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QUANTITATIVE DETERMINATION OF KAOLINITE BY X-RAY DIFFRACTION*

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ABSTRACT

An orientation index, I(00*l*)/I(060), $l=1,2$, is used to show that the degree of orientation of kaolinites ranging from well crystallized to poorly crystallized samples is high for samples giving sharp 00*l* reflections, and diminishes for samples with broader 00*l* reflections. A technique is employed involving the use of a thermoplastic cement which largely removes the preferential orientation in samples packed for *x*-ray diffractometer study. Van der Marel's experiments on the reflected basal intensities from kaolinite measured with respect to reflections from boehmite as an internal standard, are repeated, and the large variations found by him are confirmed when preferential orientation is not controlled. When the orientation is controlled, only small variations remain. Under this condition, the quantitative determination of kaolinite by *x*-ray diffraction is possible. However, the basal reflection intensities tend to diminish slightly as the reflection breadth increases, and therefore in analytical work a standard kaolinite will be preferred which gives basal reflections of the same angular width as those from the kaolinite to be determined.

INTRODUCTION

Quantitative *x*-ray diffraction provides a direct method for determining minerals in mixtures provided appropriate standards are available. Compared with other clay minerals, kaolinite presents relatively few problems because of the absence of significant amounts of isomorphous substitution. The basic assumption in determining kaolinites quantitatively by *x*-ray diffraction is that standard kaolinites can be obtained which diffract *x*-rays with the same intrinsic intensity as do the minerals to be measured. However, in a recent publication, van der Marel (1960) has brought forward data which seem to show that the reflected intensities from different kaolinites vary considerably. He gives values for the integrated intensities of the 001 reflections of a number of kaolinites ranging from about 1.9 down to 0.85 on a relative scale, a variation of about

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100%. If this is indeed true, then the quantitative assessment of kaolinite in unknown mixtures by x-ray diffraction becomes quite unreliable unless standards can be chosen which correspond in x-ray reflection characteristics with the kaolinites to be measured.

Van der Marel gives diagrams showing both peak and integrated 001 reflection intensities plotted against the surface areas of the kaolinites measured by the B.E.T. method, from which it appears that the reflected intensity diminishes with increasing surface area. This decrease of intensity is attributed to the development of an amorphous surface layer of the order of 15–25 Å thickness and/or to an increasing internal disorder in the crystal lattice. He concludes that "*it is not possible to determine quantitatively the amount of kaolinite in samples of different origin*," and that quantitative analysis is possible "*only when dealing with analyses of samples of one and the same particle size, order of crystallinity and composition.*"

One factor of considerable importance in relation to x-ray intensity measurements from kaolinite, particularly when the measurements are made by surface reflection, as in diffractometer techniques, is the marked tendency of the platy crystals to orient themselves parallel to the basal plane. Orientation is of extreme importance when measurements of the *basal* reflections are involved, as in the experiments of van der Marel. From the published account it appears that he gave little attention to this aspect of the work; he writes: "The samples were first dried at 105° C. for some hours (to prevent preferential orientation) and afterwards run with a Philips Geiger counter diffraction spectrometer. . . ." In the writers' view, this procedure is quite inadequate either to eliminate or even to control the preferential orientation of the platy clay particles.

Experiments have been undertaken, therefore, along similar lines to those of van der Marel, but with considerable attention to the question of preferential orientation. As a measure of orientation, the following intensity ratios have been measured: I(001)/I(060) and I(002)/I(060). Since orientation enhances I(001) and I(002), but diminishes I(060), these ratios provide convenient indications of the degree of orientation, and will be called "orientation indexes." It should be remarked that the prism reflection 020, although it occurs in the same angular range as the 001 and 002 reflections, is not suitable for measuring orientation because kaolinites with layer stacking disorder give diffuse scattering for the 020 and related reflections. On the other hand, the 060 and its associated reflections, $3\overline{31}$ and $33\overline{1}$, are always clearly defined and can be measured fairly accurately.

An absolute value for the orientation index for randomly oriented crystals can be calculated from the crystal structure of the mineral.

The intensity diffracted by a randomly oriented powder in a surface-reflection diffractometer is proportional to

$$F^2\,(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta) = F^2\phi(\theta),$$

where F is the structure factor and θ is the Bragg angle. This quantity was tabulated by Brindley and Robinson (1946) in their determination of the triclinic structure of kaolinite. They gave the values listed in the first and second columns of Table 1; the third column gives the calculated orientation indexes. The extent to which these results will agree with experimental values depends, of course, on the accuracy of the structure analysis as well as on the degree of preferential orientation in a powder sample. Since no attempt was made by Brindley and Robinson to refine the structure analysis beyond determining the general structural scheme, the importance of the calculated ratios must not be over-exaggerated.

TABLE 1. CALCULATED ORIENTATION INDEXES FOR KAOLINITE

hkl	$F^2\phi(\theta)\cdot 10^{-3}$	$I(00l)/I(060, 3\bar{3}\bar{1}, 33\bar{1})$
001	488	3.90
002	265	2.12
060	41.5	
$3\bar{3}\bar{1}$	42.5 } 125.4	—
$33\bar{1}$	41.4	

A purely experimental procedure is to measure the orientation indexes for many different kaolinites and to take the minimum values as representing the nearest approach to random orientation.

In the present experiments a technique has been applied for eliminating preferential orientation which appears to be largely successful, and the results now obtained go a long way towards proving that the intrinsic reflection intensities of the 001 and 002 reflections of kaolinite for different mineral samples exhibit relatively little variation, and that a large part of the variation observed by van der Marel is probably attributable to preferential orientation. His experiments and the present work both show the large variations which can arise when orientation is not adequately controlled, and the bearing of this result on the quantitative analyses of kaolinite in mixtures is very apparent.

THE PRESENT EXPERIMENTS

Materials

The experiments have been carried out using mainly a series of essentially pure kaolinites covering a range of particle sizes and degrees of crystal structure perfection which were made available through the courtesy of Mr. S. C. Lyons and the Georgia Kaolin Company. These materials have already been described by Murray and Lyons (1956); they range from very well crystallized kaolinites showing sharp *x*-ray powder diffraction lines and well defined hexagonal forms in electron micrographs, to poorly crystallized kaolinites giving diffuse *x*-ray diffractions indicative of internal stacking disorder. These kaolinites were labelled A, B, C, . . . , L by Murray and Lyons, and the same designations are used here to facilitate comparison with their studies. Data are also given for several other kaolinites, which are labelled M, N, and P, and one sample of metahalloysite from Eureka, Utah.

Internal Standard

To facilitate comparison with the results of van der Marel, the same internal standard has been employed, namely boehmite, AlO(OH), and the same kaolinite/boehmite ratio, 3:1, has been used. Weighed quantities of kaolinite and boehmite were ground together under acetone for 7 minutes and then were dried at 105° C.

The following reflections have been compared:

$$\left.\begin{array}{lll}\text{kaolinite} & (001) & d=7.15\text{ Å}\\ \text{boehmite} & (020) & d=6.11\text{ Å}\end{array}\right\}$$

$$\left.\begin{array}{lll}\text{kaolinite} & (002) & d=3.57\text{ Å}\\ \text{boehmite} & (021) & d=3.16\text{ Å}\end{array}\right\}$$

Van der Marel made use of the first pair of reflections only, but as the second pair are equally convenient they also have been used.

Elimination of Orientation

As pointed out in the Introduction, orientation of the kaolinite flakes is potentially of great importance for the question under consideration. A technique for the elimination of preferred orientation, described to the writers by Mr. David Hinckley, has been applied in a modified form. The method consists of mixing a thermoplastic organic cement* with the clay, and then crushing after the mixture has hardened. Initially the cement was softened at about 80° C., but mixing with the clay was not easy and the cement was partly lost by vaporization. The following technique was then evolved: Powdered cement* was added to the clay in the ratio 1:5 and the mixture was ground for 7 minutes. Dioxane was then added to dissolve the cement; this was done on a hot-water bath.

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* The cement used was "Lakeside, No. 70C," supplied by Hugh Courtright and Co., Chicago 20, Ill.

The cement dissolved readily and the mixing was continued with a spatula during the dissolution and eventual drying of the clay-cement mass. This had a granular texture and when fully dry was lightly ground for about 15 minutes to produce a fine powder. The material no longer had a "clayey feel."

Preliminary tests with various additions of the cement on the orientation of kaolinite as measured by the orientation index previously defined, showed that a cement:clay ratio of 1:5 was sufficient to reduce the orientation index to a minimum value.

The intensity ratios I (kaolinite)/I(boehmite), using the reflections previously listed, were measured with and without the cement addition. The measurements *without* cement were made with the object of comparing the results with those of van der Marel.

X-Ray Procedures

Measurements were made using filtered CuKα radiation and a Philips high-angle diffractometer with a scanning speed of $(\frac{1}{4})^\circ$ 2θ/minute and chart recording. *X*-ray intensities were kept within the range for which the recording system has an essentially linear characteristic. The sample was mounted in a 1″ diameter rotating holder constructed so that it could be packed from the back. To obtain uniform compaction of the powders, the same sample weight (0.5 gram) was used for each measurement. Integrated intensities were obtained by graphical integration, and each recorded value is the average of 3 runs on separately packed samples.

The angular widths of the 001 and 002 reflections were measured at half-maximum intensity. If, as van der Marel suggests, the reflected intensities are diminished by lattice disorder, then the widths of these reflections will be a useful parameter against which to plot the measured intensities. If the angular widths are related to the number of coherently reflecting planes, *i.e.*, effective crystal size, then again the widths will be a useful parameter to consider.

RESULTS

The results are presented graphically in Figs. 1, 2, 3 and 4, where closed and open circles show respectively data for samples prepared with and without the thermoplastic cement.

Results for the Orientation Index

Figures 1 and 2 show the orientation indexes for kaolinite, I(001)/I(060) and I(002)/I(060), plotted against angular breadths B(001) and B(002). The open circles (samples without cement) are widely dis-

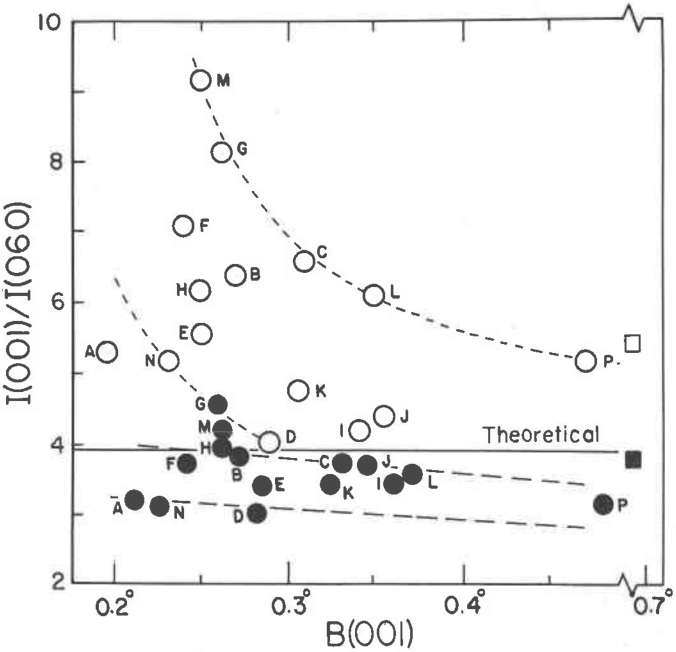

FIG. 1. Orientation index, I(001)/I(060), for fifteen kaolinite samples and one halloysite sample plotted against breadth B of the 001 reflections. Open circles for kaolinites without cement treatment. Solid circles for kaolinites with cement treatment. Squares show corresponding data for halloysite. Horizontal line shows theoretically calculated orientation index.

tributed, but have a general tendency to decrease in value as B increases. The closed circles (samples with cement) are confined to relatively narrow zones and the orientation indexes are nearly constant over the whole range of values of B.

The theoretically calculated orientation indexes also are shown in Figs. 1 and 2 by horizontal lines. Their agreement with the experimental values is particularly good for I(001)/I(060), but is less satisfactory for I(002)/I(060). The calculated value is *high* with respect to the experimental data in Fig. 1 but *low* in Fig. 2. The disagreements can be attributed, therefore, more to the approximate structure determinations than to the experimental data.

The experimental data for metahalloysite are shown by squares in Figs. 1 and 2. In order to include these values, it was necessary to break the horizontal axes, since the B values for the 001 and 002 reflections of halloysite lie far beyond the range of those for the kaolinite reflections. It is interesting to find that the halloysite reflections line up very well with those for kaolinite despite the very different morphologies of the two minerals and the fact that the structural layers of halloysite are probably curved.

It can be concluded from the data in Figs. 1 and 2 that the cement technique has been largely successful in removing preferential orientation of the clay particles and that, in the absence of such a technique, orientation has a very large influence on the reflected intensities. Furthermore, the character of the results shows that orientation increases as the angular breadth B decreases. In so far as the angular breadth is related to morphology, it may be stated tentatively that kaolinites giving sharp reflections arise from well-crystallized forms which tend to be highly oriented.

Reflected Intensities

Figures 3 and 4 show values of the intensity ratios I(001)K/I(020)B and I(002)K/I(021)B, where K and B signify kaolinite and boehmite

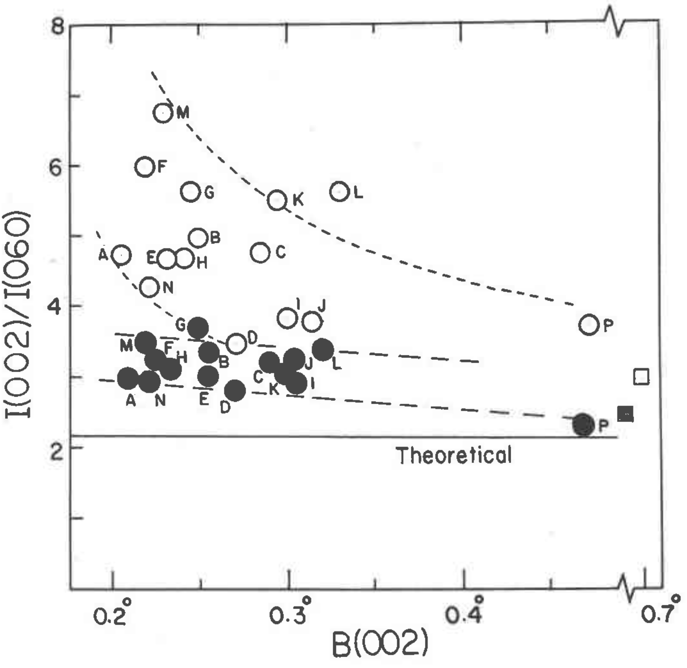

FIG. 2. Orientation index, I(002)/I(060), for fifteen kaolinite samples and one halloysite plotted against breadth B of the 002 reflections. Open circles for kaolinites without cement treatment; solid circles for kaolinites with cement treatment. Squares show corresponding data for halloysite. Horizontal line shows theoretically calculated orientation index.

respectively; the open and closed circles have the same significance as before.

Again it is seen that the open circles have wide ranges of values, with a marked tendency to decrease in magnitude as the breadth B increases. The data in Fig. 3 are comparable with those given by van der Marel in his Fig. 4. His values for I(001)K/I(020)B extend from about 1.9 down to 0.85, and the present values extend from about 2.2 down to 1.4. Both sets of values diminish as the breadth B, or as the surface area in van der Marel's Fig. 4, increases.

The closed circles in Figs. 3 and 4 are much more nearly constant and show relatively little variation as B increases. However, there remains a tendency for the intensities to diminish as the breadth B increases.

It is strikingly obvious that the intensity variations shown in Figs. 3 and 4 by the open circles run parallel with the orientation indexes given in Figs. 1 and 2. Conversely, when orientation is removed (or at least maintained constant) as shown by the solid circles in Figs. 1 and 2, the intensities in Figs. 3 and 4 also remain nearly constant.

Results for halloysite also are shown in Figs. 3 and 4. When account

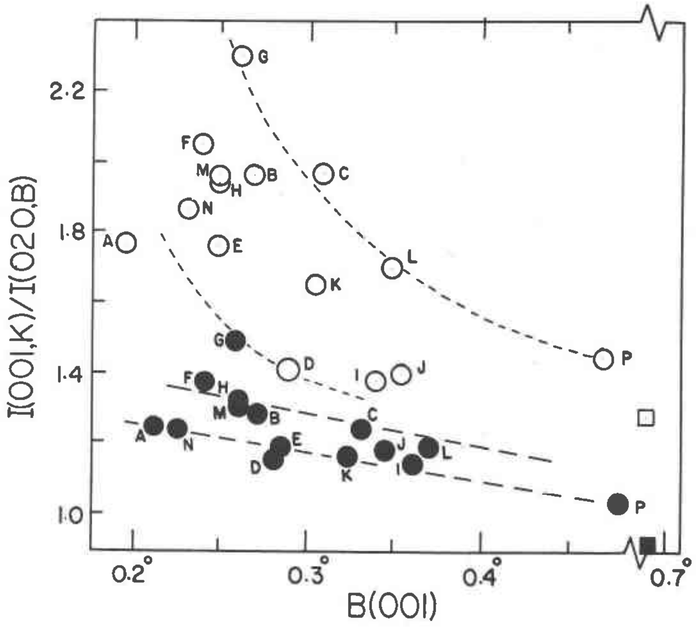

FIG. 3. Intensities of 001 reflections from fifteen kaolinite samples and one halloysite sample measured with respect to the 020 reflection from boehmite, plotted against breadth B of the 001 reflections. Open and solid circles and squares have the same significance as in Figs. 1 and 2.

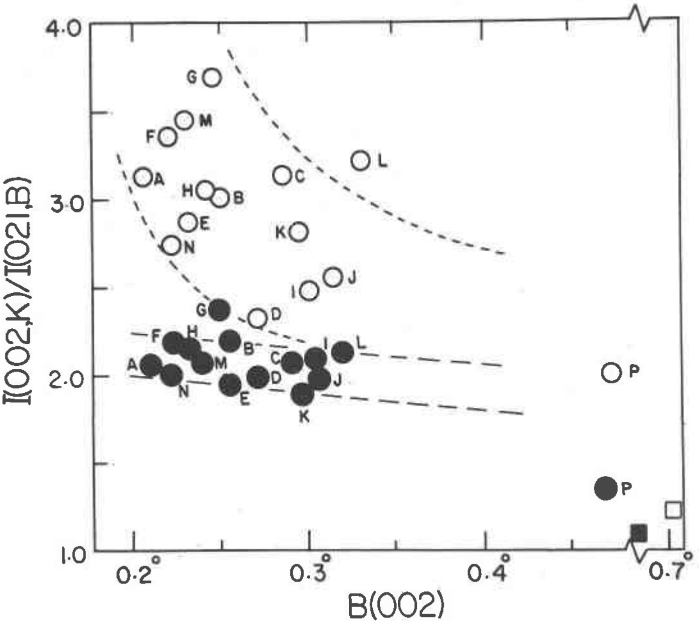

FIG. 4. Intensities of 002 reflections from fifteen kaolinite samples and one halloysite sample measured with respect to the 021 reflection from boehmite, plotted against breadth B of the 002 reflections. Open and closed circles and squares have the same significance as in Figs. 1 and 2.

is taken of the breaks in the B axis in these figures, the halloysite values are seen to lie roughly in line with those for the kaolinites, provided one accepts the conclusion that the intensities are diminishing slowly with increase of B. Indeed, the halloysite values provide additional support for this view. It is clear that for the kaolinites themselves, the decrease of intensity with increase of B is relatively small when preferential orientation is eliminated. It is not wholly negligible, however, and in the quantitative determination of kaolinites in mixtures it will be advantageous to choose standards having B values similar to those of the minerals being determined.

DISCUSSION AND CONCLUSIONS

The present experiments have confirmed those of van der Marel in showing large variations in the integrated intensities of the 001 and 002 reflections of kaolinites when no special precautions are taken to eliminate preferential orientation. An orientation index, I(00l)/I(060) with $l=1$ and 2, is used to show that preferential orientation varies considerably from one kaolinite to another, the highest orientation and the highest 00l

intensities corresponding to small values of B, the angular breadth of a basal reflection.

By using a thermoplastic cement, preferential orientation is largely eliminated (or at least controlled) and the reflected intensities are then nearly constant. Van der Marel's conclusion that "it is not possible to determine quantitatively the amount of kaolinite in samples of different origin" by *x*-ray diffraction analysis because of the large variation in reflected *x*-ray intensity is thus shown to be invalid. However, it appears that with increasing breadth of the kaolinite reflections, there is a small and not negligible tendency for the reflected intensity to diminish. Therefore it is advisable when selecting a standard kaolinite to choose one with approximately the same angular reflection breadth as the kaolinite to be measured. From the data shown in Figs. 3 and 4 it appears that it should be possible to select a kaolinite standard which reflects to within about 5% the same intensity as a kaolinite under investigation.

Van der Marel's results and those obtained in the present paper without using orientation control (*i.e.*, the open circles in Figs. 3 and 4) show the large errors which can arise in determining kaolinite by *x*-ray diffraction, if special precautions are not taken to diminish the orientation so readily assumed by clay mineral particles. An alternative solution to this problem, namely not to use basal reflections but to use more general-type reflections less subject to orientation errors, is generally impracticable. In many clay mineral mixtures in which kaolinite is present, the 001 reflection from the 7.15 Å layer spacing may be the only kaolinite reflection which is suitable for measurement and even this may be overlapped by a 002 chlorite reflection. Therefore, of necessity, the 001 and 002 kaolinite reflections, despite their sensitive dependence on preferential orientation, will be the only possible reflections which can be used in quantitative work. The present experiments emphasize the importance of eliminating (or controlling) the preferential orientation. The use of the organic cement is easy and simple and introduces very little additional labor in analytical determinations.

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