QUANTITATIVE X-RAY DETERMINATIONS OF SOME ALUMINOUS CLAY MINERALS IN ROCKS[1]

by

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ABSTRACT

x-ray diffraction traces were made of oriented aggregates of artificial binary mixtures containing approximately equal, weighed amounts of samples of illite, montmorillonite, mixed-layered combinations of illite and montmorillonite, and of kaolinite samples having different degrees of crystallinity. Measurements most suitable for quantitative purposes were obtained from the 7 Å kaolinite peaks and from the 10 Å peaks of illite and collapsed montmorillonite and collapsed mixed-layer clay. In this paper the sum of five height measurements at half-degree intervals across the peak are considered to be a measure of the area of the peak. Fireclay-type kaolinites gave 7 Å peak areas about equal to the area of the 10 Å peak of an equal amount of illite, montmorillonite, or mixed-layer clay, whereas well-crystallized kaolinites gave 7 Å peak areas generally about twice that of the 10 Å peak of an equal weight of the illite–montmorillonite minerals. Kaolinite samples having intermediate degrees of crystallinity gave 7 Å/10 Å peak area ratios intermediate between 1 : 1 and 2 : 1. The shape of the 7 Å kaolinite peak was used to evaluate the crystallinity of the kaolinite.

x-ray diffraction characteristics of the chlorite minerals from the different groups of sedimentary rocks studied vary considerably, and no uniform method has been found for their evaluation.

In the past several years many papers have appeared in which clay mineral data have been given in quantitative terms. In spite of possible limitations of the accuracy of these quantitative data, such a presentation will in most cases give a clearer idea of the distribution of clay minerals in a large group of samples than could otherwise be conveyed. In this paper are presented data on which are based the quantitative methods currently being used by the writer. It is hoped these data may be of use to others studying rocks containing similar types of clays.

A number of schemes have been proposed for quantitative evaluation of clay minerals (Talvenheimo and White, 1952; Johns, Grim and Bradley, 1954; Murray, 1954; Weaver, 1958). The writer (Schultz, 1955) described one such scheme for the types of kaolinite, illite and illite mixed-layered with a limited amount of montmorillonite that are common in underclays. Subsequent work with a wider range of clay mineral types has shown that the system used for underclays is not generally applicable to other sediments because it does not cover a sufficiently wide range of mixed-layer clay minerals, and it does not take into account variations in the degree of crystallinity of the kaolinite. The method described here can be used with a fair degree of

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accuracy for mixtures of a considerable range of the types of clay minerals common in ancient sediments, including kaolinites ranging from the well crystallized to the fireclay types and aluminous illites, montmorillonites, and a wide range of mixed-layer combinations of the two. Chlorite was the only clay mineral common in the rocks studied by the writer for which no consistent method for evaluation could be found. The chloritic minerals even in this limited number of rock types are apparently too variable in chemical composition and structural stability for consistent results.

x-ray diffractometer traces from which the data for this paper were obtained were run using filtered copper radiation, scanning at 2° per min, using a coarse collimating system and a 1 sec time constant. The samples were prepared as oriented aggregates on porous tile slides $2\frac{3}{8}$ in. long. Other conditions could give results slightly different from those of this paper, but the general pattern should be the same.

The system of evaluation is based on mixtures of equal, weighed amounts of the different types of clay minerals. Clays used in the mixtures were $<2\,\mu$ splits of nearly pure representatives of their types. The clays came mostly from the rock formations which the writer has studied in the past several years: Pennsylvanian underclays, Triassic formations of the Colorado Plateau, and the Pierre shale of late Cretaceous age. A few additional samples, mainly of well-crystallized kaolinite, were also used, because nearly pure representatives of such clays are rare in the rocks being studied.

Corrections were made for impurities in the clay samples used in the mixtures. For example, if in a mixture of equal weights of kaolinite and illite samples the original illite sample was made up entirely of this mineral but the original kaolinite sample contained 10 percent quartz in addition to the 90 percent kaolinite, then the mixture would contain 50 percent illite, 45 percent kaolinite and 5 percent quartz. Therefore, in comparing peak sizes obtained from this mixture, the ratio of the kaolinite/illite peak size would be multiplied by 50/45 in order to make the peak size ratio valid for equal weights of the two clays.

Peaks that proved to be most consistently related to the amounts of each of the minerals in the different mixtures are the first-order basal peak of the various kaolinites at about 7 Å, and the 10 Å peak of the illite–montmorillonite minerals after heat treatment sufficient to expel interlayer water and collapse the expandable layers. For this study, samples were heated at 300°C for $\frac{1}{2}$ hr, although some other heat treatment might be more suited to other groups of rocks. The 7 Å and 10 Å peaks were used because they occur close together, they are the largest peaks obtainable from these minerals, and because diffraction from few nonclay minerals interferes with them. The size of the 10 Å peak of the collapsed illite–montmorillonite clays was more consistently related to the size of the 7 Å peak of an equal weight of kaolinite than was the size of the first-order basal peak of the expanded illite–montmorillonite clays. The higher-order basal peaks of the illite–montmorillonite group were unsatisfactory because their sizes are greatly affected by mixed layering, whether the sample is hydrated, dehydrated or glycol-treated.

Because x-ray traces obtained for this study were recorded on a logarithmic scale it was impractical to measure the true areas of the peaks. Values used for comparative purposes in this paper are the sum of five measurements in counts/sec of the height of the 7 Å or 10 Å peak above the background; one measurement is at the peak position (called the peak height) and the other four are at half degree intervals on either side of the peak position, depending upon the peak shape. If the peak shape is symmetrical, two measurements are made on each flank of the peak; if the peak shape is notably asymmetrical, three of the four flank measurements are made on one
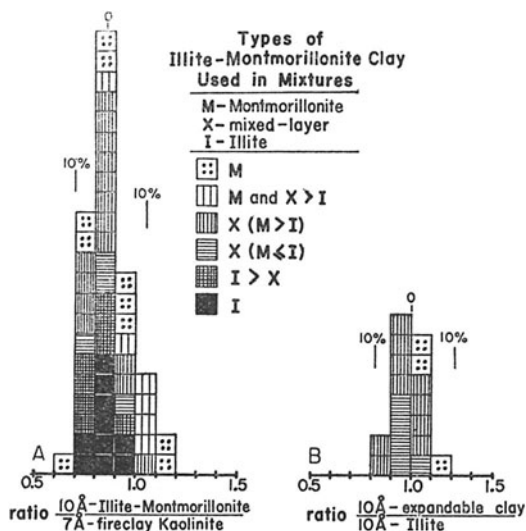

FIGURE 1.—Ratios between areas of x-ray diffraction peaks from fireclay-type kaolinite and illite–montmorillonite minerals. All measurements for the illite–montmorillonite clays are made in their collapsed state, after heat treatment to 300°C. (a) Equal amounts of kaolinite (7 Å) and illite–montmorillonite clay (10 Å). (b) Equal amounts of illite (10 Å glycol treated mixture) and expandable minerals (increase in size of the 10 Å peak after heating at 300°C).

side of the peak position. The sum of these five measurements is referred to in this paper as the area of the peak.

For this paper, 110 mixtures of equal amounts of different kaolinite and illite–montmorillonite samples were made. These mixtures fall into three groups: (a) different minerals of the illite–montmorillonite group, many of which are mixed layered, and each of which was mixed with an equal weight of the same sample of poorly crystallized kaolinite; (b) different samples of montmorillonite or mixed-layer minerals with varying proportions of expandable and nonexpandable components each of which was mixed with an equal weight of the same illite sample; (c) different kaolinite samples with varying degrees of crystallinity each of which was mixed with an equal weight of the same illite sample.

The relative areas under 7 Å and 10 Å peaks from a number of mixtures of the same fireclay-type kaolinite and an equal weight of one of the different clays of the illite–montmorillonite group are illustrated in Fig. 1(a). On Fig. 1(a) each square represents one mixture and the patterns in the squares indicate the different types of illite–montmorillonite clays mixed with the kaolinite. If the 10 Å/7 Å peak area ratio for a given mixture is between 0.9 and 1.0, for example, the mixture is represented by a square in the column between these limits. Squares representing the different illite–montmorillonite combinations are all concentrated about a value slightly less than 0.9. Apparently, in the collapsed 10 Å condition the aluminous montmorillonites, illites and mixed-layer combinations all give 10 Å peak areas which on an average are slightly smaller than the 7 Å peak of the equal weight of the poorly crystallized kaolinite with which they are mixed.

Mixtures were also made containing 50 percent illite and 50 percent of either montmorillonite or mixed-layer illite–montmorillonite. For these mixtures the area of the 10 Å peak on the trace of the glycol-treated slide is subtracted from the area of the 10 Å peak after the same slide has been heated. This difference in area is then compared with the area of the 10 Å peak from the glycol-treated slide. The 10 Å peak obtained from the glycol-treated slide results from the illitic part of the mixture only, although some correction may be necessary for the relatively small second-order basal reflection of the expandable components at about $8\frac{1}{2}$–9 Å. After heat treatment and collapse of the expandable components, both the illite and mixed-layer or montmorillonite components contribute to the size of the 10 Å reflection, so that the increase in the size of the 10 Å peak after heat treatment can be attributed to the mixed-layer or montmorillonite half of the mixture. Ratios of the 10 Å peak areas attributed to illite and to the expandable clays are shown in Fig. 1(b). The patterns indicate different types of expandable clay minerals mixed with the illite. The ratios tend to cluster near a value of 1.0 and support the conclusion derived from the mixtures with kaolinite (Fig. 1(a)), that in the collapsed state, the montmorillonites and mixed-layer montmorillonite–illites give 10 Å peaks of about the same size as that of illite.

Interpretations of relative amounts of montmorillonite and mixed-layer clay are based on the observation that, using oriented aggregate samples $2\frac{3}{8}$ in. long, the 17 Å peak of a glycol-treated montmorillonite sample is at least five times as high as the 10 Å peak of the montmorillonite in the same slide after heat treatment. (If the sample length is decreased to $1\frac{7}{8}$ in.—the longest that a Norelco diffractometer will hold—the 17 Å/10 Å peak height ratio of montmorillonite decreases to about four.) In practice, if a $2\frac{3}{8}$ in. oriented aggregate were used, and if the increase of the height of the 10 Å peak after heat treatment is more than one-fifth of the height of the 17 Å peak after glycol treatment, then some of the 10 Å peak is interpreted as due to mixed-layer clay. Such a system involves boundary problems between montmorillonite and high-montmorillonite mixed-layer clay, and the shapes of the whole sequence of basal peaks from 17 Å should be considered in the

interpretation. The method does give numerical values useful for comparative purposes.

One requirement for the use of the change-in-the-10 Å-peak-area method for evaluating the relative amounts of illite and expandable clay is that both the heated and glycol-treated slides be the same ; the clay aggregates must not buckle or crack during these treatments. Such a requirement is often difficult to fulfill when glass slides are used as backing. Such difficulties caused the writer to abandon this method during initial efforts in quantitative clay evaluation. However, introduction of porous tile plates by Kinter and Diamond (1956) as backing for the oriented clay aggregate eliminates most buckling and cracking difficulties, and in most cases makes it possible to compare directly the peak sizes on different traces obtained from the same slide.

A number of 50–50 mixtures were made of kaolinites having varying degrees of crystallinity and portions of the same illite sample. Two parameters were used as measures of the degree of crystallinity of the kaolinite samples. For the relatively pure kaolinite samples used in the mixtures, an evaluation on the basis of the nonbasal peaks similar to that of Brindley (1951, Fig. II, 4) was a simple matter. On this basis the kaolinites were classified into well crystallized, poorly crystallized (or fireclay), and intermediate types. However, the critical nonbasal peaks could not be discerned readily in natural clay mixtures in which the kaolinite was a minor component, so in practice the shape or broadness of the basal kaolinite peaks was used as a measure of the crystallinity of the kaolinites. The shape factor used was the ratio between the area and the height of the 7 Å kaolinite peak. Reflections at 7 Å with high area/height ratios correspond to the broad peaks of poorly crystallized kaolinite ; 7 Å peaks with low area/height ratios correspond to the sharp peaks of well-crystallized kaolinite. Obviously there are boundary problems between the three groups of kaolinite but, as shown on Fig. 2, there does seem to be a fairly consistent relation between the number of reflections that the different kaolinite samples give and the shapes of their 7 Å reflections.

On Fig. 2 are shown relations between the degree of crystallinity of the different samples of kaolinite, the shape of the 7 Å kaolinite peaks, and the ratios between the areas of these 7 Å peaks and the areas of the 10 Å peaks of equal amounts of the illite with which the kaolinite samples are mixed. The abscissa of the graph is the ratio of the 7 Å/10 Å peak areas, and the ordinate of the graph is the area/height ratio of the 7 Å peaks. Crystallinity of the kaolinite samples as determined from the number of nonbasal peaks observed is indicated by the different symbols. Kaolinite samples having all the x-ray reflections of well-crystallized kaolinite (+) give area/height ratios between 1.1 and about 1.3, the poorly crystallized, fireclay-type kaolinites (0) give ratios above 1.7, and kaolinite samples with intermediate degrees of crystallinity (×) give ratios between about 1.3 and 1.7. As would be expected from Fig. 1(a), mixtures containing kaolinite samples of the fireclay type give 7 Å peaks of about the same area as, or only slightly larger than, the 10 Å

peak of an equal amount of the illite. Mixtures containing well-crystallized kaolinite samples give 7 Å peaks generally of at least twice the area of the 10 Å illite peaks, and mixtures containing kaolinite samples with an intermediate degree of crystallinity give 7 Å/10 Å peak area ratios intermediate between 1 and 2.

A change in the time constant or speed or scanning will affect the relative peak sizes obtained if the peaks being compared have notably different shapes. For example, if the scanning speed were kept at 2° per min, but the time constant were changed from 1 sec to 4 sec, then the relative size of the 7 Å peak of well-crystallized kaolinite would decrease to about 85 percent of its relative size at the 1 sec time constant. In contrast, the relative size of the broad 7 Å peak of poorly crystallized kaolinite would not be affected
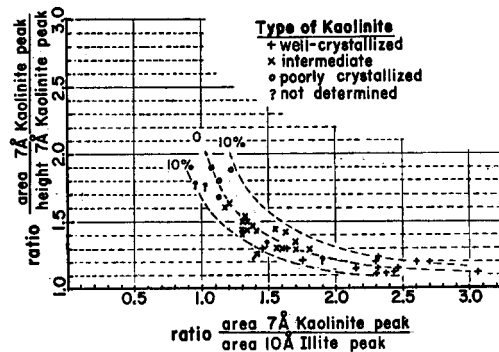

FIGURE 2.—Ratios between areas of x-ray diffraction peaks from mixtures of various types of kaolinite with equal amounts of the same illite sample. The area/height ratio of the 7 Å peak is indicated on the ordinate and the type of kaolinite as determined from the nonbasal reflections is indicated by the different symbols.

appreciably by a change in time constant because this peak has about the same shape as the 10 Å peak of the illite–montmorillonite minerals.

The scatter of area ratios in Figs. 1 and 2 is probably due to several factors :

(1) Differences in crystallinity, chemistry and atomic substitutions of the illites and montmorillonites.

(2) Operator errors in measurement of peak sizes and shapes.

(3) Errors in correcting for impurities in the samples.

(4) Differences in average particle size of the clays used in the mixtures, even within the $< 2 \mu$ fraction.

(5) Slight differences in the degree of preferred orientation of the two clay components in the same slide of a mixture.

(6) Differences in the degree of preferred orientation between slides prepared from the different mixtures, even though orientation of the two components within individual slides may be the same. The relative contribution of the angle factors (e.g. Lorentz and polarization) to the intensity

of peaks at the 7 Å and the 10 Å positions depends to some extent upon the degree of preferred orientation within a given slide. Therefore, as the degree of preferred orientation of the clay flakes varies somewhat between the slides prepared from the different mixtures, the relative contribution of these angle factors to the intensities of the 7 Å and 10 Å peaks probably varies from one mixture to the next.

All but one of these factors (no. 3) would also be encountered in evaluations of natural clay mixtures, so the spread of the measurements on Figs. 1 and 2 should be indicative of expectable accuracy in making such evaluations on natural mixtures.

Limits of error that would be involved in using average values from the data on Figs. 1 and 2 are indicated on these illustrations. On Fig. 2, a dashed lined marked 0 bisects the points for the 7 Å/10 Å peak area ratios from the 50–50 mixtures. The bordering dashed lines marked 10 percent enclose nearly all the points determined for the kaolinites studied. This indicates that the zero line can be used as a working curve to give quantitative values that are correct within 10 percent of the amount of kaolinite actually present. For example, if the trace of the kaolinite–illite mixture indicated on Fig. 2 by an arrow were interpreted on the basis of the zero working curve, and if it is assumed that the proportion of these clay minerals in the sample are unknown, then steps in the calculation of the amount of kaolinite would be as follows :

(1) The area/height ratio of the 7 Å kaolinite peak would be measured as 1.3.

(2) The 10 Å peak area would be measured, and the 7 Å/10 Å area ratio would be calculated to be 1.45. Therefore, if the area of the 10 Å peak is taken to be 1.0, then the area of the 7 Å peak would be 1.45.

(3) For kaolinite having a 7 Å area/height ratio of 1.3, the kaolinite peak area should be divided by 1.7 as read below the intersection of the 1.3 area/height ratio and the working curve (1.45/1.7 = 0.85). This step is necessary to make the 7 Å peak area value directly comparable quantitatively with the 10 Å illite peak.

(4) The ratio of kaolinite to kaolinite plus illite is calculated to be 0.85/(0.85 + 1.0) = 0.46. Of the clay in the sample, 46 percent is calculated to be kaolinite and the remaining 54 percent is attributed to illite.

These values are within 8 percent of the 50 percent kaolinite and 50 percent illite known to be in the weighed mixture, and on Fig. 2 the sample is plotted just inside the 10 percent error limit.

Most of the samples plotted on Fig. 2 are within the 10 percent error limits. Similar error limits are also plotted on Fig. 1 and here again most of the samples fall within the 10 percent limits. All the kaolinites on Fig. 2 are mixed with the same illite and all of the illite–montmorillonite clays on Fig. 1(a) are mixed with the same kaolinite. Therefore, if both the type of kaolinite and the type of illite–montmorillonite sample were varied, the errors might be cumulative. Also, an error of ±10 percent of the clay present in a mixture applies if the clay minerals are of approximately equal abundance

in the mixture. If a clay mineral comprises only 5 to 10 percent of the sample, the error in the determined abundance value would likely be considerably more than 10 percent.

The system described above for quantitative evaluations of clay mixtures has several limitations. The peak area ratios given apply only to the dioctahedral, aluminous clay minerals. For example, mixtures were made of a nontronite and of a trioctahedral mixed-layer vermiculite–illite, each with an equal weight of the same fireclay-type kaolinite used in the mixtures shown on Fig. 1(a). In the collapsed condition these nonaluminous clays gave 10 Å peaks that have from 2 to $2\frac{1}{2}$ times the area of the 7 Å kaolinite peak. Another limitation of the system is that, because oriented aggregates are used, clay particles in the mixtures must all be about the same shape. This factor gave no trouble in the rocks studied by the writer because all the clays seemed to be of the usual, platy variety. However, the ratios given on Fig. 1(a) would not apply to rocks containing a mixture of a platy illite and a tubular halloysite, for example. Still another disadvantage of this system is that it gives relative amounts instead of the more desirable absolute amounts of each clay in a sample. For an estimate of the absolute amount of clay in a sample, the writer has used the size of the nonbasal reflections obtained from an x-ray trace of an unoriented powder; the sizes of these reflections are less sensitive to slight differences in the degree of preferred orientation of the sample.

Still another disadvantage of this system, and of any other system for that matter, is that the x-ray reflections of chloritic minerals from different sediments vary considerably, and also these reflections interfere with interpretation of those from the kaolinite minerals. The only solution to this problem seems to be to determine the characteristics of the chlorite in a given group of samples and compare the chlorite diffraction intensities as best as possible with those of the other clays in the sample. For example, the chlorites in the Triassic sedimentary rocks of the Colorado Plateau consistently give 14 Å peaks of about three times the area of the 10 Å peak of an equivalent amount of aluminous illite after heat treatment at 550°C for $\frac{1}{2}$ hr. Also, the 14 Å peak from the unheated sample is from 1 to $1\frac{1}{2}$ times as high as the original 7 Å chlorite peak. Marked deviations from this ratio caused the writer to suspect the presence of kaolinite in the sample. However, this same ratio cannot be used for the Pierre shale samples which gave relatively small 14 Å reflections; the 14 Å/7 Å peak height ratio applicable to Pierre chlorites before heat treatment averages about 3/4: likewise, ratios applicable to the Triassic samples generally cannot be used for the chloritic materials in underclays because in many cases the 14 Å reflection observed on the trace of the unheated and glycol-treated samples disappears after heat treatment at 550°C.

The system for quantitative evaluation of clay minerals described above also has a number of advantages. It is fairly simple. It takes into account differences in crystallinity of the kaolinite in different samples. Such differences in the illite–montmorillonite minerals apparently are of much less

importance, at least within the samples included in this study. By using the first basal peaks obtained from oriented aggregates, one works with the biggest peaks obtainable, and thereby minimizes operator errors in measuring peak sizes and detects clays present in minor amounts. By using oriented aggregates, quantitative evaluations can be made of fairly complex mixtures of clays, including mixed-layer clays. Such evaluations would otherwise be very difficult or impossible. By using peak areas as defined herein instead of peak heights, more consistent relations are obtained between the peak sizes from the different types of clay minerals. Also, by collapsing the illite–montmorillonite minerals to 10 Å, one does not become involved with such factors as relative humidity, the uniformity of distribution of the different layers of mixed-layer minerals, and the variation in the size of the 001 mixed-layer peak with the proportion of illite to montmorillonite in the mixed-layer clay particles.

The clay samples used for the mixtures in this study are from the rock formations on which the quantitative methods derived from this paper have been used. These samples do not include a large number of standard clay samples, which may or may not be representative of the clay minerals in the rocks being studied. Anyone disposed to use these quantitative methods would do well to test them on prepared mixtures of fairly pure clay samples from the rocks undergoing study. However, attainment of fairly consistent results from the aluminous clay minerals in the underclay, Triassic and Pierre shale samples gives considerable hope that the peak area ratios given in this paper may be generally applicable to clay minerals in other rocks.

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