ORIENTING INTERNAL STANDARD METHOD FOR CLAY MINERAL X-RAY ANALYSIS

by

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ABSTRACT

Use of a platy internal standard that will orient to the same degree as clay minerals preserves the relative diffraction intensities between the basal reflections from the platy components, regardless of degree of orientation. The method is illustrated with basic zinc chloride and pyrophyllite as the internal standards for quantitative clay mineral analysis in the systems kaolinite–1Md illite and $2M_1$ muscovite–montmorillonite. Illite does not orient to the same degree as kaolinite at high illite concentrations. In such non-linear systems empirical working curves are more reliable than fixed ratios of the scattering powers of the clay minerals present. Random interstratification of 10/15.4 Å layers causes a minimum in 001/001 peak height at about 33% of the 15.4 Å component. Peak width varies in a similar but inverse pattern, so that the integrated intensity increases in a smooth curve from muscovite to montmorillonite. The major error in application of this quantitative method arises from uncertainty as to the correct allocation of peak areas in cases of overlap of the mixed-layer peak with those of discrete 10 Å and 14 Å clays also present.

INTRODUCTION

With the increased importance of X-ray techniques in the study of minerals, quantitative methods for resolving mixtures have become of considerable interest. Most methods attempt to relate the diffraction intensity from a given compound to its percentage in a mixture, normally a non-linear relationship because of differential absorption effects. With only two compounds present in a mixture relatively simple procedures suffice. By systematically varying the relative proportions of the compounds in a series of prepared mixtures, a standard working curve can be constructed by plotting the compound percentages versus some function of the relative diffraction intensities of the two compounds. With more than two compounds in a mixture it becomes impractical to attempt to duplicate by artificial mixtures all possible combinations of the components. The normal solution is to compensate for the variable absorption coefficient of the matrix inherent in such multiple combinations by the addition of a fixed amount of an internal standard

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(Clark and Reynolds, 1936). X-ray reflections from a given compound and from the internal standard are absorbed to the same degree by the matrix. Their intensity ratio, therefore, is independent of the matrix absorption. The reader is referred to Klug and Alexander (1954) for a more detailed formulation of quantitative concepts.

Quantitative analysis of clay minerals is particularly difficult because of (1) orientation effects, (2) compositional variations, including interstratification, within the clay minerals, and (3) variations in crystal perfection. In particular, the variations in composition and crystallinity of clay minerals make unlikely the development of any precise quantitative X-ray method that will be applicable to all clays. This paper is concerned primarily with the orientation effect and requires the availability of standard clays comparable in composition and crystallinity to the components of the mixtures under study.

The tendency of platy clay particles to arrange themselves in parallel orientation during sample preparation changes the intensity distribution of the basal reflections relative to the non-basal reflections from the platelets and relative to all reflections from non-platy components. The difficulty of controlling the degree of orientation from sample to sample therefore complicates quantitative methods of X-ray analysis of clays. Most previous methods have been directed either towards the attainment of a completely random distribution of particles or towards complete preferred orientation by settling techniques. Deviations from either ideal distribution of particles will cause errors in the resultant percentages of the components, except for those methods utilizing the relative intensities of the basal reflections alone. In particular, the internal standards suitable in other systems because of their non-platy morphology become ineffective in clay analysis unless a reproducible degree of orientation is possible.

The present writers propose a method using a platy internal standard that will orient to the same degree as the clay minerals themselves. The relative diffraction intensities between the basal reflections of the standard and of the clays will be preserved regardless of degree of orientation, thereby eliminating the need for reproducibility of orientation. A high degree of orientation is desirable, however, to insure that the non-basal reflections will not interfere with the basal reflections in diffractometer methods.

SELECTION OF INTERNAL STANDARD

An internal standard suitable for clay mineralogy work should possess the following characteristics:

(1) a platy morphology that will enable it to orient to the same degree as clay minerals;
(2) a strong basal reflection that will fall close to, but not overlap, those of the common clay minerals;

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(3) specific gravity and particle size similar enough to those of clay minerals that there will be no tendency for differential settling out of suspension;
(4) stability and non-reactivity to the chemical and physical treatments used to differentiate clay mineral varieties; and
(5) rarity or absence in natural clay deposits.

The following six synthetic layer-like compounds were tested as potential internal standards: $Mg(OH)_2$ (brucite), $Al(OH)_3$ (gibbsite), $Zn(OH)_2$, $CdCl_2$, SnS_2, and MoS_2. Of these, only $Zn(OH)_2$ proved suitable. The others are unsatisfactory either because of specific gravity or position of the basal reflection. The natural clay mineral pyrophyllite, which is rare or absent in most clay deposits, also proved to be a suitable internal standard.

The "zinc hydroxide" used in this study was purchased in reagent quality from A. D. Mackay Inc., who prepared it by precipitating zinc chloride with ammonium hydroxide, washing thoroughly, and drying at 110°C (personal communication). The X-ray pattern, however, is that of basic zinc chloride $ZnCl_2 \cdot 4Zn(OH)_2$ according to A.S.T.M. Powder Diffraction File card 7-155. The strong basal reflection at 7.89 Å is the 003 reflection from a hexagonal unit cell having $a = 6.34$ and $c = 23.66$ Å. Nowacki and Silverman (1961) have determined the crystal structure for basic zinc chloride and give a slightly different composition of $Zn_5(OH)_8Cl_2 \cdot H_2O$. The structure is said to consist of distorted Zn—OH packets of the brucite type with Zn occupying only three-quarters of the octahedral sites. Cl and H_2O lie in a single sheet between the $[Zn_3(OH)_8]^{2-}$ packets. Additional Zn atoms lie immediately under and above each vacant octahedral site within the packets and are coordinated tetrahedrally by 3OH + 1Cl. The reagent material used in this study will be referred to by its trade name of $Zn(OH)_2$ in the rest of the paper.

No reaction of the $Zn(OH)_2$ with glycerol has been found in the present study. The material will react very slowly with water to form ZnO and also will decompose above 300°C. $Zn(OH)_2$ is not completely satisfactory with respect to stability, therefore, for use as an internal standard. With proper experimental controls, however, it can be used successfully. Pyrophyllite may prove to be the most useful internal standard because it is stable under all the normal treatments to which clays are subjected during X-ray identification. Examples of working curves prepared with $Zn(OH)_2$ and with pyrophyllite will be presented to illustrate the principle of an orienting internal standard.

CONSTRUCTION OF WORKING CURVES

Because the method was devised for use in the study of a specific suite of Pennsylvanian shales and clays, attention was given first to construction of working curves for mixtures of 1Md illite and kaolinite. When these curves were found to give reproducible and satisfactory results, curves for $2M_1$

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muscovite, montmorillonite, and interstratified assemblages in this system were added to make the method of more general applicability.

The following clay mineral standards were selected because of their initial purity and their comparable grain sizes and degrees of perfection relative to the natural systems to be studied.

Kaolinite—API sample H-1, Murfreesboro, Arkansas—marine alteration of volcanic material.
1Md illite—API sample H-35, Fithian, Illinois—Pennsylvanian underclay.
$2M_1$ muscovite—Custer, South Dakota—fine-grained alteration product of pegmatitic orthoclase.
Montmorillonite—API sample H-27, Belle Fourche, South Dakota—marine alteration of volcanic ash.

Each sample was purified by the procedure suggested by Jackson (1956) until no impurities could be detected by X-ray powder patterns. Although Fithian illite has been reported to contain both the 1Md and the $2M_1$ mica polymorphs, only the 1Md form, slightly interstratified with expansible or chloritic layers, could be identified in the purified sample used here. Material of particle size greater than 2 microns was discarded in all cases. The finer material was stored in a 95% ethanol suspension until needed. The internal standard was centrifuged to obtain the same particle size fraction and was stored in a similar suspension.

The standard working curves for the kaolinite–illite system were prepared from a series of mixtures containing progressively varying proportions of kaolinite and illite and a constant amount of $Zn(OH)_2$. The clay samples first were evaporated from the ethanol suspension and were diluted with distilled water until they dispersed. The concentration of clay in these water suspensions was determined by weighing the amount of clay taken from a 25-ml aliquot and dried for 12 hr at 110°C. The concentration of $Zn(OH)_2$ suspended in 95% ethanol was determined in the same manner. The standard mixtures were then prepared volumetrically from the suspensions. Each mixture contained a total of 90 mg of clay plus 4.63 mg (or 5.144 wt%) of $Zn(OH)_2$. The resulting suspensions were throughly mixed, adding alcohol where necessary to produce freely-flowing mixtures, and transferred to glass slides by means of a 2-ml pipette. Each resulting oriented aggregate slide contained approximately 30 mg of clay. Diffractometer charts were obtained for duplicate slides of each mixture, and the area under each basal reflection was determined by planimeter. The best resolution and reproducibility of peaks was obtained by instrumental settings of $\frac{1}{4}°$ 2θ per minute traverse, $\frac{1}{2}°$ and 0.006 in. slits, and 16 sec time constant. CuKα radiation and a Geiger counter were used throughout. Care was taken to remain within the linear range of the counter.

Figure 1 illustrates the superimposed diffractometer charts of pure kaolinite, pure $Zn(OH)_2$, and pure 1Md illite, observed under identical conditions. The figure shows that the internal standard peak is well resolved from the kaolinite and illite peaks. The illite peak is considerably broader than the

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other peaks and is the main contributor to the background. These same points are illustrated also in Fig. 2, which shows superimposed diffractometer charts for three standard mixtures ranging from high kaolinite–low illite (curve 1) to low kaolinite–high illite (curve 3) contents. With high percentages of kaolinite there is an increase in the intensity of the $Zn(OH)_2$ peak and a corresponding decrease in both the magnitude and the slope of the background

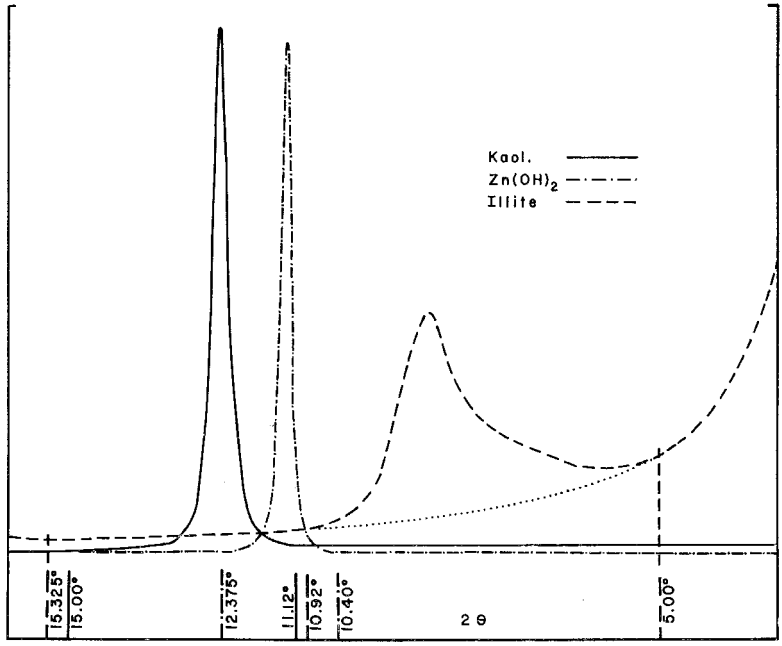


FIG. 1. Superimposed diffractometer charts for pure kaolinite, $Zn(OH)_2$, and illite. Maximum lateral limits of 2θ for each phase are shown to facilitate allocation of peak areas.

at the lower limit of the traverse at 3° 2θ. Because all three samples contain the same amount of $Zn(OH)_2$, this indicates an increase in the preferred orientation of the platy particles with increase in the percentage of kaolinite. The kaolinite orients well but the illite orients poorly. In kaolinite-rich samples that were purposely disoriented the peak intensities of all three components decreased and the slope and magnitude of the background at 3° 2θ increased. The background differences between the oriented and disoriented slides approximate those between a single crystal pattern and a powder pattern, with the background rising more rapidly as the direct beam is approached in the latter case.

Figures 1 and 2 also can be used to outline the best background base lines to the basal reflection peaks, needed to measure the integrated intensities

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of the peaks. Because a large part of this background can be assumed to be due to poor orientation of particles, a family of curves could be computed to show the ideal background distribution for cases intermediate between "single crystal" and "powder" orientations. A quicker empirical method yielding acceptable results has been used instead. The base line is constructed with French and ship's curves between two reference points selected at 5.00° and 15.325° 2θ. The point at 5.00° 2θ represents the observed low angle

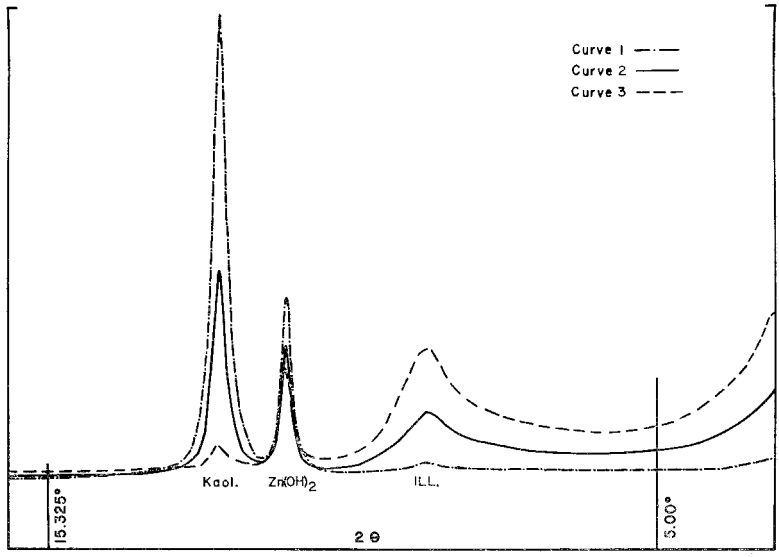


FIG. 2. Superimposed diffractometer charts for three standard mixtures having a constant weight percentage of $Zn(OH)_2$.

Curve 1—high kaolinite, low illite.
Curve 2—medium kaolinite, medium illite.
Curve 3—low kaolinite, high illite.

boundary of the 001 illite peak, whereas 15.325° 2θ represents the lowest background point between the 001 and 002 illite peaks and is unaffected by the kaolinite and $Zn(OH)_2$ backgrounds. Examples of base lines constructed in this manner are shown in dotted line under the illite peak in Fig. 1 and in solid line under the peaks of Fig. 3.

In determining the integrated intensity of each peak the area within overlapping regions has to be allocated by extrapolation of the peak shape down to the base line. To facilitate this procedure the maximum lateral extension of the peaks can be shown from Fig. 1 to be 5.00° to 10.92° 2θ for illite, 10.40° to 12.375° 2θ for $Zn(OH)_2$, and 11.12° to 15.00° 2θ for kaolinite. These limits are not symmetrical about the peak position owing to asymmetry of the peak shapes. Figure 3 illustrates a typical allocation and base line

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determination for equal amounts of illite and kaolinite. The integrated intensities of the illite and kaolinite peaks in this case have a ratio of 1.3 to 1.0 respectively, although the peak height of the kaolinite reflection is considerably greater than that of illite. Integrated intensities are to be preferred over peak heights not only because they represent the true intensities but also because they allow wider application of a given working curve to situations where variable degrees of perfection or particle size of the components may cause peak broadening without appreciable change of peak area.

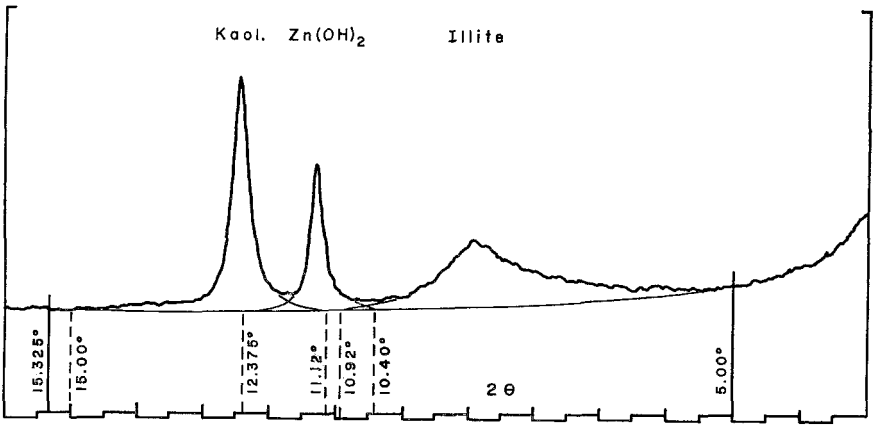


FIG. 3. Diffractometer chart for a standard mixture of equal amounts of kaolinite and illite, showing allocation of base line and peak areas.

Figure 4 shows working curves for the 1Md illite–kaolinite system. Each mixture was run in duplicate and each point represents the average of ten planimeter area determinations. The maximum deviation between duplicate points is equivalent to 4% of the clay concentration, but the average deviation is 2%. Experiments run to determine the sources of error involved indicated the major indeterminancy to be in positioning the base lines to the peaks. Minor errors are due to volumetric mixing of the standard samples and to determination of the concentration of $Zn(OH)_2$. The curves are essentially linear for kaolinite–illite ratios of 1:1 or greater. The curves progressively deviate from linearity as the illite content increases beyond the 1:1 ratio. This suggests that the phases are not orienting to the same degree at high illite concentrations, but that the relative degrees of orientation are reproducible. Empirical working curves of this type have an advantage, therefore, over quantitative methods that assume linearity and use fixed ratios of the scattering powers of the clay minerals present.

Similar techniques were employed to prepare the working curves for the $2M_1$ muscovite–montmorillonite system, illustrated in Fig. 5. Ten per cent

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of fine-grained pyrophyllite from the Kellogg mine, North Little Rock, Arkansas, was used as the internal standard for this set of curves. The pyrophyllite peak is considerably weaker than that of $Zn(OH)_2$, and a concentration of 15–20% is recommended in future work. Care had to be exercised with the montmorillonite to insure reproducibility of both the position and

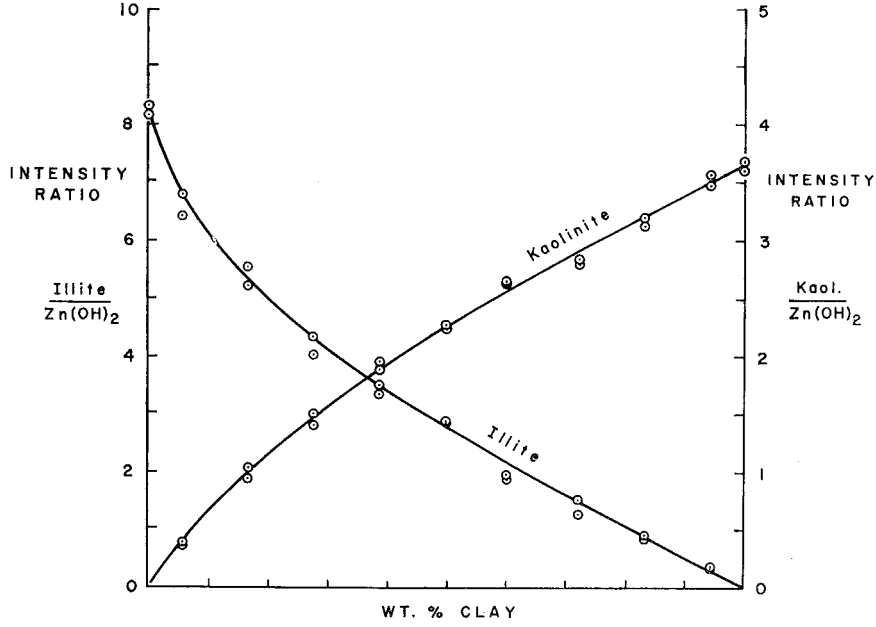


FIG. 4. Standard working curves for kaolinite and Fithian illite, showing intensity ratio of clay to $Zn(OH)_2$ as a function of weight percentage clay.

intensity of the basal reflections. Prior to mixing the clay components, the montmorillonite was Mg^{++} saturated to insure maintaining two water sheets between the layers. The 001 reflection has a spacing of 15.4 Å and a reproducible intensity if kept in a high and constant humidity atmosphere. The 002 montmorillonite reflection then has zero intensity and does not interfere with other possible clay components. Expansion of the montmorillonite layers by glycerol solvation or contraction by partial loss of interlayer water not only causes a change in the 001 montmorillonite intensity but also increases the 002 intensity to the point that it may interfere with peaks from the other components. It was found that reproducible results could be obtained by passing air under positive pressure through a saturated solution of $Na_2SO_4 \cdot 10\ H_2O$, to give 93% relative humidity, and then into the specimen chamber of the Norelco X-ray unit. Entrance and exit spigots for the air were tapped into the central hub of the scatter shield around the specimen and a Mylar film taped over the diffraction exit slot.

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The background base line in this system was drawn between reference points at 4.00° and 10.40° 2θ. The maximum lateral extension of the 002 pyrophyllite peak at 9.19 Å is between 9.00° and 10.40° 2θ, of the 002 muscovite peak at 10.01 Å between 8.25° and 9.50° 2θ, and of the 001 montmorillonite peak at 15.4 Å between 4.00° and 8.00° 2θ. The overlap between peaks is less than for the kaolinite, $Zn(OH)_2$, and illite peaks illustrated in Figs. 1–3.

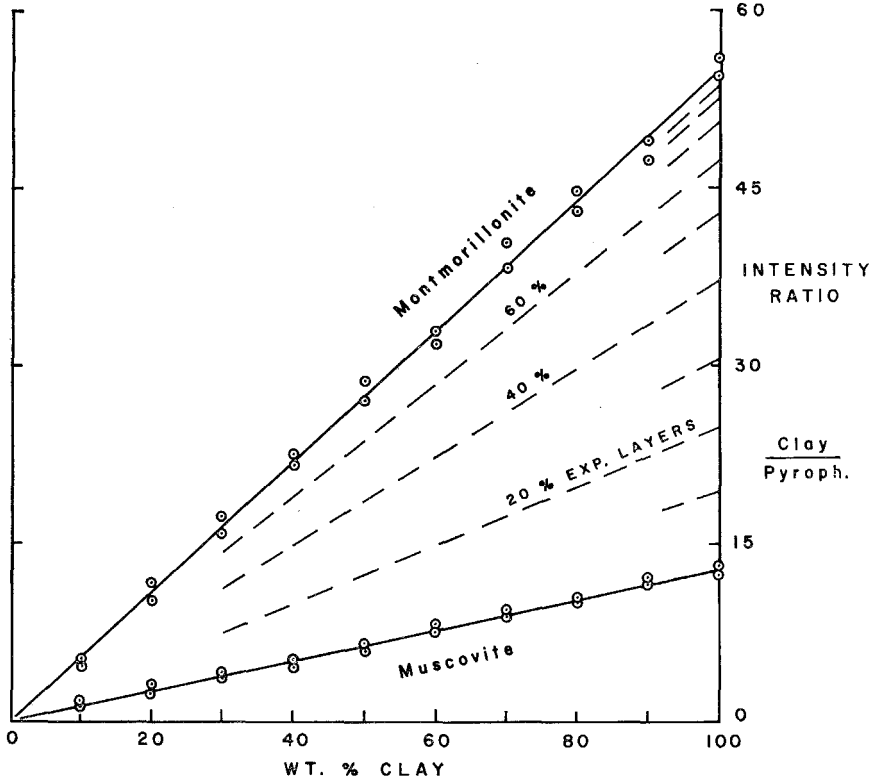


FIG. 5. Standard working curves for $2M_1$ muscovite and Belle Fourche montmorillonite, showing intensity ratio of clay to pyrophyllite as a function of weight percentage clay. Dashed lines for interstratified systems interpolated from Fig. 6*b*.

The $2M_1$ muscovite and montmorillonite working curves are linear throughout, indicating that the phases are orienting to the same degree in this system. The montmorillonite integrated intensity is 4.3 times that of muscovite for these particular specimens, but it must be kept in mind that this ratio will not necessarily be true for other montmorillonite and muscovite specimens. The deviation between duplicate points is about the same as for the kaolinite–illite system.

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Similar linear working curves have been prepared for the $2M_1$ muscovite–montmorillonite system, utilizing $Zn(OH)_2$ as the internal standard. Complete suppression of the 002 montmorillonite peak by humidity control is especially important in these samples to avoid coincidence with the $Zn(OH)_2$ peak. Because of the slow reaction of $Zn(OH)_2$ with water, it is also important to minimize the amount of time the $Zn(OH)_2$ is in contact with the high humidity atmosphere. Satisfactory results can be obtained if these precautions are observed.

INTERSTRATIFIED SYSTEMS

It was noted in preparing the working curves that the $2M_1$ muscovite peak is considerably sharper and more symmetrical than the 1Md illite peak, although the total integrated intensity of the former is smaller. This suggests interstratification within the illite. Because interstratified clay systems are common in sediments and soils, further consideration was given to the effect of interstratification on the quantitative curves presented. It is not practical to devise empirical working curves for such systems; pure end members of different degrees of interstratification are too difficult to obtain. It is possible to calculate the diffraction patterns to be expected under specified conditions, however, and to determine the general form that such curves would have. Results are presented here for the case of completely random interstratification of different percentages of muscovite and montmorillonite layers. Similar calculations could be made for other desired systems.

The diffracted intensity was computed over the range 25.0 Å to 7.4 Å for five different layer ratios intermediate between pure muscovite (10 Å) and pure montmorillonite (15.4 Å). The experimental data of Bradley (1945), modified to incorporate the proper interlayer compositions, were used for the variation of the layer structure factor over this range. These intensity values were multiplied by the mixing functions calculated by MacEwan, Ruiz Amil, and Brown (1961) for various ratios of 10/15 Å layers randomly mixed within five-layer crystallites.

The heights and widths of the resulting 001/001 diffraction peaks vary appreciably within the system. There is a minimum in the peak height at approximately 33% of the 15.4 Å component (Fig. 6*a*). The peak width varies in a similar but inverse pattern, so that the integrated intensity increases regularly from muscovite to montmorillonite (Fig. 6*b*). The latter curve can be used to interpolate tentative working curves for various 10/15 Å interstratifications intermediate between pure muscovite and pure montmorillonite. The shape of the integrated intensity curve in Fig. 6*b* is such that interstratification of a relatively small percentage of expanded layers increases the peak area markedly for interstratification up to 70%. The increase in intensity for interstratification greater than 70% is very small.

It should be emphasized that the interpolated intermediate curves shown as dashed lines on Fig. 5 are valid only for the data and the assumptions

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involved, namely the experimental intensity data, completely random mixing of 10 and 15.4 Å layers according to a five-layer crystallite mixing function model, and orientation of interstratified phases to the same degree as the pure phases. The presence of several different degrees of interstratification in the same sample, or of a third interstratified component, such as chlorite, will have additional effects not included in these calculations.

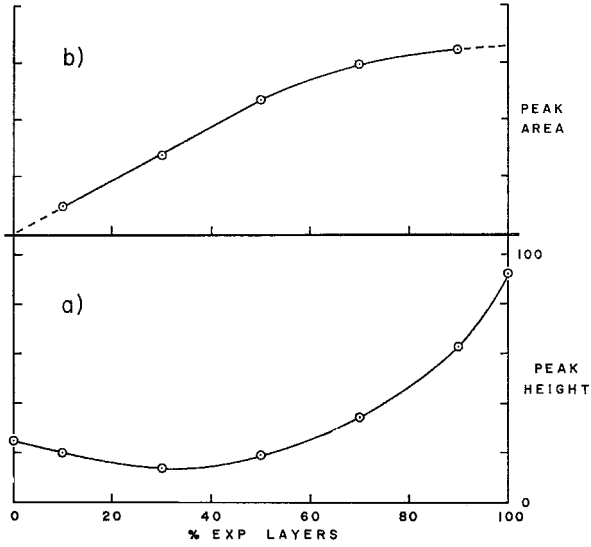


FIG. 6. Calculated peak heights and areas for random interstratification of 10 Å and 15.4 Å layers.

An alternative method of dealing with interstratified montmorillonitic layers that has been used by some workers is to collapse the higher spacings by heating so that there is only a single peak near 10 Å. Calculations by Brown (1955) and White (1962) show that such collapsed layers, which do not have interlayer K, have appreciably higher intensity 10 Å peaks than true muscovite. It should be possible to obtain quantitative results, however, by using the calculated intensity that is correct for the percentage of K present in the interstratified phase. Because of the linear nature of the muscovite working curve in Fig. 5, it is relatively easy to interpolate a family of curves corresponding to different K-contents in the 10 Å component. Probably the simplest method of determining the percentage of K present is to estimate the percentages of 15.4 Å and 10 Å layers present by use of the Hendricks–Teller spacing curves, and then to allocate the K proportionally. This assumes a full complement of K in the 10 Å component and no K in the 15.4 Å component. If discrete muscovite is present in the sample, it will also be necessary to determine the 10 Å peak intensity both before and after heating.

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APPLICATION

$Zn(OH)_2$ has been used as the internal standard in the application of this method to analysis of the clays contained within a suite of cyclothems of Desmoinesian age in northern Missouri and southern Iowa (Bailey, Brown, Cline, and Lister, in preparation). The clays present are $2M_1$ muscovite, kaolinite, interstratified illite–montmorillonite with 20–30% expansible layers, and small amounts of dioctahedral vermiculite. The scattering power of vermiculite relative to the other components was determined from the experimental data of Bradley (1945). Neither chlorite nor montmorillonite is present. This simple and homogeneous clay suite, completely dioctahedral and aluminous, is interpreted as primarily detrital and much of it derived by recycling of clays contained within older sedimentary rocks.

It is difficult to estimate the accuracy achieved with any X-ray clay method because of the variations possible in composition and degree of crystallinity. But the homogeneity of these cyclothemic clays suggests that these factors are reasonably constant throughout the suite studied. The major indeterminancy was found to arise not from errors inherent in the method itself but, for samples of high mixed-layer content, from uncertainty as to the correct allocation of peak areas in cases of overlap of the mixed-layer peak with those of muscovite and vermiculite. Some idea of the accuracy achieved can be estimated from the total clay mineral content obtained for each clay fraction. Ninety per cent of the fractions were found to give total clay mineral summations between 80% and 110%. A total somewhat less than 100% is to be expected because of the presence of small amounts of quartz and amorphous material. These results are considered satisfactory for a normal clay mineralogy study. Sample to sample variations greater than 10–15% in the relative percentages of individual clay minerals are probably significant, even though the errors in the absolute magnitudes are not known.

CONCLUSIONS

1. Use of a platy internal standard that will orient to the same degree as clay minerals preserves the relative diffraction intensities between the basal reflections of the platy components, regardless of degree of orientation. Linear working curves verifying this effect have been obtained for the $2M_1$ muscovite–montmorillonite system, using a controlled, high-humidity atmosphere and either pyrophyllite or $Zn(OH)_2$ as the internal standard.

2. Kaolinite and Fithian 1Md illite do not orient to the same degree at high illite concentrations, yielding a non-linear working curve with $Zn(OH)_2$ as the internal standard. The relative degrees of orientation are reproducible, however, so that the empirical working curves are usable. A fixed ratio of the scattering powers of the clay components is not valid in a non-linear system.

3. Calculations show that random interstratification of hydrated layers within muscovitic layers increases the integrated intensity markedly for

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interstratification up to 70%. There is a minimum in peak height, however, at approximately 33% of the 15.4 Å component.

4. Application of the method to a suite of Pennsylvanian clays indicates that the major error arises from overlap of mixed-layer peaks with those from 10 Å and 14 Å components. Summations of the clay mineral contents suggest that relative percentage variations of individual clay minerals found to be greater than 10% to 15% are probably significant.

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