

QUANTITATIVE EVALUATION OF THE KAOLINITE AND ILLITE IN UNDERCLAYS

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ABSTRACT

Oriented slides of twelve different mixtures of kaolinitic and illitic underclays were studied with the X-ray spectrometer and the resulting curves were evaluated on the basis of the area of the 001 peaks. Although the areas from the unmixed components varied greatly, within any given mixture the two clays were quantitatively comparable on the basis of a 1/1 001 peak area ratio. The considerable peak area variations from slide to slide are the result of different degrees of preferred orientation and are not due to any appreciable differences in crystallinity. Mixed-layering of expandable material with the illitic component does not affect the quantitative comparisons significantly.

INTRODUCTION

During an investigation of Pennsylvanian underclays it seemed desirable to evaluate the relative amounts of the clay minerals in a sample on as quantitative a basis as possible. Information in the literature was scant, and there was no assurance that the data available were applicable to the types of clay minerals found in underclays. Therefore, artificial mixtures were made of the two most abundant clay mineral types encountered, kaolinite and illite, in order to determine what means of evaluation was best suited to the samples being studied. X-ray spectrometer traces of the mixtures were evaluated in three ways: by comparing the peak areas of the first order basal reflections, by comparing the peak heights of the first order basal reflections, and by a comparison of the 002 kaolinite peak height with that of the nearby 003 illite peak. The kaolinite and illite were found to be best compared quantitatively on a 1/1 ratio of the relative 001 peak areas; that is, if the 001 peak areas were equal, the amounts of kaolinite and illite were equal.

KAOLINITE/ILLITE MIXTURES IN VARYING PROPORTIONS

First a series of mixtures was made of a fairly pure kaolinite from a fireclay pit near Ottawa, Illinois, with illite from the type locality near Fithian, Illinois, in ratios of kaolinite/illite of 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 by weight. Both clays were fractionated to less than 2 microns before mixing and contained very little non-clay material. The

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clays were mixed by stirring in water after which oriented slides were made by sedimentation. The slides of the mixtures were run on the X-ray spectrometer and areas under the 001 peaks of the kaolinite and illite were measured as illustrated in Figure 1. A smoothed base line curve was constructed and five computations were made for the number of counts between the base line and the spectrometer curve, one at the peak position and one at one-half degree and one degree on both sides of the peak position. The sum of these five values was considered to be the area under the peak.

Peak Area vs. Amount of Clay

Figure 2a shows a plot of the kaolinite and illite 001 peak areas vs. the weighed amount of each clay in the series of mixtures. Although the graph should theoretically give straight lines, it obviously does not. Three possible explanations were considered: (1) the surface material of the oriented slide which caused reflection of the X-rays is not representative of the clay mixture as a whole, (2) the greater adsorption of X-rays by iron-bearing illite than by the iron-free kaolinite reduced the amount of X-ray reflection in the high-illite mixtures, or (3) the degree of preferred orientation in each aggregate was not the same. To check the first possibility, the backs of the three aggregates which could be removed from the glass supporting slides were analyzed; they gave peak areas which, while less than the areas under the peaks obtained from the fronts of the slides, were very close to the same size relative to each other, indicating that the clay on the front of the slide is representative of the slide as a whole insofar as the relative amount of each clay is concerned. It was felt that adsorption could not cause deviations of the type and magnitude observed. The possibility that the preferred orientation of the clay aggregates varied was tested by taking film patterns of flakes cut from the slides. The films are reproduced in Figure 3 (b to e). A high degree of preferred orientation is indicated

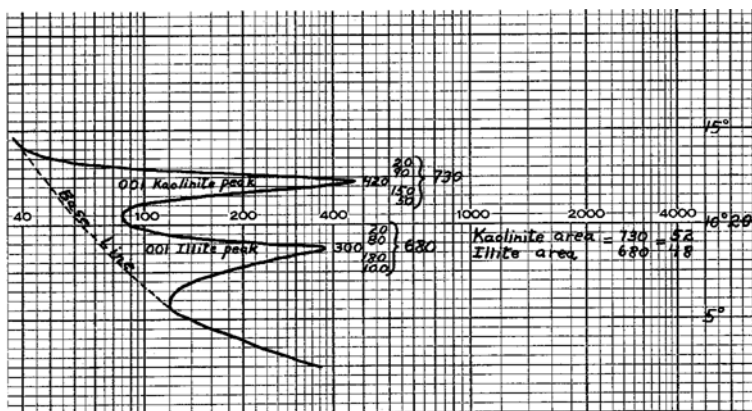


FIGURE 1. — Smoothed spectrometer trace area calculations.

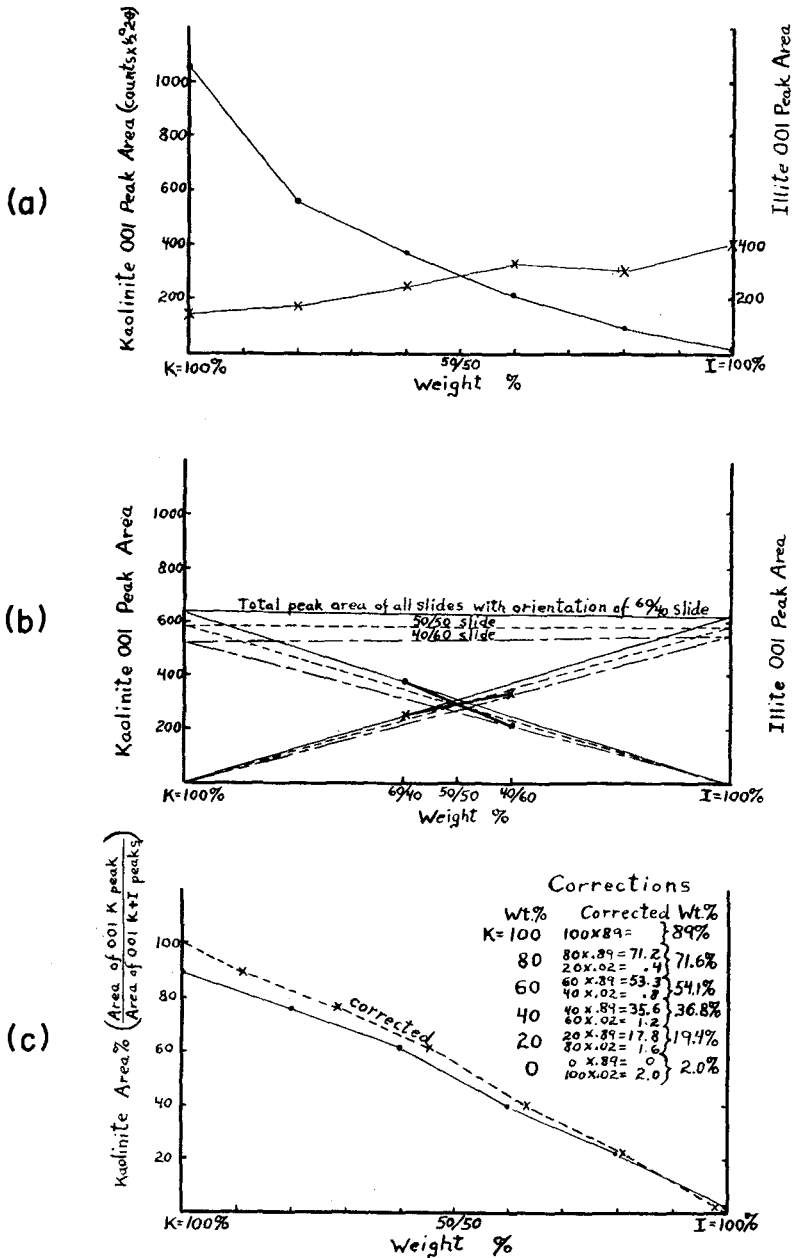


FIGURE 2.— Peak areas vs. weight percent of clay.

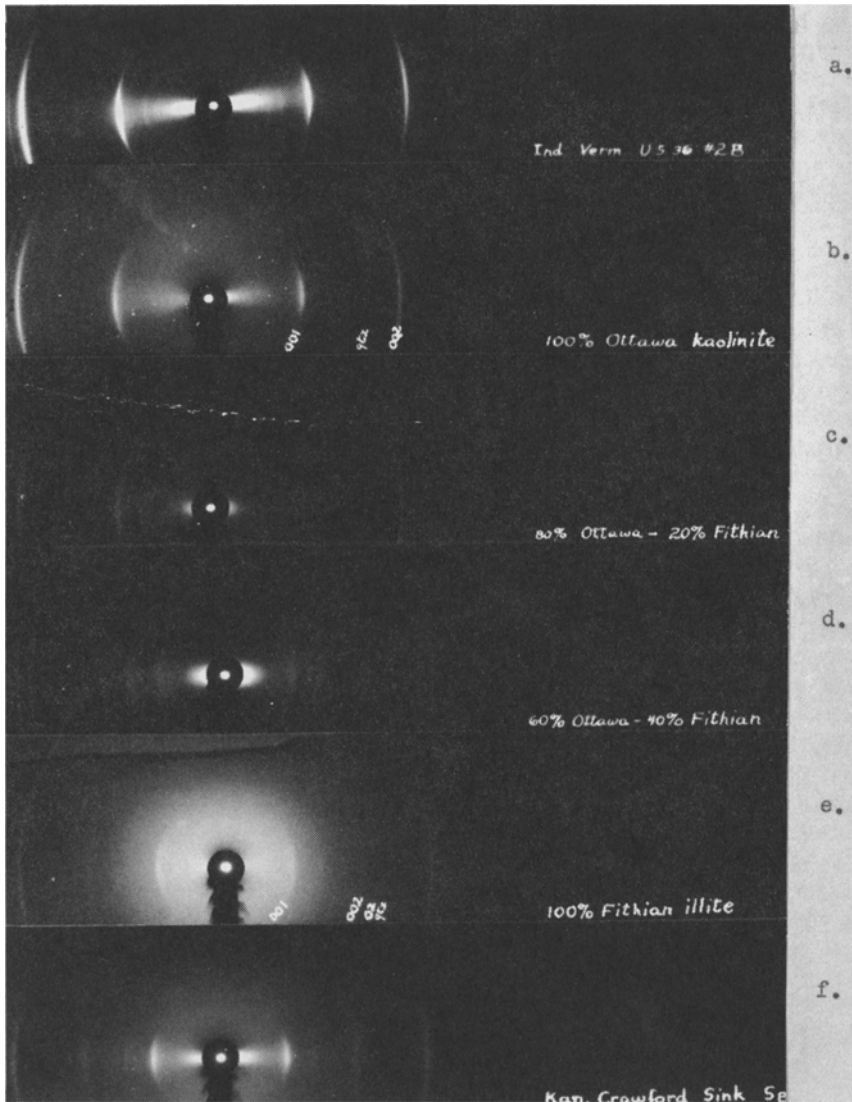


FIGURE 3.—X-ray diffraction patterns of oriented flakes.

by a strong concentration of blackening by basal reflections along the axis of the film, and an absence of blackening by prism reflections on this same axis. A completely unoriented slide gives a pattern of complete, uniformly blackened circles of all reflections. The degree of preferred orientation of the kaolinite sample (b) is greater than that of the kaolinite in the mixture, and is much greater than the illite in the 100 percent Fithian illite slide.

Yet, within any one mixture, the preferred orientation of the kaolinite and illite appears to be about the same. It is apparent that differences in the degree of preferred orientation strongly influence the peak areas produced from one slide to another. One item used to compute the reflection intensity from a sample is the polarization factor. At 2θ angles ranging from the 7 Å to the 10 Å positions, the polarization factor for a perfectly oriented aggregate is about 20 times that for an unoriented mass of clay slips, allowing more than enough latitude to explain the observed discrepancies in reflection intensities. (See Internationale Tabellen, 1935, pp. 562, 567.)

The influence of orientation on peak size was further confirmed by mixing two clays giving considerably different peak sizes with a common clay. For example, a comparison was made by mixing Fithian illite with an 001 peak area of 400 and a Kansas illite with an 001 peak area of 2,680 both with Ottawa kaolinite. The point at which the curves cross in Figure 2a shows that a 50/50 mixture of Ottawa kaolinite and Fithian illite would give peak areas approximately equal. A 50/50 mixture of the Kansas illite with Ottawa kaolinite also gives approximately equal 001 kaolinite and illite peaks. Since effects of orientation are eliminated within a single slide, the difference in the areas of the two unmixed illite samples must be due to different degrees of orientation. Oriented flake film patterns shown in Figure 3 (e and f) confirm this difference in orientation.

Flake film patterns of the Ottawa kaolinite (area — 1,055) and an Indiana kaolinite (area — 2,860) shown in Figure 3 (a and b) give another good example of the importance of preferred orientation in quantitative interpretations. The Indiana sample is better oriented. The area under the Indiana kaolinite peak is $2\frac{1}{2}$ times that under the Ottawa kaolinite peak from the unmixed slides. Yet, 50/50 mixtures of the kaolinites both with Fithian illite give area ratios of the kaolinite to illite peaks which are about the same.

Still other pairs of samples with considerably different areas under the peaks on traces from the unmixed samples were mixed with identical clays in 50/50 ratios with results similar to those mentioned above. The mixtures illustrate all possible combinations of kaolinite and illite giving extremely high and low 001 peak areas when unmixed. (See Table I for exact data.) Therefore, the great differences in the area under peaks given by different clays in different slides cannot be caused by any difference in the inherent diffracting ability of the clays due to their crystallinity or particle size; differences in peak size must be due to differences in orientation.

Relative Peak Area vs. Amount of Clay

Although any one clay in a mixture could not be evaluated quantitatively on the basis of the absolute area of its 001 peak, the amount of each clay was successfully calculated on the basis of its relative 001 peak area: that is, the peak area produced by one clay as compared with the sum of the peak area produced by both of the clays in the mixture.

Going back to Figure 2a, it was seen that the kaolinite and illite curves cross at about 50 weight percent. The kaolinite and illite curves would be straight lines if the orientation of all slides were equal. If these straight lines are constructed through the point where the observed kaolinite and illite curves cross as in Figure 2b, they intersect the 100 percent kaolinite and illite ordinates at the same heights, and a straight line between these intersections is a curve for the sum of the peak areas of any mixture having the same preferred orientation as the mixture used to construct the Area vs. Weight percent curves.

The use of a hypothetical 50/50 mixture in Figure 2b at the point where the two curves cross might be objected to. However, if straight lines are constructed through the peak areas which were actually determined for the 60/40 mixture, the lines strike the 100 percent ordinates at very close to the same distance from the base, and the sum of the peak areas for any mixture having the same orientation as the 60/40 mixture is a constant represented by the 60/40 horizontal line. As shown in the figure, the same is true for the 40/60 mixture.

At this point it is convenient to go from the specific case of Ottawa kaolinite and Fithian illite with equal reflecting abilities to the general case where the two clays have unequal reflecting abilities. In this case, there is some factor (F) such that:

$$k = Fi \quad \begin{array}{l} k = \text{reflecting ability of kaolinite} \\ i = \text{reflecting ability of illite} \end{array}$$

The equation for the Weight vs. Peak Area curves should have the form:

$$\begin{array}{ll} (1) \text{ wt K} = c \cdot \text{pk area K} & \text{K} = \text{kaolinite} \\ (2) \text{ wt I} = cF \cdot \text{pk area I} & \text{I} = \text{illite} \\ & c = \text{constant} \\ & \text{pk} = \text{peak} \end{array}$$

Adding (1) and (2):

$$(3) \text{ total wt clay} = c(\text{pk areas K} + F \cdot \text{I})$$

Dividing (1) by (3):

$$(4) \text{ K wt \%} = \frac{\text{wt K}}{\text{total wt clay}} = \frac{\text{pk area K}}{\text{pk areas K} + F \cdot \text{I}}$$

Going back to the specific case of Ottawa kaolinite and Fithian illite which have equal reflecting abilities, $F = 1$ and:

$$(5) \text{ K wt \%} = \text{K area \%}$$

Figure 2c is a graph of the kaolinite area percent vs. kaolinite weight percent as computed from Figure 2a with equation (5). The curve is very close to a straight line. The divergence of the curve at the ends is due to a small amount of illite impurity in the Ottawa kaolinite and a little kaolinite in the Fithian illite sample. On an 001 areal ratio of kaolinite/illite = 1/1, the Fithian sample contains 2 percent kaolinite and the Ottawa sample 11 percent illite. Corrections for these impurities gives the dashed line curve

in Figure 2c. This line could be straight only if the kaolinite and illite in all the mixtures have the same ability to reflect X-rays. The corrected curve of Figure 2c shows that there is a slight tendency for the kaolinite to reflect more than the illite. However, the 1/1 ratio is very close, much closer than any other simple ratio.

In the general case where the two clays being compared have unequal reflecting abilities, the above method can be used simply by multiplying the peak area of the clay with the lowest reflecting ability by a factor (F) so that its corrected reflecting ability is equal to that of the other clay as is shown in equation (4). Such a system could be used for three or more clays provided that each clay could be obtained in a fairly pure form for making artificial mixtures with known weights of the different clays.

ELEVEN 50/50 KAOLINITE/ILLITE MIXTURES

It having been established that the diffracting ability of kaolinite and illite are about the same for one pair of samples, it becomes necessary to determine how universally applicable this ratio is for plastic underclays in general. For this purpose, eleven 50/50 mixtures were made of predominantly illitic and predominantly kaolinitic underclays and spectrometer traces run of their oriented slides. Fronts and backs of all slides were interpreted and the results averaged. Where the front and back were considerably different, the mixtures were restirred and run again. Clays used in these mixtures are listed in Table I along with the areas under the 001 kaolinite and illite peaks from the unmixed clays. In the next column is the area percent of kaolinite (*i.e.* area 001 kaolinite peak/total area of 001 kaolinite and illite peaks) from the trace of the oriented slide of the mixture. Even though the peak areas of the unmixed clays vary greatly and some clays contain considerable impurities, the kaolinite area percent of the mixture does not diverge greatly from 50 percent, which indicates that the reflecting abilities of the kaolinites and the illites common in underclays are all approximately equal. This being established, the corrected weight percent of kaolinite for each mixture was calculated as in Figure 2c and is listed in Table I. Most of the area percents are very close to the corrected weight percents. In the last column of Table I are the errors which would be introduced by assuming that the area percent actually represents the weight percent of kaolinite in the mixture. Again there would be a slight tendency to overestimate the amount of kaolinite present, but even for the mixture with the greatest error, the 1/1 ratio is much closer than any other simple ratio.

EXPANDABLE CLAY IN THE ILLITE COMPONENT

The expandable component mixed-layered with the illite part of the eleven mixtures of Table I varies greatly. For example, the illites used in the # 4 and # 9 mixtures are practically unaffected by glycol treatment,

TABLE I.—50 PERCENT KAOLINITE / 50 PERCENT ILLITE MIXTURES

Samples	Peak areas of unmixed clays		Area % kaolin.	Corrected wt. % kaol.	% Error
	7 Å	10 Å			
1. 15c—# 2-horizon Fithian illite	1600 10	630 405	40.5	37.5	+4
2. 8b—# 2-horizon Fithian illite	2005 10	480 405	41	41.5	—0.5
3. 8c—# 2-horizon Fithian illite	2200 10	520 405	42	42.5	—0.5
4. 8c—# 2-horizon 32b—S-horizon	2200 155	520 2680	41.5	44	—2.5
5. 28a—# 2-horizon Fithian illite	1740 10	240 405	49	46	+3
6. 28b—# 2-horizon Fithian illite	2860 10	490 405	52	44	+6
7. 7b—M-horizon 13b—P-horizon	1255 45	440 435	47	42	+5
8. 28b—M-horizon Fithian illite	1650 10	660 405	43.5	37	+6.5
9. Ottawa kaolinite 32b—S-horizon	1055 155	140 2680	52	47	+5
10. Ottawa kaolinite 24b—# 6-horizon	1055 25	140 635	47	46	+1
11. Ottawa kaolinite 20a—# 6-horizon	1055 15	140 2290	43	45	—2
average error					+2.2%

whereas the 001 peak from the illite of the # 11 mixture shifts to a 13 Å position which would correspond to about 43 percent montmorillonite mixed-layered with the non-expandable illite (*i.e.* 13 Å is 43 percent of the way between 10 Å and 17 Å). The close agreement of the corrected weight percent and the area percent for all the mixtures indicates that the mixed-layered montmorillonite, when dried at 45° C to 50° C and not treated with glycol, has little effect on the diffracting ability of the illitic component. Glycol reduces the reflecting ability of the mixed-layered minerals considerably, so that computations should be made before glycol treatment.

The similar reflecting ability of illite and mixed-layered illite-montmorillonite was the main reason why peak area instead of the more easily determined peak height was used for the quantitative interpretations. Whereas mixed-layered expandable material affected the 001 peak area very little, it spread the peaks out and greatly decreased the peak height of all the basal reflections, particularly the first and third order. The coincidence of the strongest quartz reflection with the 003 illite peak is another reason why the 002 kaolinite and the 003 illite pair of peaks were not used for quantitative comparison.

CONCLUSIONS

The amount of kaolinite and illite in an underclay sample is best evaluated on the basis of a 1/1 ratio of the 001 peak areas. It should be emphasized that this ratio is intended only for plastic underclays. It may well not be applicable for hydrothermal clays or recent sediments, for example. If a well crystallized type of kaolinite, such as the Georgia variety, were involved, it most certainly would not apply. However, the general method should be useful in evaluating the amounts of clay in rock types other than underclays. By using relative peak areas instead of absolute peak areas or heights, difficulties arising from different degrees of preferred orientation, considerable mixed layering, or differential adsorption are eliminated.

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