# STUDY OF SOME CHEMICALLY ANALYZED OHIO CLAYS BY X–RAY DIFFRACTION AND DIFFERENTIAL THERMAL ANALYSIS

DUNCAN McCONNELL, ALFRED A. LEVINSON AND LIBERTO DE PABLO–GALAN

*Department of Mineralogy, College of Engineering, The Ohio State University, Columbus 10*

Several studies of Ohio clays have been completed in past years principally by means of chemical and microscopic methods, and the results were related to ceramic properties and uses. Noteworthy among the earlier studies are those of Stout *et al*. (1923) on the coal formation clays; Lamborn *et al*. (1938) on shales and surface clays; Stout *et al*. (1931) on the Lawrence clay; and Stout (1940) on the Clarion clay. Recently the use of two methods of mineralogical analysis, namely x-ray diffraction and differential thermal analysis (d.t.a.), have become increasingly significant in their adaptability to the study of clays and shales. These techniques reportedly lend themselves to quantitative or semi-quantitative determinations of the minerals present in clays.

The earlier studies made no attempt to determine the relative amounts of the individual mineral species found in the clays although it was realized that the variations in the mineral content were responsible for the variations in the ceramic properties. As an initial project of several proposed investigations of Ohio clays, about 40 of the chemically analyzed and petrographically examined coal formation clays, originally described by Stout *et al*. (1923), were restudied by the more modern x-ray and d.t.a. methods. This study had the objectives of (1) determining quantitatively the minerals present, (2) attempting to correlate the chemical data with the several mineralogical phases present, and (3) evaluating the ceramic characteristics in terms of differences in mineral compositions.

All specimens studied are from clays which underlay the coals of Pennsylvanian age in eastern and southeastern Ohio. A detailed description of each clay, including its geological and geographical occurrence, as well as the results of petrographic study and ceramic tests, are given in Stout *et al*. (1923). Each sample studied and reported in this paper is numbered to correspond with the page in Stout *et al*. (1923) on which the chemical analysis appears. Other pertinent data, such as the petrographic examination and ceramic tests, are given in appropriate sections of the same work.

## EQUIPMENT AND METHOD OF STUDY

Differential thermal analysis (d.t.a.) consists of detecting and recording thermal effects that occur at different temperatures. As applied here, it measures the changes in thermal energy content of a material while the temperature is raised 10° per min. from room temperature to about 1050°C. The equipment used in this study is essentially identical with that described by McConnell and Earley (1951). Thermograms were obtained for all samples except number 127.

Filtered copper x-radiation was used throughout the study. Powder diffraction photographs (using a camera diameter of 114.6 mm.) and x-ray goniometric measurements were obtained for all samples using the Norelco "large-angle" apparatus. For these measurements, bulk samples were used, rather than fractions (*e.g.*, finer than 2 microns), because: (1) there is reason to believe the samples had been ground prior to chemical analysis at the time of original study (Stout *et al*., 1923), and thus the present size distribution is not representative of the original clay; (2) only small amounts of some specimens were available; (3) experimentation has shown that the same proportions of the clay minerals are indicated by bulk

samples as by sedimented fractions, although the intensity maxima for sedimented materials are usually larger; and (4) the chemical analyses were made on the same bulk clays rather than any particular fraction. The use in our x-ray studies of compacted samples, rather than sedimented samples, seems to be justified by the results of Mitchell (1953). He found that well oriented samples could be obtained by compaction.

Without additional qualitative mineralogical information, a chemical analysis of a clay is of limited value in deducing either the mineral composition of the clay or its usefullness to the ceramic industry. For example, the following samples, all from the same clay bed (Lower Kittanning) and from the same mine in Tuscarawas County, show the following percentages of some significant constituents (Stout *et al.*, 1923):

| Number | SiO₂ | Al₂O₃ | K₂O | Position in bed |
|--------|------|-------|-----|-----------------|
| 313 | 54.16 | 25.12 | 1.71 | Top |
| 314 | 52.31 | 29.52 | .34 | Middle |
| 316 | 55.93 | 24.83 | 3.02 | Lower part |

If it is known that these clays contain kaolinite and mica, however, the ratios of these minerals might be surmised from the $K_2O$ content to be approximately $1:1.2$, $1:0.3$ and $1:2.2$, respectively, as found by a combination of methods. McCaughey (Stout *et al.*, 1923) employed the petrographic microscope, whereas the present investigations attempted to obtain correlations by other means.

The quantitative estimations by means of x-ray diffraction were made by using the method of Murray (1954a). Murray (p. 57) calculated the theoretical diffracting power of the (001) plane of kaolinite to be about three times that of the (001) plane of a mica (so-called "illite"). From measurement of the intensities from the basal planes of kaolinite and "illite," the relative proportions of these clay minerals were determined. The method is subject to criticism, however, because it is known that kaolinites and "illites" show variable intensities of reflection depending upon differences in perfection of crystallization, isomorphous substitution (particularly of Fe), and crystal size. Nevertheless, this method still seems to be reliable and, as will be shown below, other methods are less so. This procedure appears to give good semi-quantitative results.

Qualitative or semi-quantitative information was obtained also from the powder diffraction patterns and from the thermograms. Finally the chemical data were calculated in such a manner as to give the best correlations with the other determinations.

### MINERALOGICAL COMPOSITION OF THE CLAYS

As pointed out by Stout *et al.* (1923) the clays of Ohio are rocks; that is, they are composed of several minerals in varying proportions and are rarely uniform for any large area. In particular, the Ohio underclays are composed chiefly of a micaceous constituent, kaolinite and quartz. Usually these three principal minerals comprise 90 to 95 percent of the clay. Other substances found in small amounts in practically all the underclays are rutile, limonite, pyrite, siderite and organic matter. Occasionally, calcite, dolomite, zircon, tourmaline, etc. were found. Our discussion of the minerals in the clays will be limited primarily to the micaceous mineral, kaolinite, and quartz, although other minerals that were detected by d.t.a. or x-ray analysis will be noted.

### *The Micaceous Minerals*

In his petrographic descriptions of the individual samples, McCaughey (Stout *et al.*, 1923) refers to "muscovite" and "sericite," the distinction being that the

former occurs as bright, splendent flakes of relatively large size usually in the "sand" fraction, whereas the latter occurs as fine needles or shreds in the "clay" portion. The term "illite," which is commonly used today to describe the micaceous constituent of argillaceous sediments, was not proposed until 1937 by Grim, Bray and Bradley. "Illite" has subsequently been applied to micas with a considerable range in composition, some of which are high in silica and water and low in potash when compared with muscovite (Grim et al., 1937). Other persons have used "illite" for micas of sedimentary rocks which have a normal silica content but are high in water and low in potash. The latter are often called hydromuscovite or hydrous mica. Carr et al. (1953) have described hydrous mica from a Yorkshire fireclay, which is considered to be remarkably well developed and has a normal silica content. It is possible that the material originally called "muscovite" (Stout et al., 1923) may be similar in composition as well as size and crystalline development but, inasmuch as the pure mica has not been chemically analyzed, this supposition cannot be verified.

A small amount of coarse-grained mica of specimen 342 has been isolated from the fraction which did not pass a 50 mesh screen, and some flakes are as large as ¾ mm. Although a detailed description of the micaceous constituents in the Ohio underclays has not been undertaken, preliminary examination shows the mica to have the optic angle characteristic of muscovite (approx. 35°). X-ray study indicates that this mica is the 2-layer monoclinic (2M) muscovite-type polymorph. In order to compare the crystalline properties of the large mica flakes with the fine-grained material ("sericite") from the same sample, a fraction which passed the 325 mesh screen was heated at 600°C for half an hour so that the structure of any kaolinite present would be destroyed. Only the x-ray diffraction lines characteristic of a 2M polymorph (in addition to weak lines of quartz) were observed, indicating that the coarse and fine flakes are virtually identical structurally after such treatment. The fine-grained mica of specimen 206 was studied similarly with similar results. In both cases the x-ray lines were remarkably sharp considering the small particle size. An attempt was made to determine the structure of the micaceous constituent in the fine fractions (2 microns and finer) of several specimens, but the results were inconclusive. The various mica polymorphs of illite or hydrous mica, as well as their identification, are discussed by Levinson (1955) and Yoder and Eugster (1955).

Table 1 shows that the micaceous constituent is commonly the most abundant of the clay minerals and also the most abundant of all minerals. Further investigation of the micaceous minerals in the underclays may reveal that the coarse-grained flakes have chemical properties similar to those of the hydrous mica described by Carr et al. (1953), whereas the finest grained mica may have a chemical composition similar to the illites described by Grim (1937). It is also possible that polymorphic structures other than 2M will be found. In addition some mixed-layer clays may be present because a few specimens (402, 453, 468, etc.) show the normal 10Å mica reflection to be broad and slightly displaced toward a smaller diffraction angle. Treatment with ethylene glycol failed to indicate any expandable layers among those specimens with suspected mixed-layers structures, but the possibility of a chlorite or some other non-expandable mixed-layer clay mineral remains. The thermograms, with the possible exception of specimens 313, 314, 327 and 402, show no indication of any clay mineral other than kaolinite or illite, although admittedly some of the thermal reactions could be too small to be recorded. The same four specimens showed a small endotherm at approximately 750°C. Although this valley is characteristic of some chlorites, no chlorite could be positively identified by x-ray methods and thus the significance of this d.t.a. inflection remains to be explained. On the basis of the work of Yoder and Eugster (1955) montmorillonite or some mixed-layer structure was suspected, but none could be identified with certainty either by d.t.a. or x-ray methods.

## Kaolinite

Throughout the work of Stout *et al.* (1923) "clay" has been used both to denote a fine particle size (the clay separate or fraction) and a rock composition—principally a mixture of a mica, kaolinite and quartz. Only in a few places does "kaolinite" appear in the mineralogical descriptions. However, it should be emphasized that it is kaolinite which gives some of the Ohio clays their plasticity and other desirable ceramic properties.

TABLE 1

*Ratios of illite to kaolinite and types of thermograms for Ohio coal measure clays*

| Sample Number* | Source Formation | Illite to Kaolinite | Thermogram |
|---|---|---|---|
| 127 | Sciotoville | 0.3 | Not obtained |
| 140 | Sciotoville | 3.3 | Type 2 |
| 152 | Quakertown | 4.5 | Similar to type 2 |
| 164 | Middle Mercer | 4.0 | Similar to type 2 |
| 170 | Flint Ridge | 1.4 | Type 4 |
| 178 | Flint Ridge | 2.2 | Similar to type 2 |
| 184 | Upper Mercer | 3.7 | Similar to type 2 |
| 193 | Bedford | 2.4 | Similar to type 2 |
| 199 | Tionesta | 0.8 | Similar to type 1 |
| 206 | Tionesta | 1.5 | Similar to type 4 |
| 210 | Tionesta | 2.0 | Similar to type 4 |
| 230 | Brookville | 3.0 | Similar to types 3 (pyrite) and 4 |
| 233 | Brookville | 0.9 | Similar to types 3 (pyrite) and 4 |
| 236 | Brookville | 1.9 | Similar to type 4 |
| 252 | Clarion | 1.8 | Similar to type 4 |
| 258 | Clarion | 0.8 | Similar to type 1 |
| 262 | Clarion | 1.7 | Similar to type 4 |
| 264 | Clarion | 2.1 | Similar to type 2 |
| 279 | Lower Kittanning | 1.1 | Similar to type 4 |
| 291 | Lower Kittanning | 1.6 | Similar to type 4 |
| 301 | Lower Kittanning | 0.8 | Similar to type 4 |
| 307 | Lower Kittanning | 1.0 | Similar to type 4 |
| {313** | Lower Kittanning | 1.2 | Similar to types 3 (pyrite) and 4 |
| {314 | Lower Kittanning | 0.3 | Similar to types 1 and 3 (pyrite) |
| {316 | Lower Kittanning | 2.2 | Similar to types 2 and 3 (pyrite) |
| 324 | Lower Kittanning | 1.1 | Similar to type 4 |
| 327 | Lower Kittanning | 0.0 | Similar to types 1 and 3 (pyrite) |
| {341 | Lower Kittanning | 1.7 | Similar to types 3 (pyrite) and 4 |
| {342 | Lower Kittanning | 2.9 | Similar to types 2 and 3 (pyrite) |
| 346 | Lower Kittanning | 2.5 | Similar to types 2 and 3 (pyrite) |
| 348 | Lower Kittanning | 2.9 | Similar to types 2 and 3 (pyrite) |
| 350 | Lower Kittanning | 2.7 | Similar to types 2 and 3 (pyrite) |
| 375 | Oak Hill | 2.4 | Similar to type 2 |
| 379 | Oak Hill | 0.0 | Type 1 |
| 402 | Middle Kittanning | 1.5 | Similar to types 3 (pyrite) and 4 |
| 404 | Middle Kittanning | 2.8 | Similar to types 2 and 3 (pyrite) |
| 412 | Middle Kittanning | 3.2 | Similar to type 2 |
| {437 | Upper Freeport | 1.8 | Similar to type 2 |
| {438 | Upper Freeport | 2.5 | Similar to type 2 |
| 446 | Mahoning | 1.4 | Similar to type 4 |
| 453 | Anderson | 3.0 | Similar to types 2 and 3 (calcite) |
| 468 | Meigs Creek | 4.0 | Similar to type 3 and 3 (pyrite and coal) |

* The number of each sample corresponds with the page in Stout *et al.* (1923) on which the chemical analysis of the sample is given. Detailed mineralogical descriptions and results of ceramic tests may be found on the same and adjoining pages of the same reference.

** Specimens such as 313, 314 and 316, which are bracketed, are from different elevations of the same clay formation at one particular location.

Brindley and Robinson (1947) have shown that the kaolinite-type mineral found in fireclays (synonymous with underclay or "coal measures" clay) is structurally distinctive from other kaolinite-type minerals. In particular, it appears to be a member of the series intermediate between very well crystallized kaolinite which gives sharp diffraction lines and very poorly crystallized meta-halloysite which generally gives broad, diffuse bands. Murray (1954b) has studied a similar series and shown that there are characteristic differences in the size of d.t.a. inflections among kaolinites, depending upon the perfection of crystallization.

Using the criteria established by Brindley and Robinson (1947) and Murray (1954b), we have found that the kaolinite in the coal formations is of two general types. The flint clays (314, 327, 379) and specimen 127 have structures which may be classed as well crystallized kaolinites; noteworthy is the fact that these are the clays with smallest concentrations of mica and quartz. The high degree of crystallinity is implied by the intense reflections at approximately 4.35 and 4.17 Å. Furthermore, reflections at 4.17 and 4.12 Å were resolved for the three flint clays, thus satisfying Brindley's (1951 p. 51) criterion for a well crystallized kaolinite. All other kaolinites of the underclays give x-ray patterns which are characterized by a poorer degree of crystallinity, either similar to Brindley and Robinson's (1947) "fireclay" with a weak reflection at about 4.14 Å, or similar to the better of the several poorly crystallized kaolinites described by Murray (1954b) as not giving this reflection. Nevertheless, these kaolinites do not approach closely either metahalloysite or dehydrated halloysite of the authors cited. In general, it may be said that the vast majority of kaolinites in the underclays show similarities in crystallographic perfection; the four notable exceptions have been cited above.

### Quartz

The third abundant mineral in the underclays is quartz. It is found in two types of occurrence: (1) in relatively coarse and probably detrital grains in the "sand" fraction or (2) as very small grains intimately associated with the kaolinite and illite of the clay fraction and in clay aggregates. Stout et al. (1923, p. 519) suggest the possible occurrence of some secondary quartz in the form of chalcedony. The quantity of quartz varies considerably. In a few cases it may be virtually absent, as in specimen 127, whereas in others (e.g., specimen 342) it may compromise at least 40 percent of the clay.

### DIFFERENTIAL THERMAL ANALYSIS

Figure 1 illustrates several characteristics of the thermograms obtained from the Ohio clays, as well as those for several pure minerals. As a generalization the following types are represented:

(1) *High-kaolinite clays* exhibit a large endothermal valley at about 600°C and a large exothermal peak at about 950°C. The 950°C peak is uniquely attributable to kaolinite, and its intensity has been used by some persons as an indication of the degree of crystallinity. The 600°C valley, on the other hand, may result in part from the thermal effects of illite and quartz. The high-kaolinite clays are usually low in illite and quartz and are illustrated ideally by the flint clays.

(2) *High-illite*, low-kaolinite clays exhibit subdued endothermal valleys at 600°C because the thermal reaction of illite is proportionately much smaller than that of kaolinite. They give a subdued, broad, exothermal 950°C peak because of the low kaolinite content. A second endothermal valley for illite (at about 900°C) precedes the 950°C exothermal peak of kaolinite and is often discernable. The relative intensities of the 900°C and 950°C inflections may be used as a rough indication of the clay mineral content. A clay high in quartz, low in illite and containing some kaolinite would give a similar curve.

(3) *Clays with specific impurities* are easily recognized. Pyrite, for example, can be detected in concentrations as small as two percent by means of its peak in the range 400–500°C. Calcite was found in sample 453 by means of its valley at about 850°C; its presence was confirmed by x-ray methods. Coal fragments were found in sample 468 by means of a large exothermal peak in the vicinity of 700°C.
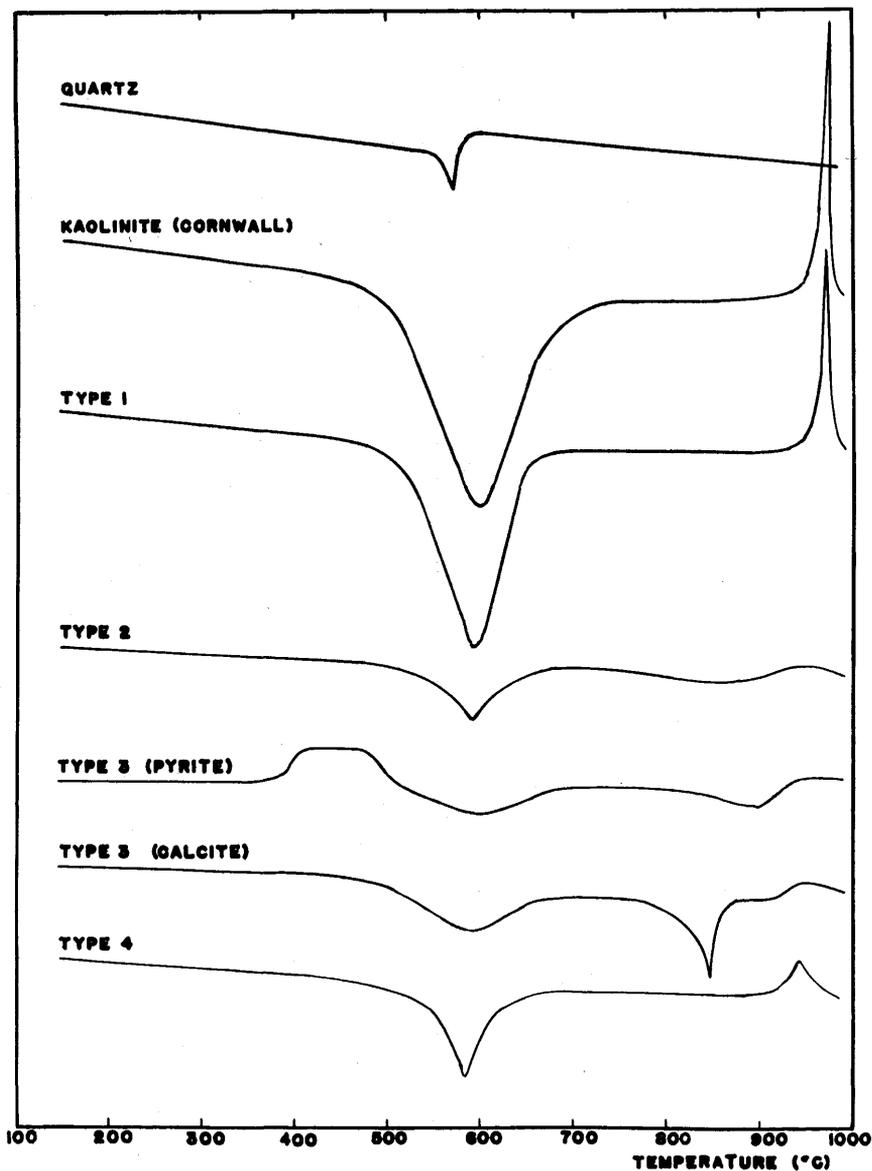


FIGURE 1. Thermograms of: 1. Quartz (Novaculite), Arkansas. 2. Kaolinite, Cornwall, England. 3. Type 1, specimen No. 379. 4. Type 2, specimen No. 140. 5. Type 3 (pyrite), specimen No. 468. 6. Type 3 (calcite), specimen No. 453. 7. Type 4, specimen No. 170.

Inasmuch as practically all the clays contained enough organic matter to mask or decrease the intensity of thermal effects near 500°C, all samples were treated with 30 percent hydrogen peroxide in order to eliminate the organic matter. The presence of significant amounts of quartz usually cannot be detected by d.t.a. methods in the presence of even small quantities of kaolinite and illite because the 573°C valley corresponding to the quartz inversion is relatively small. In table 1, clays containing significant amounts of the impurities noted are classified as type 3 and are further classified according to other characteristics.

(4) *Typical mixtures* containing kaolinite, illite and quartz, but no mineral in sufficient concentration to permit classification as type 1 or 2. In this group both illite and kaolinite range from about 30–50 percent and the ratio of kaolinite to illite ranges from about 1 : 1 to about 1 : 2. Quartz accounts for the remainder of the bulk sample, except that as much as 5 percent of impurities may be present also. The d.t.a. curves of clays of this type show considerable variation.

## CLAY MINERAL COMPOSITION

The method described by Murray (1954a) and others for determining the clay mineral ratios by means of x-ray spectrometer measurements has proved to be the only reproducible method. On two different occasions, using different instrumental settings and different portions of the specimens, the results were quite similar with respect to the ratios of illite to kaolinite. Such was not the case with the 4.25 Å line for quartz, however, so a reliable estimate of the quartz content apparently cannot be obtained by this method. The presence of quartz in the samples undoubtedly reduced the preferential orientation of mica and kaolinite flakes, but did not affect the ratios of (001) intensities of these minerals. A desirable consequence of the presence of quartz is the improvement of (11*l*), (0*kl*) and other reflections upon which differentiation of the mica polymorphs and the degree of crystallinity of the kaolinite are based.

In general, it appears that the kaolinite and illite in the underclays are probably of similar particle size, and thus particle size can be dismissed as a serious problem in comparing intensities from the respective (001) planes. The obvious exception for the bulk clay is the coarse-grained "muscovite" described above. This mica is not common, and in many clays it is rare or absent. Carr *et al.* (1953) noted that only 5 g. of coarse-grained hydrous mica was recovered from a 2 kilogram sample of the Yorkshire fireclay. It seems that the "muscovite" in the Ohio underclays is no more abundant. The effect of isomorphous substitution, particularly of Fe for Al in the illite, is probably not of considerable significance with respect to altering the intensity of the (001) reflection. The intensity of the (002) reflection of illites examined in this study is at least half that of the corresponding (001) illite reflection and nearly always approximates three-fourths of this intensity. Brindley (1951, p. 162) and others have shown that highly aluminous dioctahedral micas should produce first and second order basal reflections of comparable intensities, whereas for those high in iron the second order reflection should be weak or missing. Therefore the iron content of these illites is probably low.

Other effects, such as differences in the degree of crystallinity, which might cause departures from the theoretical ratios of reflecting powers of the (001) planes for illite and kaolinite, have been disregarded in our investigations. Should future studies show that the diffraction intensity ratio of 1 : 3, as used in our compilation, is not applicable to the Ohio clays, the data presented in table 1 can be modified accordingly. The ratios in table 1 do not indicate relative proportions of illite or kaolinite among different samples, but merely the relative amount of illite for each sample. The percent of quartz, which makes up the remaining bulk of the clays, is extremely variable from sample to sample; its ratios could not be satisfactorily determined by any method utilized in these investigations.

## CORRELATION OF DATA

An attempt was made to correlate the data obtained from the d.t.a. and x-ray studies with the chemical analyses published by Stout *et al.* (1923) in order to determine quantitatively the mineral phases present.   The problem was attacked first by calculating the percentages of the minerals present in the bulk clay from the chemical analysis by assuming ideal mineral compositions for pyrite, kaolinite, quartz, rutile and other minerals observed by microscopic examination, and an average composition for illite.   The procedures were: (1) all sulfur and an equivalent amount of iron was alloted to pyrite; (2) the remaining Fe and equivalent inorganic carbon were calculated as siderite; (3) any remaining inorganic carbon was calculated as calcite, or less commonly, dolomite; (4) all Ca and Mg not assigned to calcite or dolomite was assumed to occur in illite; (5) illite was calculated on the assumption that it contains on the average 6.5 percent potash, sufficient Al, Mg and Fe to occupy octahedral positions, and Si for tetrahedral positions; (6) all remaining Al and equivalent Si were calculated as kaolinite; and (7) all remaining Si was taken as quartz.   Calculations were then made of the predicted areas for the endotherms at about 600°C based on the contributions of the calculated minerals.   The relatively minor contribution of quartz was necessarily disregarded. The predicted areas were then compared with those obtained experimentally. The correlations thus obtained were only fair, in general, and in some cases were poor.   Inasmuch as the areas under d.t.a. inflections for most clay minerals depend upon composition, particle size, degree of crystallinity, etc. such data are semi-quantitative at best.

Other methods of calculating the mineral compositions of the clays were attempted and they were also compared with the d.t.a. results.   The correlations were, likewise, not quantitative.   The literature does not record successful quantitative analyses of similar clays involving three major minerals by thermographic methods; most determinations involve merely two minerals or are reports of data on prepared mixtures.

From the chemical analyses, particularly the $K_2O + Na_2O$ contents in relationship to the $Al_2O_3$, a rough estimate of the ratio of illite to kaolinite can be obtained. These ratios are of the same order of magnitude as those listed in table 1.   The estimation is based upon the fact that the alkalies undoubtedly occur in illite, whereas the aluminum, with the exception of that occupying octahedral mica positions, belongs to the kaolinite.   Therefore, if the $Al_2O_3$ contents of several samples to be compared are the same, those with the greater alkali contents would be expected to have higher illite to kaolinite ratios.   However, isomorphous substitutions in the micas, preclude accurate estimations.

## DISCUSSION

The data presented in this paper indicate conclusively that the Ohio underclays are extremely variable in mineral composition.   Variations in the ratios of the clay minerals (illite to kaolinite) occurs not only laterally within a particular stratum, but vertically within relatively short distances.   The Lower Kittanning clay (also called "number 5" clay), one of the most important industrial clays in Ohio, has an illite to kaolinite average ratio of approximately 1.5.   On the basis of the limited data of table 1, other less valuable clays show larger ratios.

That the ceramic properties of the bulk clay depend upon the mineral constituents has long been recognized.   Illite and kaolinite have decidedly different ceramic properties.   Numerous authors have discussed the influence of clay minerals on the ceramic properties and have also stressed the significance of particle size.   A high proportion of illite in a clay would result in a correspondingly high percentage of alkali ions which act as fluxes at high temperatures and lower the fusion point of the mass.   A high proportion of kaolinite results in a more

refractory clay.  According to Carr *et al.* (1952) the fine-grained illite in some Yorkshire clays contributes a large firing shrinkage and little after-contraction, whereas coarse-grained illite (probably similar to the "muscovite" described in this paper) does not strongly influence the firing shrinkage, but has a marked effect on the after-contraction.  Others have shown that high-illite clays often fire to yellow or brown colors as a result of the presence of iron.  Plasticity, as well as other properties, are also dependent upon the mineral composition, in addition to other factors.

The role of impurities, particularly quartz, pyrite and siderite are well known, but it is interesting to note the effect of pyrite in samples 402 and 468, and calcite in sample 453, which contain the largest concentrations of these impurities (table 1 and fig. 1).  Stout *et al.* (1923) reported that these samples bloated and that 453 and 468 could probably be used for lightweight aggregate.  It is now generally recognized that calcite and pyrite are sources of bloating gases; in the case of specimen 468, coal fragments may also contribute.

Several questions were not adequately resolved in the present investigations and are worthy of further consideration, as follows:

(1)   Possible differences in structures and compositions of the two texturally distinctive micas that occur in the underclays.  Mixed-layer types of clay minerals might be found as a consequence of further study.

(2)   More information on the kaolinite might permit characterization of the very well crystallized and the poorly crystallized ("fireclay") types and thus indicate structural or compositional differences.

(3)   The changes in clay mineral ratios in different size fractions might prove of practical interest in predicting firing properties.

(4)   A reliable method for estimation of quartz has not been developed for application to mixtures of this sort.

The ability to determine the mineralogical composition, and consequently predict the usefulness, of a clay by x-ray and differential thermal anlaysis has been considered in some detail in the light of experience with chemically analyzed Ohio underclays.  Although these methods contribute valuable increments of information, they do not necessarily replace the petrographic microscope, and its use should not be abandoned.

## SUMMARY

Examination of 42 samples of Pennsylvanian underclays of Ohio has indicated that they are composed predominantly of kaolinite, at least one micaceous constituent, and quartz.

From the x-ray diffraction data it is feasible to establish semi-quantitative ratios for illite to kaolinite that are reasonably consistent with the chemical analyses.  Differential thermal analysis did not yield reliable estimates of the component minerals, but did contribute information of practical value.  The underclays produced thermograms that can be classified according to four types, which are generally indicative of the kaolinite content and, in the case of type 3, indicated significant quantities of other material.

The mineralogical constituents of these underclays are correlated with known ceramic characteristics.

Professor Wm. J. McCaughey provided the collection of analysed clays for which he had previously prepared petrographic descriptions (Stout *et al.*, 1923).

## REFERENCES CITED

**Brindley, G. W.** (Editor) 1951. X-ray Identification and Crystal Structures of Clay Minerals. Mineralogical Society of Great Britain, London.

————, and **K. Robinson.** 1947. An X-ray study of some kaolinitic fireclays. Trans. Brit. Ceram. Soc. 46: 49–62.

**Carr, K., R. W. Grimshaw,** and **A. L. Roberts.** 1953. A hydrous mica from Yorkshire fireclay. Mineral. Mag. 30: 139–144.

————, **J. Hargraeves, R. W. Grimshaw,** and **A. L. Roberts.** 1952. The constitution of refractory clays. Part V. The relationship between constitution and properties with special reference to the influence of micaceous minerals. Trans. Brit. Ceram. Soc. 51: 345–354.

**Grim, R. E., R. M. Bray,** and **W. F. Bradley.** 1937. The mica in argillaceous sediments. Am. Mineral. 22: 813–829.

**Lamborn, R. E., C. R. Austin,** and **D. Schaaf.** 1938. Shales and surface clays of Ohio. Ohio Geol. Surv. Bull. 39.

**Levinson, A. A.** 1955. Studies in the mica group: Polymorphism among illites and hydrous micas. Am. Mineral. 40: 41–49.

**McConnell, D.,** and **J. W. Earley.** 1951. Apparatus for differential thermal analysis. Journ. Amer. Ceram. Soc. 34: 183–187.

**Mitchell, W. A.** 1953. Oriented-aggregate specimens of clay for X-ray analysis made by pressure. Clay Minerals Bull. 2: 76–78.

**Murray, H. H.** 1954a. Genesis of clay minerals in some Pennsylvanian shales of Indiana and Illinois. Clays and clay minerals. Proc. Second Nat. Conference on Clays and Clay Minerals, University of Missouri, October 15–17, 1953. Nat. Acad. Sci., Publ. 327: 47–67.

————. 1954b. Structural variations of some kaolinites in relation to dehydrated halloysite. Am. Mineral. 39: 97–108.

**de Pablo-Galan, L.** Study of chemically analyzed Ohio clays by X-ray diffraction and differential thermal analysis. Unpublished Master's Thesis, The Ohio State University (August, 1955).

**Stout, W.** 1940. Clarion clay of Hope and Lincoln Furnace Fields. Ohio Geol. Surv. Bull. 40.

————, **M. C. Shaw, G. A. Bole,** and **D. Schaaf.** 1931. The Lawrence clay of Lawrence County. Ohio Geol. Surv. Bull. 36.

————, **R. T. Stull, W. J. McCaughey,** and **D. J. Demorest.** 1923. Coal Formation clays of Ohio. Ohio Geol. Surv. Bull. 26.

**Yoder, H. S.,** and **H. P. Eugster.** 1955. Synthetic and natural muscovites. Geochim. Cosmochim. Acta 8: 225–280.