged for 8 months; note the presence of tube-like or rolled forms, and curled flaky masses.

Discussion

The material under consideration is a kaolinite-group mineral exhibiting some of the characteristics of kaolinite (notably a platy habit, and ability to orient with respect to (001)) and also of endellite (10 Å spacing which collapses to 7.3 Å with gentle heating, expansion in ethylene glycol, and a diffraction pattern indicating highly random layer displacements parallel to (001)). It could be called "tabular endellite", if endellite does not necessarily imply rolled or tubular particles. It could be called "hydrated kaolinite" by analogy with "hydrated halloysite" and thereby arouse another heated nomenclatural controversy. A new name can scarcely be introduced without careful re-consideration of existing names. Elsewhere, Brindley and Souza Santos (1966) have outlined three possible nomenclatures for these minerals.

Temporarily the problem of nomenclature can be shelved and attention focussed on the more fundamental question of the classification of the kaolinite-group minerals. Dickite and nacrite need not be considered now since they are sufficiently distinct not to cause confusion.

Given a collection of kaolinite-halloysite-endellite-like minerals to sort out into boxes, the present writers would begin with four boxes, labelled respectively:

(1) d = 7.15–7.20 Å; platy and near platy forms.
(2) d = 7.2–7.5 Å; variously rolled and tubular forms.
(3) d ≃ 10 Å; platy and near platy forms.
(4) d ≃ 10 Å; rolled and tubular forms.

There might be some question about minerals going into box 4 because their morphology could not easily be observed; placing them in an electron microscope would convert them to the status of minerals in box 2. Possibly the glycerol technique described by Sand and Comer (1955), supplemented by the carbon replica method used by Bates and Comer (1955), would provide a method of examining these tubular forms without their collapse. It is to be expected that chemical analyses would show $Al_2O_3/SiO_2/H_2O$ ratios of 1/2/2 for minerals in boxes (1) and (2), and 1/2/4 for those in boxes (3) and (4). This preliminary sorting into four boxes would take no heed of structural order, except to remove dickites and nacrites to special containers.

The writers then would sub-divide the minerals in each box according to the degree of crystal-structure order. Box 1 would require at least three sub-divisions:

1A. Minerals with a high degree of crystal-structure order, which would be indicated by many *hkl* diffraction lines without exclusion of particular indices.
1B. Minerals with considerable structural disorder, mainly displacements of $nb/3$, indi-

cated by absence or considerable weakening of diffraction lines with $k \neq 3n$, and by appearance of diffraction bands, particularly the 02, 11 band.

1C. Minerals with still greater disorder produced by layer displacements, showing mainly diffuse bands of x-ray scattering.

Minerals placed in box 2 also will show varying degrees of structural order and disorder, as the descriptions given by Honjo et al. (1954) and by the present writers (Souza Santos et al., 1965) indicate. More detailed electron diffraction studies of single particles will be required to establish a better understanding of these minerals.[1]

The mineral described in the present paper might be the only immediate occupant of box 3. However, the absence of other samples may be a consequence of most materials having been dried (naturally or otherwise) before examination by x-ray diffraction. Samples placed in box 4 are not amenable to single particle, electron diffraction study because they will dehydrate under the conditions used. X-ray powder diffraction is probably unable to give detailed information but ability or inability to show orientation effects would give a preliminary indication whether to put a 10 Å mineral in box 3, or 4.

Further consideration can be given to the grouping within boxes 1 and 2. Figure 3 shows schematically a sub-division based on crystal-structure order, which varies vertically, and gross structure as shown by particle morphology, which varies horizontally. The vertical scale ranges from the crystallographically well-ordered minerals at the top, through one-dimensionally disordered minerals, to those where two-dimensional disorder is prominent or dominant. The vertical scale might even be continued to those minerals, like allophane, which do not show layer stacking order of any kind. However, this last remark raises questions which are beyond the scope of the present paper.

The horizontal variation from platy forms, through increasingly curved and rolled forms, to fully rolled forms is in some respects an over-simplification. One knows that there is much variety among the rolled forms. For example, Bates (1955) showed electron micrographs of material from British Guiana containing tubes having an hexagonal cross-section. However, it is difficult to place these and other examples in the scheme of classification because x-ray and electron diffraction data of the same materials were not always given.

The area between the diagonal dashed lines in Fig. 3 corresponds to the univariant classification in which crystal-structure order and gross structure (or morphology) follow more or less closely together. It is evident now that a univariant system ranging from structurally well-ordered
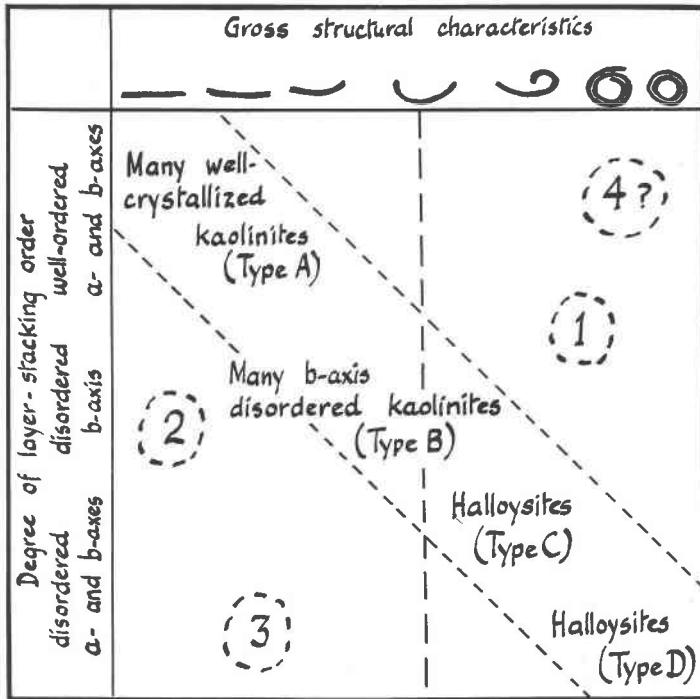
[1] See, "Note Added in Proof."

Fig. 3. Schematic divariant classification of kaolinite-halloysite type minerals. Types A, B, C, D are described by Brindley, P. and H. de Souza Santos (1963). Diagonal dashed lines correspond to a roughly univariant range of minerals. The vertical dashed line corresponds to a rather arbitrary kaolinite-halloysite boundary. (1) Mineral from Piedade, described by Souza Santos, P. and H. de, and Brindley (1965). (2) Kaolinite from Pugu, Sample D, described by Robertson, Brindley and Mackenzie (1954). (3) Mineral from Poços de Caldas described in the present paper. (4) This *may be* the position for the halloysite occurring in British Guiana kaolinite, and containing tubes with hexagonal cross-section, as described by Bates (1955).

platy forms of kaolinite to structurally disordered, rolled and tubular forms of halloysite cannot cover the variety of minerals found in nature. The locations of the numbered clays shown in Fig. 3 are not precisely defined, but they serve to show that examples are now known which fall outside the univariant scheme.

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NOTE ADDED IN PROOF

Attention should be directed also to the recent paper by F. V. Chukhrov and B. B. Zvyagin: Halloysite, a crystallochemically and mineralogically distinct species, *Proc. Intern. Clay Conf., Jerusalem, Israel*, 111–25 (1966), where it is claimed that halloysite has a structure with two layers per unit cell.