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MINERALOGICAL STUDIES OF KAOLINITE-HALLOYSITE CLAYS:
PART I. IDENTIFICATION PROBLEMS[1]

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ABSTRACT

X-ray diffraction and morphological characteristics of kaolinite, halloysite and intermediate forms are reviewed. Four recognizably different *x*-ray diffraction patterns (labelled types A, B, C, D) are recorded for essentially monomineralic materials and these correspond to increasing amounts of layer stacking disorder. A sequence of morphological forms also exists extending from platy, through lath-like and curved forms, to fully rolled and tubular forms. *X*-ray patterns of types A and B arise generally from platy forms (*i.e.*, kaolinites) and patterns of types C and D from curled and variously rolled forms (i.e., halloysites). However, the latter correspondence may not hold in all cases since platy crystals (kaolinites) may conceivably exist with highly disordered stacking sequence giving rise to *x*-ray patterns of types C and D. Preferential orientation of platy crystals gives enhancement of basal *x*-ray reflections and provides a useful distinguishing characteristic between kaolinites and halloysites. Electron microscope data provide direct evidence on the morphology of a clay material provided the sampling procedure gives a true picture of clay content. Problems are discussed which arise in the identification of kaolin minerals in mixtures of kaolinite and halloysite by *x*-ray diffraction and by electron microscope techniques.

INTRODUCTION

Among minerals described as kaolinite and halloysite, varieties exist differing in particle morphology and in degree of structural order. Those exhibiting extreme characteristics can usually be classified unambiguously, more particularly when they occur in monomineralic samples. Varieties with intermediate characteristics are more difficult to classify, and when they occur in mixtures the results are likely to be ambiguous. The present study was complete when a paper by Beutelspacher and van der Marel (1961) came to hand dealing with the same problems. Their survey is broader than the present one in that they consider, besides *x*-ray diffraction and electron microscope data, also infra-red and differential thermal analysis data, and they describe results for a variety of clay materials containing many different impurities. The present study is concerned with *x*-ray diffraction and electron microscope data for kaolin clays which are mainly monomineralic. The diffraction data tend to fall into four categories which are not sharply defined but grade into each

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other. There is some correspondence between diffraction and morphological data, but it is neither exact nor invariable. The ambiguities which arise when mixtures of kaolin minerals are involved are illustrated.

The two studies in many respects are complementary to each other. In view of the wide literature coverage provided by Beutelspacher and van der Marel, 170 references in all, it is unnecessary to repeat their detailed survey of other work. The present paper will be oriented towards giving the ideas which have developed from the writers' own studies without an exhaustive discussion of every related item which can be found in the literature.

Nomenclature. "Kaolin mineral" is used as a general group term covering kaolinite, halloysite and intermediate forms. "Kaolin clay" signifies a clay in which these minerals predominate. The specific minerals, dickite and nacrite, also are covered by these terms but do not arise in the present paper. Halloysite is used for a mineral with composition approximately $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$; the corresponding mineral with approximately $4H_2O$ is not considered in this paper.

STRUCTURE AND MORPHOLOGY OF KAOLINITE AND HALLOYSITE

In its most nearly ideal form, kaolinite consists of platy particles in which the structural layers have a high degree of stacking regularity and the x-ray powder pattern consists of many clearly defined reflections (Fig. 1A). The particles have the form of flat plates, commonly exhibiting angles of 120°, and frequently approach an hexagonal form (Fig. 2A).

In its most characteristic form, halloysite consists of rounded lath-like, tubular or rolled particles, with considerable variations in width (diameter) and length, but the ratio length/width lies in the range 3–6 for many samples (Bates and Comer, 1959). The structural layers scatter x-rays in a manner largely incoherent from layer to layer (Brindley and Robinson, 1948). This incoherence, together with the curvature of the layers gives rise to bands of scattering in regions where kaolinite gives groups of reflections (Fig. 1D). An electron micrograph of the material giving the pattern of Fig. 1D is shown in Fig. 2D.

Other diffraction characteristics which distinguish these extreme types arise from their morphological differences. The platy particles of kaolinite are very readily oriented on the basal (001) planes and the corresponding reflections, chiefly 001 and 002, are enhanced with respect to other reflections. The tubular form of halloysite precludes this kind of orientation, and the basal reflections are relatively less intense, and the peaks tend to be lower than the maximum of the 02,11 diffraction band. Figures 1A and 1D were obtained by a technique (see later) giving relatively little preferred orientation, but any method of sample preparation which pur-

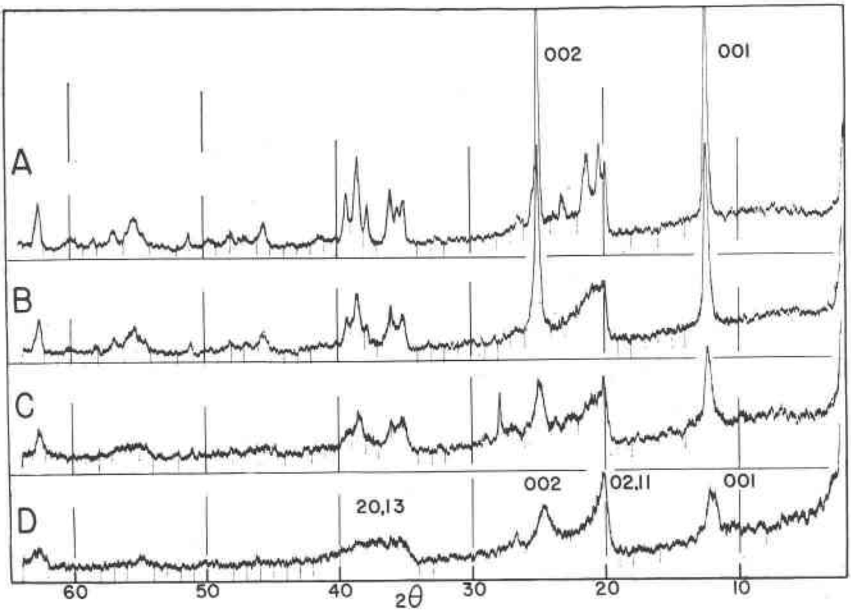

Fig. 1. *X*-ray powder diffraction patterns of monomineralic kaolin minerals. (A) Well-ordered, well-formed platy material, enhanced basal reflections (kaolinite). (B) Platy material with b-axis disordered sequence, enhanced basal reflections (disordered kaolinite). (C) Layer sequence partially disordered with respect to both *a*- and *b*-axes, little enhancement of basal reflections, rolled forms (halloysite). (D) Highly disordered layer sequence, no enhancement of basal reflections, tubular form (halloysite).

posely orients the platy particles gives considerable enhancement of the basal intensities from kaolinite, and little or no enhancement of these reflections from halloysite.

The angular breadth and symmetry of the basal reflections and the lattice spacing (measured at half maximum intensity) provide additional distinguishing characteristics. For halloysite, the 001 reflection is usually broad and tends to be asymmetric (Fig. 1D), and the lattice spacing usually lies in the range 7.2–7.3 Å. For kaolinite, this reflection is sharp and symmetrical, and the lattice spacing is in the range 7.15–7.17 Å.

DISORDERED KAOLINITES

Many kaolinites exhibit a type of stacking disorder in which the layers have random displacements of *nb*/3; this was described by Brindley and Robinson (1946, 1947). Figure 1B shows a typical powder diffraction pattern, and the corresponding electron micrograph is given in Fig. 2B. The particles are platy with hexagonal outlines and smaller in size than those shown in Fig. 2A. Similar material from Pugu, Tanganyika, was de-

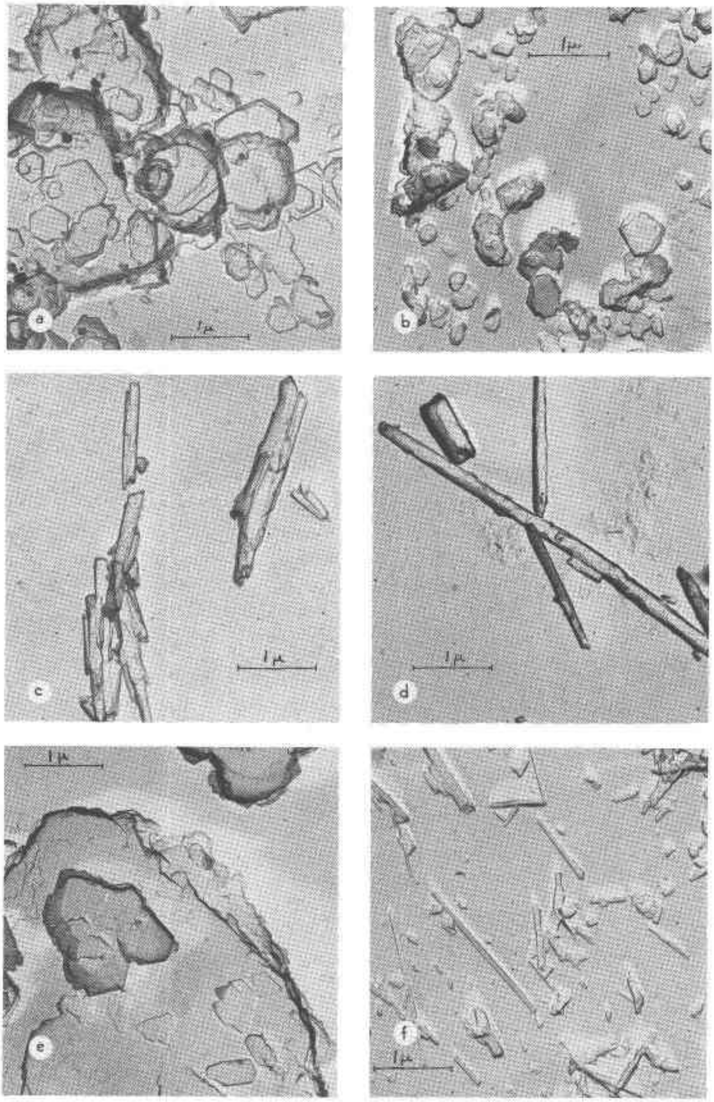

FIG. 2. Electron micrographs.

(A) Kaolinite A: Tuscaloosa Formation. Georgia Kaolin Co.
(B) Kaolinite J: Tuscaloosa Formation. Georgia Kaolin Co.
(C) Halloysite, 2012: Utah, U.S.A.
(D) Halloysite, 2007: Utah, U.S.A.
(E) Kaolinite #24: Minas Gerais, Brazil.
(F) Halloysite, #59: Minas Gerais, Brazil.

scribed fully by Robertson *et al.* (1954). Other kaolin clays giving *x*-ray diagrams of the type shown in Fig. 1B consist of platy crystals with very irregular outlines. There does not appear to be a unique correlation between crystal shape or crystal size, and stacking disorder with respect to the *b* axis.

When the *x*-ray diffraction pattern of halloysite was recognized as arising from a disorderly stacking of layers with respect to both *a* and *b* axes, then it seemed reasonable to suppose that all degrees of stacking order-disorder might exist between fully ordered kaolinite, one-dimensionally disordered kaolinite, and halloysite fully disordered in two dimensions. The recognition of the tubular morphology of halloysite by Bates *et al.* (1950), confirmed by many subsequent studies, gave rise to doubts whether a *continuous* range of stacking order could exist.

With improvements in electron microscope techniques and with continued examination of many different clays, the idea of a continuous range of mineral types has been resuscitated. Bates and Comer (1959: see pp. 245–6) have written that "it is logical to have in the kaolinite group a complete morphological series from hexagonal plates to elongate plates to "laths with hexagonal tendencies" to curved laths to tubes to the more amorphous curls and rounded grains of allophane."

It would be out of place here to attempt a detailed survey of electron microscopic data. The work of Bramao *et al.* (1952), which refers particularly to kaolin minerals in soils, is among the few morphological studies which also give detailed consideration to *x*-ray data. In numerous papers, Oberlin (1957) and Oberlin and colleagues (1957, 1958, 1959) have described kaolin flakes exhibiting rolled and curled forms produced under natural conditions and also in the laboratory. Gastuche (1959) has described experiments leading to the production of rolled flakes, and Fripiat (1958) has made similar observations on kaolin minerals in tropical soils.

In several publications it has been asserted that kaolin minerals exist having the morphology of halloysite but yielding the *x*-ray diffraction characteristics of kaolinite. De Keyser and Degueldre (1954) made this assertion first for a clay from Les Eyzies, but Brindley and Comer (1956) examined similar material and showed that the results could be explained as arising from a mixture of the two minerals. Visconti *et al.* (1956) made similar claims for some Brazilian kaolins, and their results have been questioned by Urban (1958). Honjo *et al.* (1954) have found evidence by single crystal electron diffraction that a higher state of order may exist in the halloysite structure than *x*-ray powder diffraction data have indicated.

It is evident that a re-evaluation of the *x*-ray and microscopic data is needed. The problems arising when mixtures of kaolin minerals are studied also call for careful examination.

Experimental Methods and Materials

Electron microscope techniques. Particular care has been taken to use techniques which will avoid accidental fractionation of a clay, and damage to the clay particles by mechanical processes such as grinding. It is very important to obtain micrographs which are truly representative of the whole clay in its initial condition.

A method developed by P. and H. de Souza Santos (1957) uses an aerosol spray. The clay sample is dispersed in water containing a little ammonia and is disaggregated mechanically between two glass slides. The disaggregated and dispersed clay is transferred to a nebulizer and the aerosol droplets allowed to fall on collodion-covered grids.

The preshadowed carbon replica technique of Comer and Turley (1955) has been applied as follows: The clay is spread between two glass slides, shadowed by platinum in a high vacuum, and then covered with a carbon film which forms the replica. The clay is dissolved in HF and the replica transferred to collodion covered grids.

Micrographs reproduced in Fig. 2 were obtained by the second method using an R.C.A. E.M.U. type D instrument with an instrumental magnification of ×6900. The final magnification shown in Fig. 2 is about ×20,000.

X-ray diffraction technique. A Philips high-angle *x*-ray diffractometer has been used with CuKα radiation and a normal scanning speed of $1°2\theta$/min. A back-filled rotating sample holder has been employed which previous experience has shown reduces considerably the preferential orientation of platy particles as compared with the degree of orientation obtained with front-filled sample holders. However, since the preferred orientation of platy particles is a useful distinguishing characteristic, it is undesirable to take more elaborate steps as in the "wax technique" described by Brindley and Kurtossy (1961). Weighed samples of 0.5 g were used in order to obtain a consistent packing density from sample to sample.

Materials studied. These include a wide range of Brazilian kaolins which will be considered further in Parts II and III, a range of Georgia kaolins kindly made available by Mr. S. C. Lyons of the Georgia Kaolin Company and described by Murray and Lyons (1956), and a range of halloysites made available by Dr. T. F. Bates and described by Bates and Comer (1959). Other samples were examined which need not be mentioned individually.

Specifically the present paper deals with the following clays:

Kaolinite A and J—Tuscaloosa Formation (Cretaceous) Georgia Kaolin Co., Dry Branch, Georgia.
Kaolinite #24 —Jazida Roca Grande, Ibitiguaia, Juiz de Fora County, Minas Gerais, Brazil.
Halloysite 2007 —New Park Mine, Utah, U.S.A.
Halloysite 2012 —Fox deposit, Utah.
Halloysite #59 —Fazenda Avai, Sta. Helena, Pequeri County, Minas Gerais, Brazil.

Preparation of mixtures. Clays were dried for 24 hr. at 110° C., and 1 g samples of mixtures of kaolinite and halloysite were prepared containing respectively 5, 10, 15, 20, 25, 30, 35 and 40% by weight of kaolinite. Two sets of mixtures were studied containing respectively kaolinite No. 24 and halloysite 2007, and the same kaolinite with halloysite No. 59. The materials were mixed with a steel spatula, first in the dry state, and later with acetone to form a homogeneous paste. The paste was air-dried, lightly crushed and passed through a 100 mesh sieve. After sieving, 0.5 g was placed in the rotating holder for *x*-ray diffraction, after which the material was examined by electron microscopy by the second method described.

DIFFRACTION AND MORPHOLOGICAL DATA FOR MONOMINERALIC KAOLIN CLAYS

On the basis of the present experiments and earlier work, the present writers believe that essentially monomineralic kaolin clays give four recognizably different kinds of powder diffraction patterns. These are illustrated in Fig. 1 (A, B, C, D) and micrographs of the corresponding materials are given in Fig. 2 (A, B, C, D). These diagrams and materials will be referred to as Types A, B, C and D.

The relative intensities of the reflections shown in Fig. 1 depend on the experimental arrangements employed and notably on the small but still significant preferential basal plane orientation of platy crystals. Other investigators wishing to compare their results with those reported here should use similar techniques. Powder smears on glass slides give highly oriented arrangements of platy particles, and the resulting diffraction data are not directly comparable with those given here.

The type A diagram (Fig. 1) is that of a well-ordered, well-formed kaolinite with some preferred basal plane orientation. The type D pattern is that of a well-formed tubular halloysite with probably no preferred basal plane orientation.

Material described as *b*-axis disordered kaolinite corresponds to type B. As stated previously, the morphology of this type of kaolin mineral is variable. It is always platy and is readily oriented on the basal plane; the

001 and 002 reflections usually appear stronger than the maximum of the diffuse band, 02,11, and this is shown in Fig. 1B. It is seen also that most of the well-defined reflections from kaolinite in the range $34° < 2\theta < 40°$ (CuKα radiation) are present in the type B pattern, whereas the type D pattern gives a diffuse, and almost featureless band in this angular range.

Much interest attaches to materials which fall between types B and D. Figure 1C is a diffraction pattern of such a material. It resembles types B and D in that the 02,11 band is diffuse in the range $20° < 2\theta < 30°$ (CuKα radiation). The 20,13 band, $34° < 2\theta < 40°$, is less continuous than that in Fig. 1D but is less well resolved into separate reflections than in Fig. 1B. The basal reflections show about the same intensities as the peak of the 02,11 band. They are slightly enhanced as compared with the basal reflections in Fig. 1D, but are not enhanced much further even by intentional orientation procedures. This latter observation, together with the breadth of the 001 reflection and frequently some asymmetry in the profile, suggests curved layers akin to those in halloysites of type D.

The morphology of materials giving the type C diffraction pattern is variable. Negatively it can be said that the particles are not flat plates (this is consistent with the absence of marked ability to give preferential orientation), nor are they exactly like the well-formed tubes giving the type D pattern. There seems to exist an intermediate state which may be approached from either side, *i.e.*, flat sheets or laths may be in the process of curling and rolling and thus tending towards the tubular halloysite form, or halloysite particles may be splitting or unrolling as appears to be the case in Fig. 2C. It is consistent with this idea that type C patterns can be found which are closer to both type B and type D patterns. In other words, there exists a range of morphological forms and a range of diffraction patterns between the type B and type D states.

Distinctions Between Kaolinites and Halloysites

A basic question is where to draw the dividing line between kaolinites and halloysites.

The present writers suggest that the division comes between types B and C, and that the platy forms are kaolinite, and the rolled, curled, and tubular forms are halloysite. In other words, it is proposed that these names relate primarily to morphological varieties. This is largely in line with the description given by Bates and Comer (1959): they write,

> ". . . halloysite is used for material which appears in electron micrographs in the form of tubes or of laths with a large enough ratio of length/width to suggest a genetic relationship to tubes. The term kaolinite refers to platy particles that show 'pseudo hexagonal' angles and vary from equidimensional to elongate."

The present writers consider that the "genetic relationship" of Bates and Comer is an unnecessary qualification, and that a kaolinite flake, which is beginning to curl or roll and may (or may not) eventually attain the fully developed halloysite form, should be called halloysite as soon as a "significant" degree of rolling or curling has developed. It is difficult to give a precise definition of "significant" in this context, and herein lies the uncertain boundary between kaolinites and halloysites.

A second question can be asked as follows: If the names kaolinite and halloysite relate primarily to morphological varieties, can they be identified by *x*-ray powder diffraction? The preceding section has discussed *two* kinds of *x*-ray diffraction characteristics.

In the first place, stacking disorder of different kinds appears to be related to morphology. Platy forms exhibit disorder with respect to the *b* axis and may be called kaolinites. Forms which are disordered with respect to both *a* and *b* axes appear to be rolled, curled, or tubular and therefore should be called halloysites. But is the latter relationship a *necessary* relationship? It is conceivable that platy forms may exist with a high degree of disorder with respect to both *a* and *b* axes, and such forms would give diffraction patterns of type C or type D. Their platy morphology would require that they be called kaolinites, although the *x*-ray pattern would indicate halloysite. *One cannot presuppose that type C and type D x-ray patterns necessarily arise from curved layers.*

The second *x*-ray characteristic is the enhancement of basal reflections by preferential orientation of platy forms. A morphological distinction between kaolinite and halloysite may be recognized from this feature of the *x*-ray data. A "significant degree" of curling or rolling of layers might be considered as the amount required to inhibit a marked preferred orientation of well-dispersed kaolin particles.

It is possible that the present discussion is excessively cautious for it seems very likely that *most* kaolin clays with the high degree of stacking disorder shown by diffraction patterns of types C and D will owe this disorder to curvature of the layers and their resultant misfit. Therefore the present writers adopt the view that, generally, patterns of types C and D can be taken to indicate some form of halloysite, but it will be preferable to confirm this by morphological examination.

As will now be shown, the practical problems arising from mixtures of minerals are of major importance in the interpretation of *x*-ray diffraction patterns.

DIFFRACTION DATA FOR KAOLINITE-HALLOYSITE MIXTURES

Various mixtures have been studied showing the dominating effect of kaolinite on the *x*-ray diffraction patterns, and the results are illustrated in Figs. 3 and 4.

Figure 3 shows data for mixtures of a well-crystallized kaolinite (Sample #24; diffraction pattern Fig. 3A; electron micrograph Fig. 2E) and a well-formed halloysite (Sample 2007; diffraction pattern Figs. 3F and 1D; electron micrograph Fig. 2D). Additions of 5% and 10% kaolinite to halloysite, Figs. 3E, 3D, produce scarcely noticeable changes in the diffraction pattern, but with 20% and 25% kaolinite, Fig. 3C, the composite pattern resembles that of the type C material in Fig. 1C. With 40% kaolinite, Fig. 3B, the kaolinite characteristics are clearly seen, and in the absence of a very careful examination the material would be identified as a slightly disordered kaolinite, approaching nearer to type A than to type B. In other words, 60% halloysite is almost completely "submerged" by 40% of kaolinite.

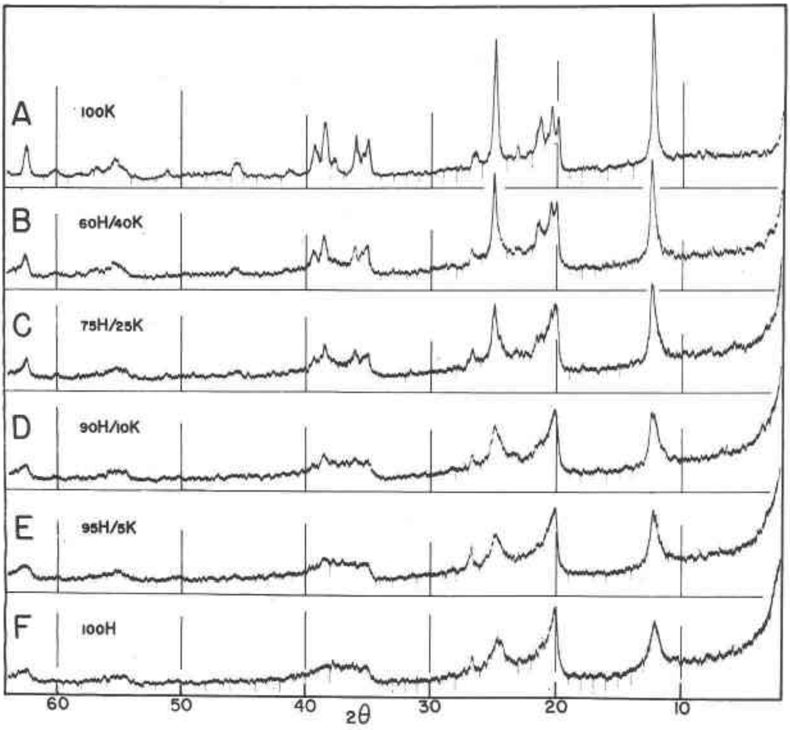

FIG. 3. *X*-ray powder diffraction patterns of prepared mixtures of kaolinite and halloysite in the proportions indicated. Kaolinite #24 (Minas Gerais, Brazil); Halloysite, 2007, (Utah, U.S.A.).

Figure 4 shows data for mixtures of the same kaolinite (Sample #24) with a second halloysite (Sample #59; diffraction pattern Fig. 4F; electron micrograph Fig. 2F). This halloysite appears lath-like and its diffraction pattern resembles the type C pattern in Fig. 1. It also contains a mica impurity, and the strong mica reflections are labelled M in Fig. 4F. No Fig. 4A is given for the pure kaolinite since this is already given in Fig. 3A. With a 5% addition of kaolinite, Fig. 4E, there is little change in the diffraction pattern, but with a 10% addition of kaolinite, Fig. 4D, the pattern begins to resemble that of type B in Fig. 1. With additions of 20% and 25% of kaolinite, Fig. 4C, the material would be identified as a kaolinite with some degree of *b*-axis disorder, probably nearer to type B than type A. With 40% of kaolinite in the mixture, the material would be recognized as approximating to a well-ordered kaolinite, and 60% of halloysite would be overlooked in all but the most careful *x*-ray examination. Even as much as 75% of halloysite could easily be overlooked in this series of mixtures.

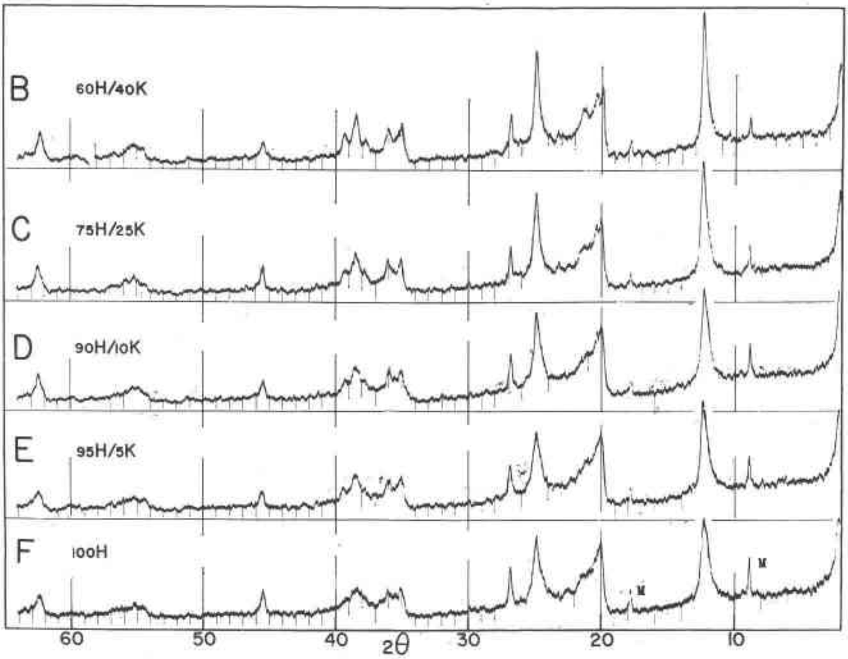

FIG. 4. *X*-ray powder diffraction patterns of prepared mixtures of kaolinite and halloysite. Kaolinite #24 (Minas Gerais, Brazil) and halloysite #59 (Minas Gerais, Brazil).

It is abundantly clear that kaolinite-halloysite mixtures can be misidentified very easily from *x*-ray powder diffraction data alone. Since the characteristics of the individual components affect the composite diagrams, one cannot say exactly how the resultant patterns depend on percentage amounts. However, it is certainly true that in the presence of kaolinite as much as 60% or even larger proportions of halloysite can be overlooked. If a clay is principally halloysite, probably no more than about 10–15% of kaolinite could be present without a significant modification of the diffraction pattern and a resulting misinterpretation of the nature of the material.

Electron Microscopy of Kaolin Clays

From the foregoing discussions it might appear that an electron microscopic examination of a kaolin clay would resolve the ambiguities of the *x*-ray data. However, electron microscopy also has its inherent problems. Provided techniques are employed which give a true sampling of the material and avoid accidental fractionation, then the microscopic data will resolve many of the ambiguities.

Tests made on the mixtures used for the *x*-ray work have shown that 10% of platy forms (*i.e.* kaolinite) will not be overlooked with proper sampling techniques, but in taking a drop of a dilute suspension this amount of kaolinite might easily be reduced to a proportion where it is overlooked. A mixture containing 60% or more of tubular or rolled halloysite would certainly reveal the halloysite in electron micrographs, but the converse question now arises: Could 20–40% of kaolinite be "lost" in an electron microscope examination? This question is of cardinal importance in relation to the tubular kaolins of Brazil and is discussed at length in the following paper. Therefore it will not be considered here, beyond the bald statement that without adequate care such an amount of kaolinite (*i.e.* platy forms) might be overlooked.

Conclusions

Essentially monomineralic kaolin minerals occur giving four recognizably different *x*-ray powder diagrams labelled types A, B, C and D. These correspond to increasing amounts of layer stacking disorder. A sequence of morphological forms also exists extending from platy crystals, through lath-like and curved forms, to fully rolled and tubular forms. It is suggested that "kaolinite" and "halloysite" be used primarily to distinguish platy forms from curved and rolled forms, but the dividing line is not sharp. *X*-ray diagrams of types A and B appear to correspond with kaolinite. Diagrams of types C and D are likely to correspond with curled and fully rolled forms of halloysite, but this correspondence may not hold in all cases. Preferential orientation due to platy morphology enhances basal reflections, and this enhancement or lack of it is a useful pointer to kaolinite or halloysite. Serious problems are shown to arise in the identification of kaolin minerals in mixtures of kaolinite and halloysite. As much as 60% or even more of halloysite may be overlooked in an *x*-ray diagram of a halloysite-kaolinite mixture. A clay containing mainly halloysite with 10–20% of kaolinite could be misinterpreted very easily from *x*-ray data alone. Electron microscopy can resolve these ambiguities, but unless suitable techniques are used, it also can lead to incorrect conclusions.

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