

EFFECTS OF MICRO-SIZED MIXTURES OF KAOLIN MINERALS ON PROPERTIES OF KAOLINITES

W. D. KELLER AND R. P. HAENNI

University of Missouri-Columbia

(Received 3 April 1978)

Abstract—“Kaolinites” from classic, large deposits of kaolin are shown commonly in scanning electron micrographs to be mixtures, at least in part, in microdimensions, of kaolin-mineral polymorphs.

Artificial mixtures of selected kaolin polymorphs simulating the natural mixtures, also micrographed, show crystallinities intermediate between the crystallinities of the end members in X-ray powder diffractograms. Thus, *apparent* crystallinity interpreted from diffractograms of a kaolin specimen may be a product of kaolin-mineral mixture in microdimensions as well as from ordering in the crystals. Evaluation of the crystallinity of a kaolin from powder diffraction may be suspect if independent means, such as SEM, are not used to assess the monomineralic character of that kaolin specimen.

Analogous to the apparent crystallinity of a “kaolinite” being the product of a mixture, so may other widely ranging properties of “kaolinite” be products of kaolin-mineral mixtures in microdimensions. These properties include DTA, IR, chemical composition, free energies of formation, and industrial applications.

Specifications for a monomineralic, nearly ideal kaolinite are considered—the Keokuk geode variety possesses desired crystallographic and chemical properties.

Key Words—Crystallinity, Halloysite, Kaolin, Kaolinite.

INTRODUCTION

Ideal kaolinite can be specifically defined in terms of crystal structure, chemical composition, and other mineralogic properties. In reality, however, and as described in the literature, the numerical data on the fundamental properties of “kaolinite” vary so widely that their limits are circumscribed with difficulty. From a viewpoint of orthodox mineralogy, a question may be asked if the mineral kaolinite does, indeed, vary that much inherently, or whether other external factors modify the data.

An example of wide variation in the degree of perfection of crystallinity in kaolinite was documented in the classic paper by Murray and Lyons (1956) where they showed the range to be from nearly perfect to extremely low in kaolinites from one region, “Georgia kaolin.” The degree of imperfection, and/or apparent imperfection, in crystallization of kaolinite, as determined by X-ray powder diffraction, has been attributed to variable quality of crystallization quantifiable by a crystallinity index (Hinckley, 1963), by defects in the crystals, and especially by degrees of order-disorder (Brindley and Robinson, 1946; Brindley, 1961; Plancon and Tchoubar, 1977).

We would add that the X-ray powder diffractogram includes effects of another factor which can be crucially important in interpreting the crystallinity of the “kaolinite.” This is the effect of a mixture in the X-ray specimen, of two or more kaolin minerals which may have widely disparate mineralogic properties. The purpose of this paper is to show evidence from scan electron micrographs (SEM) that such polymorphic kaolin minerals are, indeed, commonly and intimately inter-

mixed in microdimensions. Furthermore, when such mixtures are simulated, or reproduced artificially, they modify the powder diffractograms in proportion to minerals present. Inferences will be further drawn on the possibly confusing effect of mixtures of kaolin minerals on other mineralogic properties which unknowingly have been assigned to presumably “pure” kaolinite.

OBSERVATIONS FROM SCANNING ELECTRON MICROGRAPHS

A year ago, one of us (WDK) observed in a scanning electron micrograph (SEM), Figure 1, of kaolin-saprolite at Sparta, Georgia, a natural mixture of two kaolin minerals (plates and elongates) within the small area of an SEM field of view (Keller, 1977a). This specimen represents a randomly collected sample of residual saprolite over granite—not a sedimentary, transported mixture. This particular view of the specimen was positioned to show a ratio of about 50:50 for books and elongates. Quite obviously, the field of view could have been modified through a range from 0 to 100% elongates to 100% to 0 books by raising or lowering the specimen in the microscope. An analysis could, therefore, be run on this specimen so as to report characteristic properties for Sparta kaolin-saprolite all the way from those possessed by plates to those of elongate mineral. Quite probably the data on crystallinity in this specimen would thus be significantly different, depending upon where within the view it was taken.

Such variability in kaolin mineralogy is common in natural deposits and is widespread in occurrence. For example, a residual kaolin deposit on Belitung, Indonesia (Murray et al., 1974) contains both books and

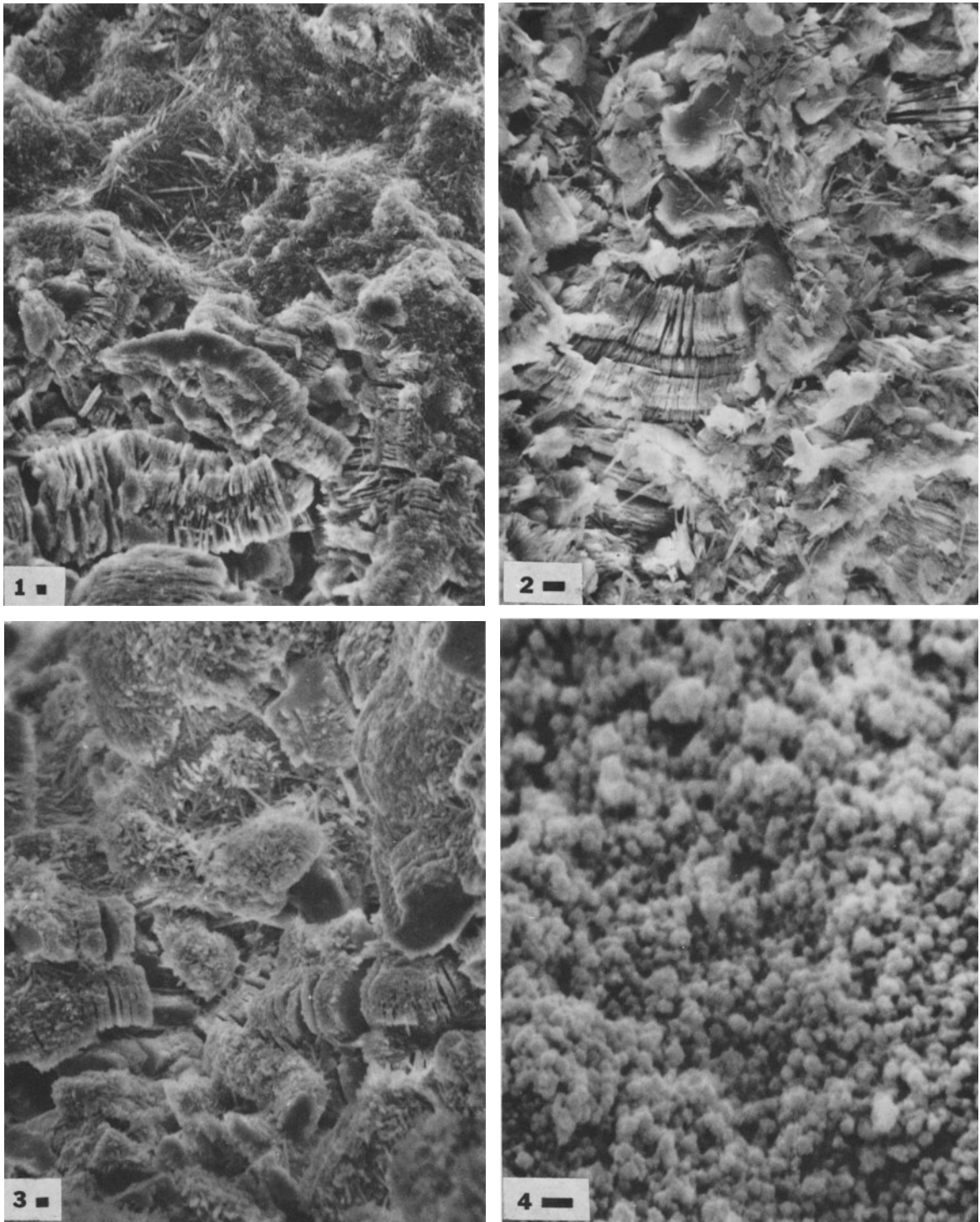


Fig. 1. Scan electron micrograph of sapolite on Sparta Granite, Martin Marietta quarry, Sparta, Ga. Note both plates of kaolinite and elongates of halloysite comprise this specimen of residual kaolin, 1000 \times . The length of the bar at the figure number represents 1 μ m, unless otherwise designated.

Fig. 2. Mixture of plates and elongates in residual kaolin, Belitung Island, Indonesia, 3000 \times . Specimen furnished by H. H. Murray.

Fig. 3. "Gaerome" ("Frog-eye") residual clay, Yamaka mine, Japan. Both books and elongates of kaolin are present, 2000 \times .

Fig. 4. Spherical halloysite weathered from pumice, Yamaka mine, Japan, 5000 \times .

elongates (Figure 2). In Japan, "Gaerome" residual kaolin, as from the Yamaka mine (Nagasawa et al., 1976), contains both morphologies (Figure 3). Furthermore, spherical halloysite (Figure 4) occurs in the same mine, (Yamaka) weathered from a layer of pumice (Nagasawa et al., 1976; Keller, 1977b). Hydrothermal kaolin at the largest kaolin deposit in Mexico, the Zaragoza mine in San Luis Potosí, Mexico, was illustrated by TEM to contain a mixture of plates and elongates (Keller and Hanson, 1968). At the Sombrerete, Mexico, hydrothermal deposit, veins of elongates transect bodies of platy kaolin (Keller and Hanson, 1969; illustrated by Keller and Hanson, 1975). Numerous publications in the past, e.g., Brazil kaolin by Brindley et al. (1963), have described, or illustrated with TEM, mixed morphologies of kaolin in commercial deposits. Indeed, Brindley et al. recognized in 1963 that a problem was created in kaolin mineralogy by mixtures of kaolin morphologies (plates and tubular or rolled halloysite) in a given sample. They were more limited, however, by the techniques of transmission electron microscopy (TEM) in 1963 than are available with SEM today.

X-RAY DIFFRACTOGRAMS OF MIXTURES OF KAOLIN MORPHOLOGIES

A convenient method to observe experimentally the effect of mixing kaolin morphologies on the crystallinity property of the specimen is by the X-ray powder diffractograms of the mixtures. Concurrently, SEM's may also be taken of the same mixtures. To this point, we mixed as "end members" a typical elongate kaolin, halloysite (2H₂O) from Spruce Pine, N.C., with, respectively, the API Reference kaolinite No. 6, McNamee Pit, Bath, S.C., the API Murfreesboro, AR, No. 1, and the exceptionally well-crystallized Keokuk-geode kaolinite (Keller et al., 1966).

The clays were scraped to a powder from the outcrop samples so as to avoid possible disordering which might have been caused by grinding. Dry portions of the clay powders were weighed in ratios of 25, 50, and 75% of Spruce Pine clay to the other kaolinities. These powders were further mixed by shaking in water (as in nonabrasive aqueous transport) for 12 hr on a mechanical shaker and subsequently dried. The mixed powders were mounted in aluminum holders for X-ray diffraction; Cu-K α radiation was used, and samples were run at 2° two-theta/min (also unpublished diffractograms at 1°/min). Additional runs were made at ¼°/min across 21–22° two-theta for resolving the 4.13 and 4.18 Å reflections, recommended by Brindley (1961) as follows: "the partial resolution of the doublet 11 $\bar{1}$ and 1 $\bar{1}$ 1, with spacings 4.18 and 4.13 Å as an indication of a well-crystallized kaolinite In diffractometer records, the 4.13 Å peak gives a step or inflection on the side of the 4.18 Å peak."

MIXTURES OF KEOKUK KAOLINITE AND SPRUCE PINE HALLOYSITE

The first illustrated example of kaolin mixture shows Spruce Pine halloysite with the Keokuk geode kaolinite (Hayes, 1963; Keller et al., 1966). The Spruce Pine clay is micrographed in SEM Figures 5 and 6, and its powder diffractogram shown in Figures 7E, 13E, and 17E. It is characteristically poorly ordered and, in the 21–22° enlargement, shows no hint of resolved 4.13 and 4.18 Å peaks. The Keokuk kaolinite is very well crystallized in external morphology (Figure 8). It is so well crystallized internally that the late W. F. Bradley found in "one sample of it all the X-ray reflections that have been reported for kaolinite" (oral communication) (Figure 7A). The supplementary trace (21–22°), extending from the main diffractogram to the left, shows the very strong 4.18 Å peak and the prominent shelf for the 4.13 Å reflection, as described by Brindley (1961).

In all the diffractogram traces shown, instrumental settings were the same so that peak dimensions can be directly compared.

A mixture of 75% (by weight) of Keokuk kaolinite with 25% S.P. (Spruce Pine) halloysite yields the diffractogram in Figure 7B, and the SEM in Figure 9. In the diffractogram all of the peaks, especially the 060, are slightly lower in height, than in Figure 7A. In the supplementary trace (21–22°) the 4.18 peak is lower and stubbier, and the 4.13 shelf is more tapered than in the 100% Keokuk. In the SEM (Figure 10) the mixing has resulted mainly in partial coating of some of the Keokuk plates.

In the 50:50 mixture (Figure 7C) the peaks in the diffractogram are about 70% of their heights produced from the unmixed Keokuk kaolinite. In the supplementary trace the 4.18 and 4.13 peaks are well resolved, although the height of the 4.18 peak is only slightly more than one half the height in Figure 7A. The Keokuk kaolinite maintains its crystallinity effect better in the 50:50 mixture than do the other kaolinities in the same ratio.

In the SEM (Figure 10) the elongates coat more of the plates than where they constitute 25% of the mixture; they have also aggregated, or segregated, to form small clumps that are about the same size as the stacks of Keokuk plates.

At 25 Keokuk:75 S.P. (Figure 7D) the peaks are noticeably subdued, and some are lost in both high- and low-intensity reflection angles. In the supplementary trace, the peak is one third the height of Figure 7A and the shelf of 4.13 is slanted. It is doubtful, if this X-ray trace were independently examined, that it would be interpreted to represent the presence of 25%, or any, of very highly ordered kaolinite as is the Keokuk. In the SEM (Figure 11) the coating of the plates is notably increased and clumps of the halloysite are nearly continuous.

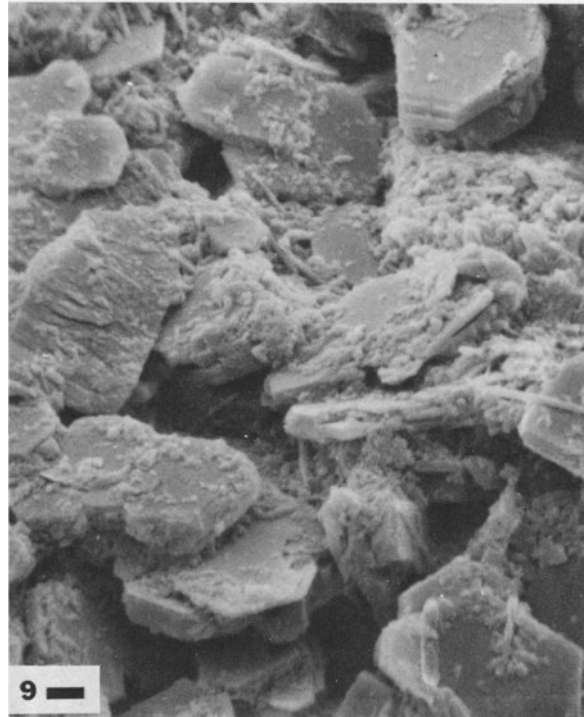
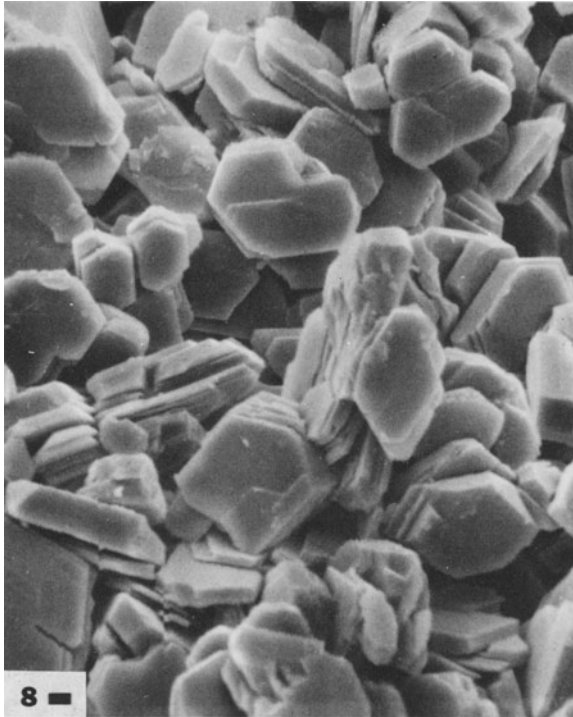
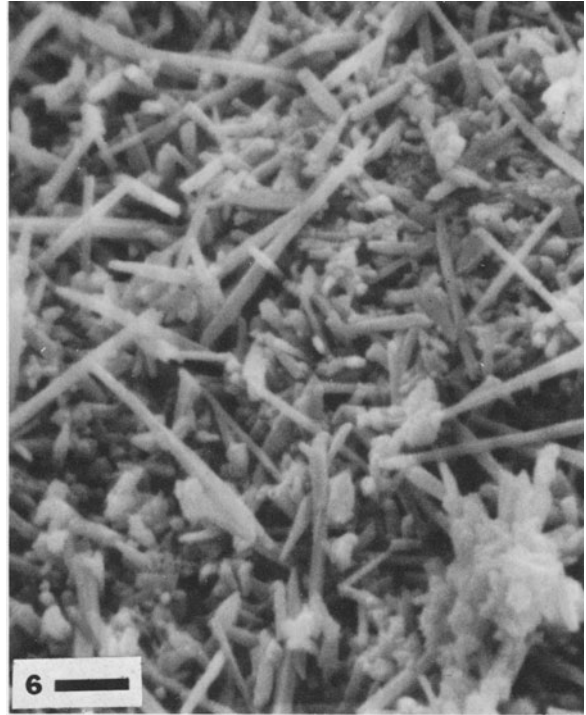
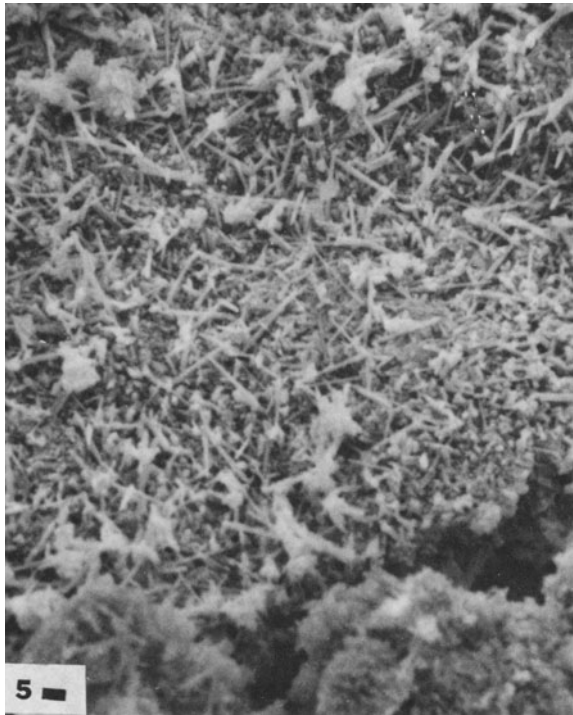


Fig. 5. Spruce Pine, N.C., halloysite, from the Gusher Knob locality, 3000 \times .

Fig. 6. Same specimen as Figure 5, 10,000 \times .

Fig. 8. SEM of Keokuk, Iowa, kaolinite, 3000 \times .

Fig. 9. SEM of mixture, 75 Keokuk:25 Spruce Pine, 5000 \times .

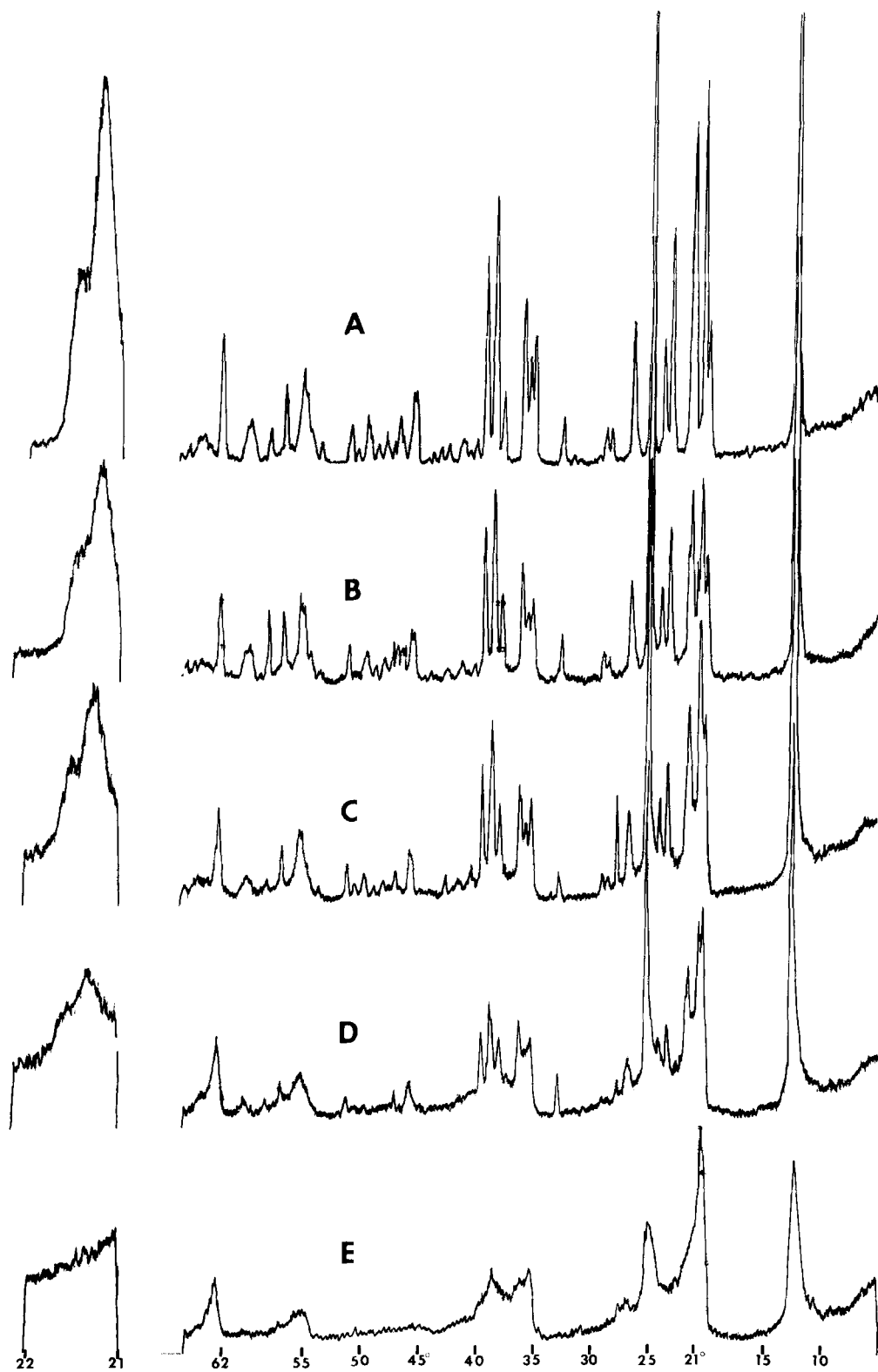


Fig. 7. X-ray diffractograms of Keokuk kaolinite, A; 75:25 ratio with Spruce Pine clay, B; 50:50 ratio, C; 25:75 ratio, D; Spruce Pine halloysite, E.

"GEORGIA-KAOLIN" TYPE AND SPRUCE PINE HALLOYSITE

To represent "Georgia kaolin," an API Reference kaolin, McNamee Pit, No. 6, Bath, S.C., was used. This sample is from the original API collection; therefore, the data in the original publication of API Project 49 may be validly used. The SEM of this kaolin is shown in Figure 12, and its X-ray powder diffractogram in Figure 13A. Although this kaolin is not nearly as well crystallized as is the Keokuk kaolinite, it is a fairly well ordered representative of commercial-size deposits. It displays peaks in the 10–65° diffractogram comparable to the 50:50 Keokuk-S.P. mixture.

Not much change in diffractogram occurs when 25% of the clay is replaced by S.P. halloysite (Figure 13B). The SEM (Figure 14) shows partial coating of the books and plates by elongates, analogous to that of 75% Keokuk clay.

With a 50:50 ratio (Figure 13C) some of the pyramidal reflections are either lost or significantly attenuated. Comparing this specimen with that of Figure 13A ("pure" McNamee), it clearly does not appear to be as well crystallized as Figure 13A. The rise in reflection between 21° and 22° has moved in the 21° direction. In the SEM (Figure 15) clumping of the larger quantity of Spruce Pine clay becomes more prominent.

In a 25:75 ratio of the McNamee kaolin to S.P. halloysite, the crystallinity and diffractogram (Figure 13C) have been dominated by the properties of halloysite. The sharpness of several peaks has been subdued to band-type reflection. In the 21–22° region, the reduced height of the rise is further moved toward the lower two-theta direction. The SEM (Figure 16) shows thick coating of elongates on the books, and interlacing clumps of the Spruce Pine clay.

MURFREESBORO KAOLINITE—S.P. HALLOYSITE MIXTURE

The Murfreesboro, AR, API kaolinite, No. 1, is one of the better-ordered kaolinites of the API Reference set (Figure 17A) although morphologically it resembles the McNamee (Georgia-type) more than the Keokuk clay (see SEM, Figure 18). In the supplementary diffractogram trace, the 4.18 Å peak is strong and high, but shows only a slant of the 4.13 reflection.

With reduction of kaolinite to a 75:25 ratio (Figure 17B), a considerable reduction in peak height results in a loss of the weaker reflections present in the "A" specimen. The height of the peak in the 21–22° area is reduced about 30% and the shape of the peak is changed.

Reduction to a 50:50 ratio (Figure 17C) continues the same trend as in Figure 17B. Likewise, the 21–22° reflection is diminished and, as with the McNamee kaolin, it has moved in the 21° direction. Comparing the 50:50 "C" diffractogram with the "A" (100% Murfreesboro) diffractogram, the crystallinity in "C" ap-

pears sufficiently lower that the "C" easily would be differentiable from the "A" clay. Thus, a 50:50 mix, as in the Sparta specimen (Figure 1) indeed produces a significant effect on apparent crystallinity. Its SEM (Figure 19) shows clumping of the elongates accompanied by coating of the relatively large aggregates of the Murfreesboro clay.

Where the halloysite fraction predominates, 25K:75H (Figure 17D), its diffractogram approaches that of 100% Spruce Pine halloysite (Figure 17E). The 21–22° reflection indicates low crystallinity. If specimen "D" were X-rayed from a newly collected field sample, not knowing that the specimen was mixed, it is doubtful that the crystallinity as interpreted from the diffractogram would be correlated with the degree of perfection seen in Figure 17A.

It can be safely concluded the X-ray powder diffractogram of an artificial mixture (and presumably a natural one) does not necessarily reveal the crystallinities of the end members.

CONCLUSIONS AND INFERENCES

Artificial mixtures of kaolin polymorphs yield X-ray powder diffractograms different from those of the end members, but are proportionally intermediate to them. Presumably natural mixtures would behave the same way.

Mixtures of kaolin plates and elongates in microdimensions, shown in SEM, are common in large, important kaolin deposits of the world.

An appraisal of the crystallinity of a kaolinite based on its X-ray powder diffractogram is vulnerable to error unless the specimen is independently confirmed to be monomineralic. SEM is useful to determine the homogeneity of a kaolin specimen.

Many reports in the literature on the crystallinity of kaolins and/or kaolin deposits fall in the category described above.

Generalizations interpreting the kaolin mineralogy, genesis, diagenesis, and geologic history of kaolin deposits based on diffraction data of specimens which have not also been examined by electron microscopy for mineral composition should be considered with caution.

It follows that reference samples of powdered "kaolinite" prepared by pulverizing and homogenizing a large quantity (hundreds of kilos) of kaolin will almost certainly be polymineralic in kaolin minerals! If so, such samples will not truly represent a kaolinite—one kaolinite—they represent kaolin. The tentative definition of kaolin suggested by the Committee on Correlation of Age and Genesis of Kaolin seems appropriate: "Kaolin is an earthy rock characterized by a significant content of kaolin minerals."

Likewise, experimental work otherwise carefully done is weakened in applicability if it is reported as rep-

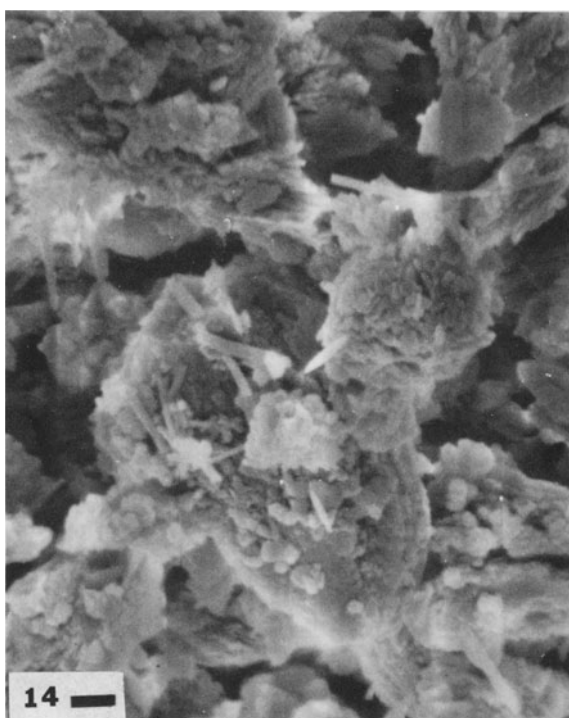
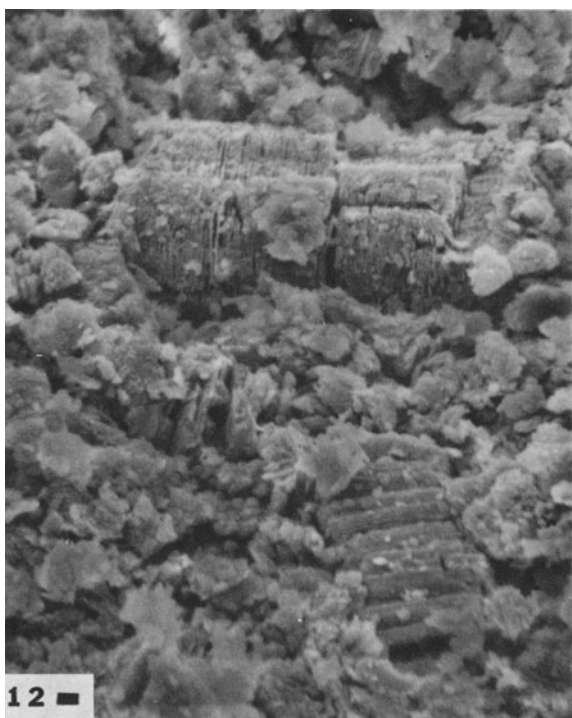
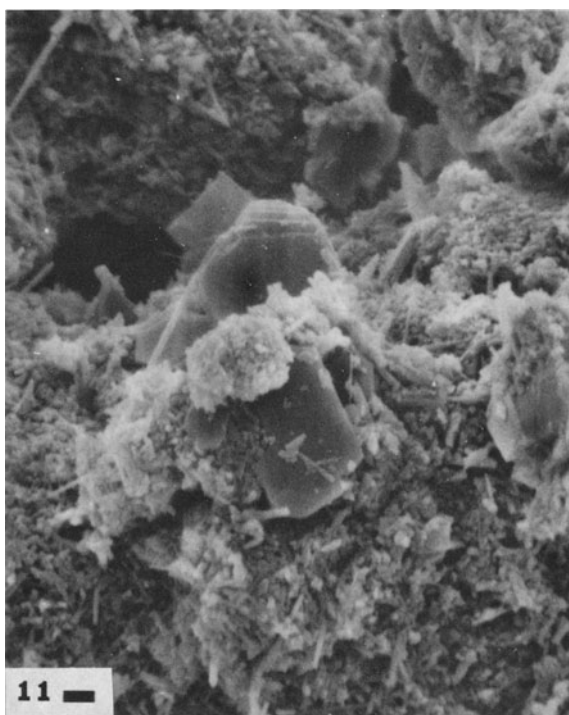
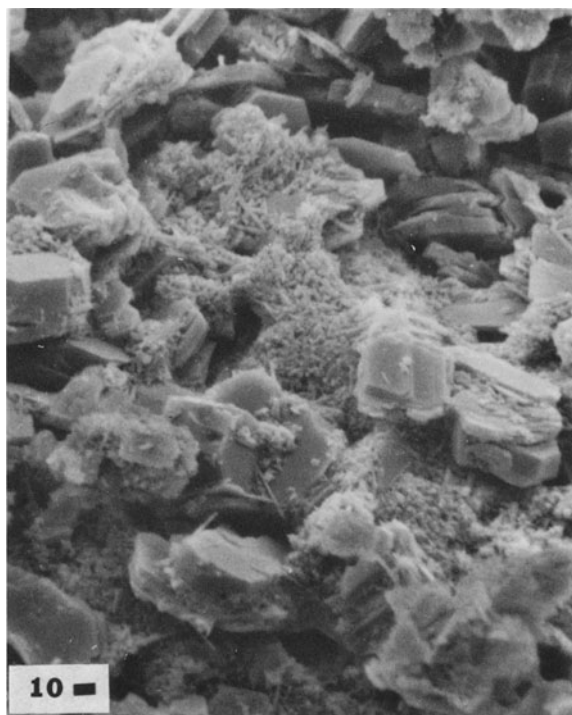


Fig. 10. SEM of mixture, 50 Keokuk:50 Spruce Pine, 3000 \times .

Fig. 11. SEM of mixture, 25 Keokuk:75 Spruce Pine, 4000 \times .

Fig. 12. SEM of API Reference kaolinite, McNamee Pit, Bath, S.C., No. 6, 3000 \times .

Fig. 14. SEM of mixture, 75 McNamee:25 Spruce Pine, 3000 \times .

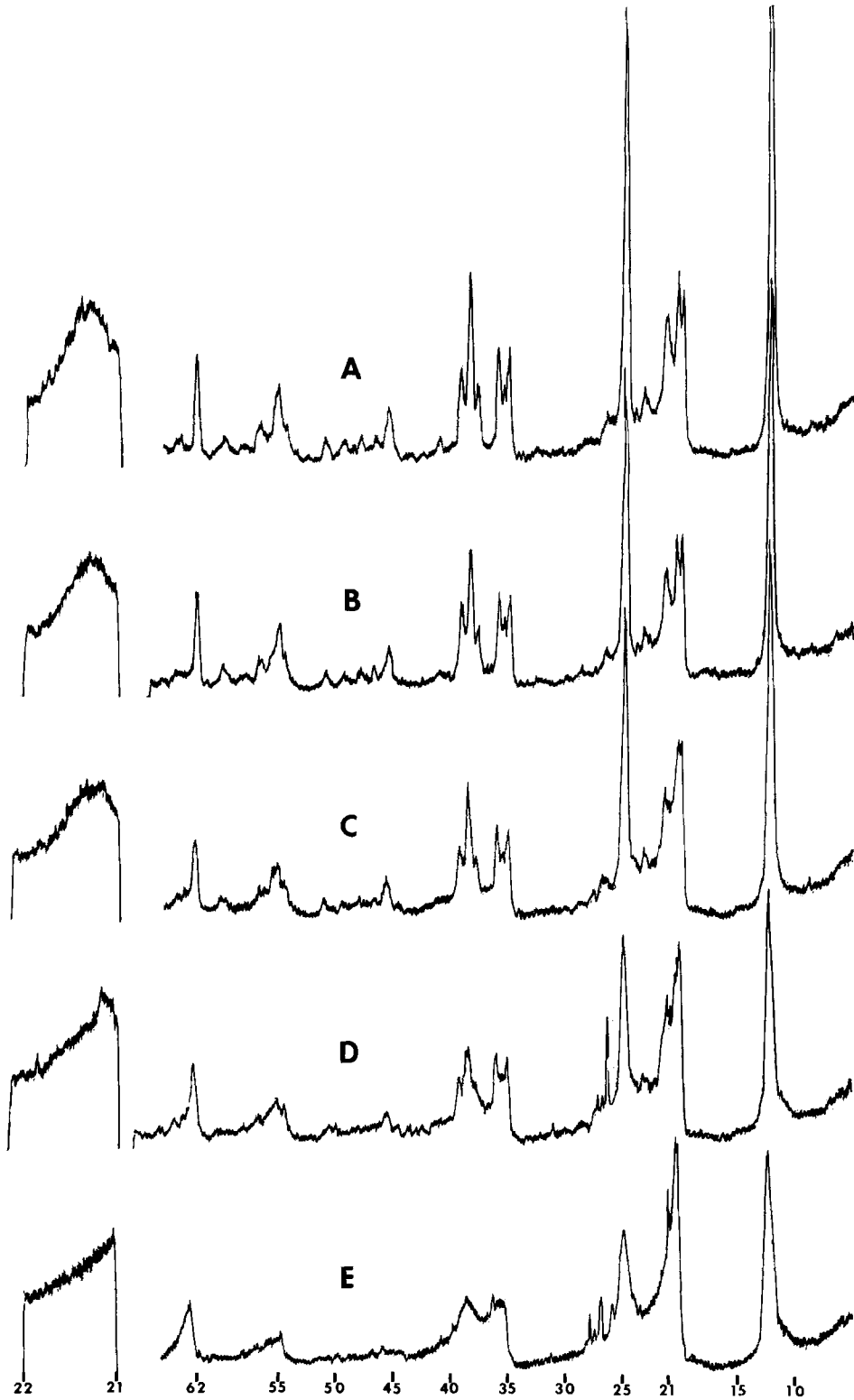


Fig. 13. X-ray diffractograms of McNamee kaolinite, A; 75:25 ratio with Spruce Pine clay, B; 50:50 ratio, C; 25:75 ratio, D; Spruce Pine halloysite, E.

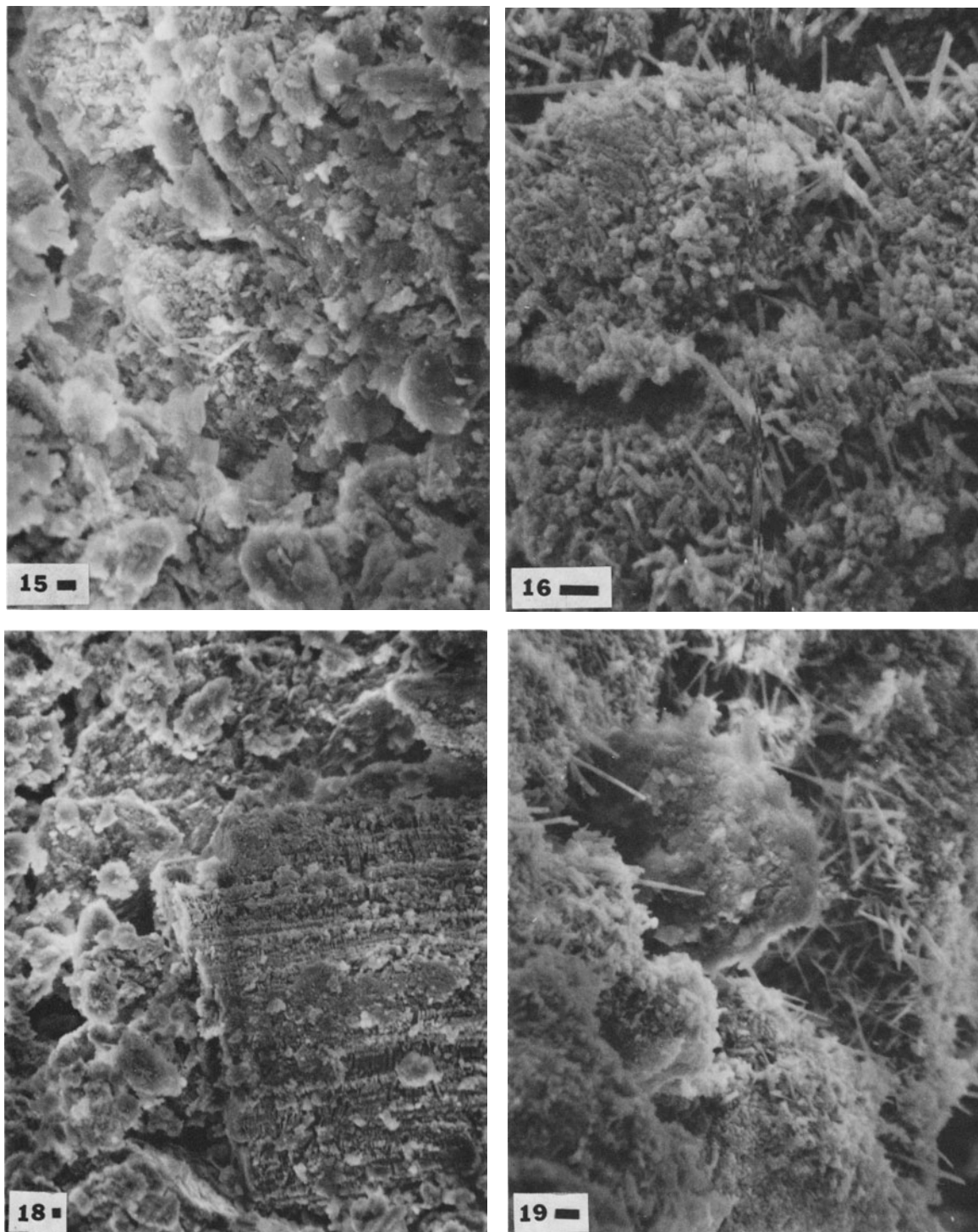


Fig. 15. SEM of mixture, 50 McNamee:50 Spruce Pine, 3000 \times .

Fig. 16. SEM of mixture, 25 McNamee:75 Spruce Pine, 5000 \times .

Fig. 18. SEM of API Reference kaolinite, Murfreesboro, Ark., No. 1, 1000 \times .

Fig. 19. SEM of mixture, 50 Murfreesboro:50 Spruce Pine, 4000 \times .

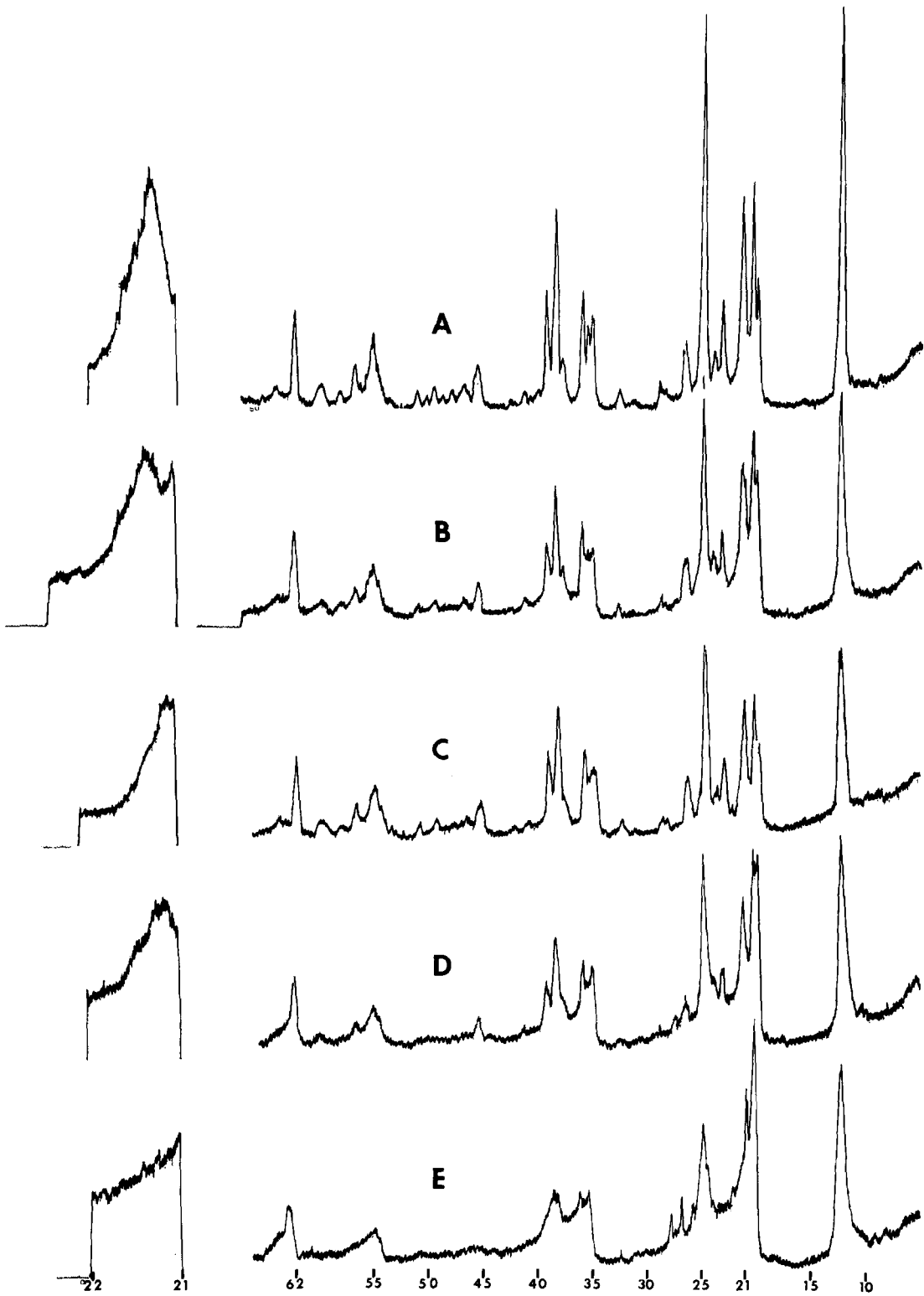


Fig. 17. X-ray diffractograms of Murfreesboro kaolinite A; 75:25 ratio with Spruce Pine clay, B; 50:50 ratio, C; 25:75 ratio, D; Spruce Pine halloysite, E.

representing a large region, e.g., "representing Georgia kaolin"—there are many varieties of "Georgia kaolin" (or Cornwall, Zettlitz, etc.).

Certain inferences and extrapolations to other important properties of kaolin seem to be logically justifiable, or at least merit consideration, from the observations made on X-ray powder diffractograms in this report, as follows. These include DTA, IR, bulk elemental chemical composition, and determination of free energies of formation.

The peak dehydroxylation temperatures of kaolin minerals determined with DTA apparatus range from about 540°C for halloysite (Bedford, Ind.; Spruce Pine, N.C., of Carter's Ridge 5) to 690°C for Keokuk kaolinite (API Reference Minerals, Preliminary Report No. 3; Keller et al., 1966). May not many, or at least some, of the intermediate values be products of mixtures of kaolin minerals in a polyminerale specimen?

The array of kaolin IR spectra in the IR Atlas by Van der Marel and Beutelspacher (1976) range, for example in the 3600 to 3800 wave-number interval for OH absorption, from two strong absorptions by halloysite to the four sharp absorption peaks for typical platy kaolinite. May not some of the intermediate spectra represent kaolin mixtures of microdimensions as in the Sparta saprolite (Figure 1)?

The chemical compositions of "kaolinites" apparently deviate as much from the ideal as do crystallinities, DTA, and IR. According to Weaver and Pollard (1973, p. 131), writing on kaolinite, "Although hundreds of chemical analyses of this clay have been made, there is still little known for certain about the exact composition of most (all?) samples. The ideal composition for kaolinites is: 46.54% SiO₂, 39.5% Al₂O₃, 13.96% H₂O, however, in nature, this exact composition is seldom, if ever, found." We suggest that most "kaolinites" are not mineralogically pure; they may contain traces of nonkaolin minerals and/or mixtures of kaolin polymorphs.

Values of the free energies of formation determined for kaolinite, and other kaolin minerals, have extended over a wider spread than seemed desirable. Reesman (1966) determined, by dissolution methods, the free energies of formation of 40 kaolin specimens from 31 domestic and foreign deposits. These included book or stack varieties, elongate halloysite and endellite, "fire clays," flint clays, ball clays, and hydrothermal and weathered types. These yielded values ranging from -896 kcal/formula weight (both Dry Branch, Ga., and halloysite-endellite, Bedford, Ind.) to -905 kcal/formula weight (Keokuk kaolinite). We had no satisfactory explanation in 1966 for so wide a variation in properties of what we thought to be a "single" mineral, kaolinite, but selected for publication a value preferred then (Reesman and Keller, 1968). Now, 12 years later, after seeing in SEM numerous mixtures of polymorphic

kaolin, the most reasonable explanation for much of the variability appears to be nonuniformity and nonhomogeneity in the mineralogy of the "kaolinite" specimens. If it is granted that different kaolins do, indeed, have different free energies of formation, some of the otherwise anomalous relationships in nature of kaolin minerals with other aluminum silicates are reconcilable.

In the industrial use of kaolin, e.g., in fillers, coating, refractories, etc., variations in properties within one geologic deposit are an almost universal experience. May they be due to mixtures of kaolin minerals in microdimensions?

In the face of many lines of evidence of wide diversity in kaolinite mineralogy, the question may be asked, "has an example of ideal, or near ideal, kaolinite been observed?" What should be its specifications? The Keokuk-geode kaolinite (Keller et al., 1966) approaches the ideal in kaolinite crystallinity, and its chemical composition is within analytical limits of the ideal composition. Its peak dehydroxylation temperature at 690°C is anomalous, or appears to be anomalous for most kaolin—but what is the ideal DTA dehydroxylation temperature of pure, well-crystallized kaolinite?

Pure, monomineralic kaolinite is elusive.

ACKNOWLEDGMENTS

The research for this paper was supported by the Earth Sciences Section, National Science Foundation, NSF Grant EAR 76-18804. Special thanks are due Prof. W. D. Johns for a constructive review of this paper.

REFERENCES

- API Reference Clay Minerals (1949) *Research Project 49, Reference clay localities, United States*, 2, 103 pp.
- Brindley, G. W. (1961) Kaolin, serpentine, and kindred minerals. In *The X-ray Identification and Crystal Structures of Clay Minerals* (Edited by Brown, G.), pp. 51-131. Mineral. Soc., London.
- Brindley, G. W., de Souza Santos, P. and de Souza Santos, H. (1963) Mineralogical studies of kaolinite-halloysite clays: Part I, Identification problems: *Am. Mineral.* **48**, 897-910. Part II: *Am. Mineral.* **49**, 1543-1548.
- Brindley, G. W. and Robinson, K. (1946) Randomness in the structures of kaolinic clay minerals: *Trans. Faraday Soc.* **42B**, 198-205.
- Hayes, J. B. (1963) Kaolinite from Warsaw geodes, Keokuk region, Iowa: *Iowa Acad. Sci. Proc.* **70**, 261-272.
- Hinckley, D. N. (1963) Variability in "crystallinity" values among the kaolin deposits of the coastal plain of Georgia and South Carolina: *Clays & Clay Minerals, 11th Nat. Conf.* pp. 229-235, Pergamon Press, Oxford.
- Keller, W. D. (1977a) Scan electron micrographs of kaolins collected from diverse environments of origin—IV. Georgia kaolin and kaolinizing source rocks: *Clays & Clay Minerals* **25**, 311-346.
- Keller, W. D. (1977b) Scan electron micrographs of kaolins collected from diverse environments of origin—V. Kaolins collected in Australia and Japan on field trips of the Sixth and Seventh Clay Conferences: *Clays & Clay Minerals* **25**, 347-364.
- Keller, W. D. and Hanson, R. F. (1968) Hydrothermal alteration of a rhyolite flow breccia near San Luis Potosi, Mexico, to refractory kaolin: *Clays & Clay Minerals* **16**, 223-229.

- Keller, W. D. and Hanson, R. F. (1969) Hydrothermal argillation of volcanic pipes in Mexico: *Clays & Clay Minerals* 17, 9–12.
- Keller, W. D. and Hanson, R. F. (1975) Dissimilar fabrics by scan electron microscopy of sedimentary versus hydrothermal kaolins in Mexico: *Clays & Clay Minerals* 23, 201–204.
- Keller, W. D., Pickett, E. E. and Reesman, A. L. (1966) Elevated dehydroxylation temperature of the Keokuk geode kaolinite—a possible reference mineral: *Proc. Int. Clay Conf.*, Jerusalem 1, 75–85.
- Murray, H. H. and Lyons, S. C. (1956) Correlation of paper-coating quality with degree of crystal perfection of kaolinite: *Proc. 4th Clay Conf.*, NAS-NRC Pub. 456, 31–40.
- Murray, H. H., Partridge, P. and Post, J. L. (1974) Residual kaolin formation on the Island of Belitung, Indonesia: *Abstr. 23rd Annu. Clay Minerals Conf.*, p. 49.
- Nagasawa, K., Tsuzaki, Y., Takeshi, H. and Togashi, Y. (1976) Geology of the Seto, Shokoan, and Itaya Kaolin Deposits, A Guide to Field Investigations, 7th Symp. on Genesis of Kaolin: Mimeographed Field Guide distributed by H. Minato, 31 pp.
- Plancon, A. and Tchoubar, C. (1977) Determination of structural defects in phyllosilicates by X-ray powder diffraction—I. Principle of calculation of the diffraction phenomena—II. Nature and proportion of defects in natural kaolinites: *Clays & Clay Minerals*, 25, 430–450.
- Reesman, A. L. (1966) A study of clay mineral dissolution: Ph.D. Thesis, University of Missouri-Columbia.
- Reesman, A. L. and Keller, W. D. (1968) Aqueous solubility studies of high-alumina and clay minerals: *Am. Mineral.* 53, 929–942.
- Van der Marel, H. W. and Beutelspacher, H. (1976) *Atlas of infrared spectroscopy of clay minerals and their mixtures*: Elsevier, Amsterdam, 396 pp.
- Weaver, C. E. and Pollard, L. D. (1973) *The chemistry of clay minerals*: Elsevier, Amsterdam, 213 pp.

Резюме- "Каолиниты" из классических, больших месторождений каолина, на микро-снимках, сделанных с помощью развертывающего электронного микроскопа, обычно выглядят как смеси, по крайней мере частично, в микро-размерах, каолин-минеральных полиморфных веществ.

Искусственные смеси выбранных каолиновых полиморфных веществ, моделирующих естественные смеси, на микроснимках также выявляют кристалличность, промежуточную между конечными членами на дифрактограммах, полученных порошковым методом рентгеноструктурного анализа. Таким образом кажущаяся кристалличность, определяемая по дифрактограмме образца каолина, может быть результатом каолин-минеральной смеси в микро-размерах, а также следствием упорядочения в кристаллах. Оценка кристалличности каолина по данным порошковой дифракции может быть сомнительной, если не использовать независимые средства, такие как РЕМ, чтобы оценить мономинеральный характер данного образца каолина. Аналогично кажущаяся кристалличности "каолинита", которая на самом деле является продуктом смеси, другие многочисленные свойства "каолинита" могут быть продуктами каолин-минеральных смесей в микро-размерах. Эти свойства включают ДТА, ИКС, химический состав, свободные энергии формирования и особенности промышленных применений.

Рассматриваются характерные особенности образца мономинерального, близкого к идеальному, каолинита-разновидности жеоды Кеокук, имеющей требуемые кристаллографические и химические свойства.

Kurzreferat- Es kann gezeigt werden durch SEM Messungen, daß 'Kaoliniten' aus klassischen, großen Kaolinablagerungen im allgemeinen, wenigstens zum Teil in Mikrodimensionen aus Mischungen von Kaolinmineralpolymorphen bestehen. Künstliche Mischungen von ausgesuchten Kaolinpolymorphen, welche die natürlichen Mischungen simulierten, zeigten in SEM Kristallinitäten, welche zwischen den Kristallinitäten der Endmitglieder in Röntgenpulverdiagrammen liegen. Daher kann es sein, daß die scheinbare Kristallinität, die von Pulverdiagrammen eines Kaolins interpretiert wurden, ein Produkt einer Kaolinmineralmischung, sowohl von Mikrodimensionen wie auch von der Ordnung in den Kristallen her gesehen, ist. Auswertung der Kristallinitäten eines Kaolins durch Pulverdiagramme kann verdächtig sein, falls unabhängige Messungen wie SEM nicht benutzt werden, um den monomineralischen Charakter der Kaolinprobe zu bestimmen. In Analogie zu der scheinbaren Kristallinität eines Kaoliniten, das ein Produkt einer Mischung ist, kann es sein, daß andere weitreichende Eigenschaften von Kaolinit Produkte von Kaolinmineralmischungen sind. Diese Eigenschaften umfassen DTA, IR, chemische Zusammensetzung, Freie Energien der Formation und industrielle Anwendungen. Spezifizierung für eine Probe eines monomineralischen, fast idealen Kaoliniten werden berücksichtigt--die Keokukgeodenart besitzt die gewünschten kristallographischen und chemischen Eigenschaften.

Résumé—Les "kaolinites" provenant de larges dépôts classiques de kaolin apparaissent souvent dans les micrographes électroniques comme des mélanges, du moins en partie, en micro-dimensions, de polymorphes du minerai kaolin. Des mélanges artificiels de polymorphes de kaolin sélectionnés simulant les mélanges naturels, également micrographiés, montrent des cristallinités intermédiaires entre les cristallinités des termes extrêmes des diffractogrammes aux rayons-X. Ainsi la cristallinité apparente interprétée des diffractogrammes d'un échantillon de kaolin peut être le produit d'un mélange de minerai de kaolin en micro-dimensions, de même que d'un rangement dans les cristaux. L'évaluation de la cristallinité d'un kaolin par diffraction poudrée peut être suspecte si une méthode indépendante, telle le microscope électronique, n'est pas utilisée pour assurer le caractère monominéral de cet échantillon de kaolin. De même que la cristallinité d'une "kaolinite" peut être le produit d'un mélange, d'autres propriétés très variées de la "kaolinite" peuvent être les produits de mélanges du minerai kaolin en micro-dimensions. Ces propriétés comprennent l'analyse thermique différentielle (D T A), I R, la composition chimique, les énergies libres de formation et les applications industrielles. Des spécifications pour un spécimen d'une kaolinite monominérale, quasi idéale, sont considérées -- l'espèce de la géode Keokuk possède les propriétés cristallographiques et chimiques voulues.