

IDENTIFICATION OF CLAY MINERALS BY X-RAY DIFFRACTION ANALYSIS

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ABSTRACT

Since X-ray diffraction patterns are directly related to crystal structures, X-ray identification is, in principal, better suited to the recognition of structural groups and structural varieties than of chemical species.

Well-formed kaolin, mica, and chlorite structures give rise to characteristic 7, 10 and 14Å spacings which are relatively easily identified. Hydrated forms, such as hydrated halloysite ($d=10\text{Å}$) and montmorillonoids under normal conditions ($d=14\text{Å}$), are recognized either by low-temperature dehydration giving characteristically diminished spacings, or by the formation of organic complexes giving characteristically increased spacings. This introduces at once the principle that X-ray identification may, and generally does, entail the study of mineral modification by suitable chemical and/or thermal treatment.

The main requirements in the X-ray technique are: (1) Ability to record long spacings up to 25Å or even higher values; (2) well focused lines with good resolution; (3) absence of background scattering and white radiation anomalies. Of these, (1) and (3) lie within the control of the investigator, but (2) depends partly on the material.

The main difficulties of X-ray identification are: (1) The multiplicity of lines when many components are present, and (2) poorly defined diagrams arising from poor crystallinity and/or small size of crystals. The first can be treated experimentally, but the second is inherent in the problem. Simplification of X-ray diagrams is possible by sedimentation, acid treatment and thermal treatment and by the use of orientated specimens. Poor quality powder diagrams (if not due to poor technique) are of interest in themselves and may still give valuable information concerning the clay minerals, more particularly when monomineralic or mainly monomineralic fractions are used. Line profiles give valuable indications of randomly displaced layers and of interstratified sequences.

The recognition of chemical species by X-rays is difficult but some progress can be made if pure or nearly pure specimens are obtainable. The recognition of di- and tri-octahedral minerals by the (060) spacing is well known but the recognition of micas and chlorites in any greater detail is difficult. A consideration of basal spacings and basal intensities may make more specific identification possible.

INTRODUCTION

The problem of identifying clay minerals by X-ray diffraction analysis may usefully be considered in relation to the scheme of classification, already outlined in Table 1 of the previous paper *Structural Mineralogy of Clays to this Conference*, in which minerals are subdivided successively into chemical categories, structural groups and sub-groups, chemical species, and structural varieties. Since X-ray diffraction analysis is concerned primarily with structural aspects of clay minerals, it is clear that the method is most suited to the recognition of structural groups and structural varieties. Differentiation between chemical species tends to be difficult except in cases where the structural varieties are themselves indicative of particular chemical species. Apart from this possibility, the recognition of chemical species requires consideration of the manner in which the fine details of X-ray diffraction patterns depend on chemical constitution. From this standpoint, atoms differ in size and in scattering power. Structurally similar minerals of different chemical composition may therefore show characteristic differences in lattice parameters and/or in the intensities of their X-ray diffraction effects.

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The subject of X-ray identification of clay minerals has been reviewed up to 1950 by a number of writers in *X-ray Identification and Crystal Structures of Clay Minerals*, edited by the present writer and published by the Mineralogical Society of Great Britain. This discusses the principles of identification and gives lists of X-ray powder data. *Clay Mineral Standards*, edited by Kerr (1950), also contains a section listing X-ray powder data for clay minerals. Data are also to be found in the American Society for Testing Materials card index of X-ray diffraction data. The present article gives a broad survey of the subject and indicates some present trends.

EVALUATION OF STRUCTURAL GROUPS AND SUB-GROUPS

Use of Basal Reflections. The majority of clay minerals have layer silicate structures with a marked basal cleavage and platy habit. The basal reflections, generally designated 00 l , are usually easily recognized more particularly when preferentially orientated aggregates are employed. These reflections, if indexed 001, 002, 003, etc., give directly the thickness of the structural layers. The unit cell of the structure may, and often does, contain more than one such layer depending on the manner in which the layers are stacked on each other. The stacking sequence determines the particular structural variety of the mineral and generally is less easily determined than the layer thickness. The latter determines, in a broad sense, the layer type and so suffices to place a mineral in a particular structural group or sub-group.

Layer spacings of about 7, 10 and 14Å are the ones most commonly observed and they are broadly characteristic of particular kinds of layers.

Ambiguities in their interpretation can usually be resolved by (a) knowing the sequence of basal intensities, and (b) applying auxiliary techniques, such as the use of characteristic thermal and chemical properties of the minerals, in conjunction with X-ray examination. In addition, it is often useful to use orientated aggregates which for platy minerals can be obtained by careful sedimentation onto a glass plate. This greatly enhances the basal reflections and largely suppresses others, so that an easier interpretation of these reflections is obtained (Nagelschmidt, 1941; MacEwan, 1951).

The problems involved are generally not difficult if pure and sufficiently well-crystallized material is examined and the experimental technique is adequate. But clay minerals are frequently neither pure nor well-crystallized and the problems encountered may be considerable.

Interpretation of 10Å Spacings. Ten-Å spacings indicate unexpanded mica-type layers or the presence of hydrated halloysite. Since the sequence of lines from these is quite different they are not likely to be confused. Further, micas tend to be preferentially orientated parallel to the basal planes while halloysite, owing to its morphology, shows no such orientation. The most decisive test, however, is that hydrated halloysite readily dehydrates at 100°C, to a spacing of 7.2 to 7.4Å.

Interpretation of 7Å Spacings. A true spacing of 7Å (as distinct from a second-order reflection from a 14Å spacing) indicates a kaolin-type mineral in the sense used in the preceding paper *Structural Mineralogy of Clays* in this symposium. There is usually no difficulty in recognizing this type of layer structure. Uncertainties are likely to arise only if a mineral giving a 14Å spacing is also present, for then the 7Å line may be a second-order reflection from the 14Å spacing. Diagnosis now rests on removing the component giving the 14Å line or at least modifying it so that it no longer possesses a 14Å spacing. If a kaolin-type mineral is present, then the 7Å line will persist provided it has not also been affected by the treatment. An important source of error or uncertainty which must not be forgotten is that some minerals having 14Å spacings tend to give extremely weak odd-order and strong even-order reflections. Therefore a weak 14Å line and a strong 7Å line does not necessarily mean a small amount of a "14Å" mineral and a predominance of a "7Å" mineral. The interpretation requires a careful evaluation of the particular minerals which are present.

Interpretation of 14Å Spacings. These are generally due to chlorites, vermiculites and montmorillonoids and we are to consider how to differentiate between these.

Heat treatment in air to 400°-500°C causes vermiculites and montmorillonoids to collapse to a spacing of about 9.5 to 10.5Å (the exact value depending on the interlayer cations) whereas chlorites are unaffected. Further, at 600-700°C chlorites are modified by partial dehydration in such a way that the 14Å reflection is, indeed, of enhanced intensity. This effect is of particular interest in regard to iron-bearing chlorites which normally give a very weak 14Å reflection. Treatment at 500-600°C also effectively removes kaolin components thus concentrating attention on the chlorite problem.

On the other hand, since chlorites are soluble in warm dilute HCl, they may be removed from a mixture so that a kaolin component can be more easily recognized. Kaolin-type minerals, such as chamosite, however, will also be removed by this treatment.

The swelling characteristics of clay minerals also constitute a powerful tool. Montmorillonoids swell in glycerol or ethylene glycol to a spacing of 17.7Å while chlorites are unaffected. This 17.7Å reflection is also relatively strong thus facilitating the recognition of small percentages (MacEwan, 1946, has claimed that 1 percent can be detected). The layers of glycerol-montmorillonoids are more uniformly spaced than those of hydrated montmorillonoids and a clearer succession of higher orders is obtained.

With regard to vermiculite, Walker (1949) considers that they "can be positively identified by leaching with a solution of an ammonium salt, which causes the displacement of the 14Å line to about 11Å even if glycerol is afterwards added to the sample."

Walker admirably summarises the position in his three-way test which consists in leaching with an ammonium salt solution, or boiling gently for a few minutes in such a solution, and then adding glycerol to the washed and dried residue. Lines at 11, 14 and 17.7Å indicate respectively vermiculite, chlorite, and montmorillonite. He recommends, however, that if a chlorite

is indicated by this test, an appropriate heat-treatment test should be applied in confirmation.

Swelling chlorites, however, do exist, as Stephen and MacEwan (1949) have reported, so that some care will still be necessary before a decision can be made that a mineral is not a chlorite on the grounds that a swelling of the lattice is observed.

Interpretation of Non-integral Basal Reflections. Mixed-layer mineral types are now being recognized with increasing frequency, particularly among soil clays, (see, for example, a paper by Jackson et al., 1952). Similarities in the layer structures of clay minerals make the occurrence of mixed structures, such as mica-montmorillonites and chlorite-montmorillonites, easily possible. Such structures are essentially of mica type throughout but with different cations between layers, so that some layers are capable and others incapable of swelling. Partially hydrated halloysite may also come in this category; it appears to retain some interlayer water when the greater part of the mineral is dehydrated. Illites fall either in this category or on the border line, for the 10Å reflection from illite has a characteristically shaded appearance in powder photographs which suggests an admixture of mainly 10Å spacings with some larger spacings.

It was the apparently continuous expansion of the first basal spacing of montmorillonite without corresponding changes in other orders of reflection which led Hendricks and Teller (1942) to study the diffraction characteristics of layer structures having a random sequence of unequal layers. The numerical analysis is simplest when it can be assumed that all the layers scatter equally but possess different spacings. An example of this kind was studied by Brindley and Goodyear (1948) in connection with the hydration of halloysite. On the assumption that all the layers scattered equally and had a random distribution of 7.2 and 10.0Å spacings, and from the position of the first observed spacing, the proportion of hydrated layers was determined, and hence the amount of interlayer water in partially hydrated material. A satisfactory correlation was obtained with the directly measured water content.

A detailed numerical analysis of the positions of reflections from mixed-layer structures in relation to the proportion of the two kinds of layer which are intermixed has been carried out by Brown and MacEwan (1951) on the basis of the simplifying assumption that the layers scatter equally and differ only in their spacings. How nearly this represents the actual state of affairs will depend on the interlayer material. When this consists mainly of water molecules, as for example in an inhomogeneously expanded, or hydrated, montmorillonoid or halloysite, the approximation is a good one, but in the case of intermixed mica and chlorite layers it will not be quantitatively good though it will probably lead to the right qualitative picture.

More recently Méring (1949) has given a new and more general analysis of this problem and has taken into account the effect of crystal size (i.e. the number of diffracting layers) and the variation of structure factor with angle, and has given (Méring, 1950) a number of illustrative examples.

The main characteristics of this type of diffraction are:

(i) A non-integral series of basal reflections. Successive reflections do not correspond to integral values of n in the Bragg reflection law, $n\lambda = 2d \sin \theta$. If d is calculated from the angular position of the first observed reflection, the value so obtained is a statistical average and does not correspond exactly to the spacing of any particular layer.

(ii) A variable line breadth. Some reflections appear broad and others comparatively sharp. As a simple example we may consider a random mixture of 10Å and 15Å layers. The first observed reflection will lie between these extremes and be nearer the one or the other depending on the proportion of the two, but for about equal proportions a rather broad line at 12 to 13Å would be expected. In such an example, a sharp line at 5Å would occur, this corresponding exactly to the second order of the 10Å spacing and third order of the 15Å spacing. This example illustrates also the difficulty of attaching a particular order to an observed line in such cases.

(iii) Unequal movement of lines when the component spacings are modified. This is obtained, for example, by changing the degree of hydration or by forming an organic complex. The analysis by Brown and MacEwan (1951) is invaluable for interpreting such effects.

The interpretation of mixed-layer structures presents a more difficult problem than the recognition of regular structures. The main experimental requirement is to obtain X-ray diagrams of the pure mineral. Then, provided one of the component layers can be modified by heat-treatment or by organic or other reagents, Brown and MacEwan's tabulations should give considerable information regarding the kinds of layers which are present.

Ideally, as MacEwan has explained in this Conference, it should be possible by use of a Patterson type analysis, as used in crystal structure determinations, to determine the probability of finding after a layer of type A a second layer of type A (with characteristic AA separation) or a layer of a different type B (with its characteristic separation, AB). To carry out an analysis of this kind requires a complete knowledge of the variation of scattered X-ray intensity with angle and therefore it is only possible for pure mono-mineralic specimens. However, it promises to be a very important development because it will give information not only of the kinds of layers which are present in a mixed-layer sequence, but also of the degree of ordering of the layers.

X-RAY TECHNIQUE

The identification of clay minerals by X-ray analysis depends on the use of a satisfactory experimental technique. The main requirements are:

- (i) Ability to record long spacings up to about 25Å or even higher values.
- (ii) Well focused lines with good resolution.
- (iii) Absence of background scattering and white radiation anomalies.

Of these, (i) and (iii) lie within the control of the investigator, but (ii) depends partly on the character of the material.

Experimental Methods. Both photographic and Geiger counter methods of recording are widely used. It must be emphasized that these are alternative methods of recording X-ray diffraction data and that many factors which influence the diffracted intensities are common to both techniques. The effects due to crystal orientation and to inhomogeneous absorption of X-rays in multi-component specimens are equally important in both methods.

The Geiger counter spectrometer with continuous automatic recording of reflected intensity is particularly useful for obtaining accurate intensity and spacing measurements. As compared with the most accurate photographic techniques, absolute measurements of lattice spacings with the spectrometer may be somewhat less accurate (c.f. Wilson, 1950) but for clay mineral measurements, which are mainly at low θ -values, the spectrometer gives spacing data at least as accurate as the best photographic measurements, while the direct recording of intensity is a considerable advantage over photographic and micro-photometric determinations.

As regards sensitivity in the recording of weak reflections, the Geiger counter method is claimed to be as sensitive as photographic recording, but this is probably not valid for all forms of the instrument and it calls for careful consideration so that weak but valuable reflections are not overlooked through the use of this very convenient instrument. The recording spectrometer is especially useful when it is required to examine a small angular range of the diffraction diagram for a range of specimens.

Long Spacing Measurements. While the basic layer types have spacings of about 7, 10 and 14 to 15 Å, and glycerol-montmorillonite has a spacing of 17.7 Å, a number of larger spacings have been recorded in recent years. Bradley (1950) obtained a basal spacing of 25.0 Å with the mineral rectorite which contains a regular alternation of pyrophyllite-type and vermiculite-type layers. Alexanian and Wey (1951) recorded a spacing of about 32Å from a montmorillonite from Camp Bertheaux (Morocco). Caillère, Mathieu-Sicaud, and Hénin (1950) described a mica-like mineral from Alleverd with a spacing of about 22Å. These observations show the importance of extending spacing measurements to values beyond 20Å as a matter of routine procedure.

The study of long spacings from hydrated Na-montmorillonite by Norrish and MacEwan, which are reported at this Conference, emphasises still further the importance of developing adequate techniques for long spacing measurements.

X-ray Powder Cameras for Clay Mineral Studies. Cameras of commercial design for routine X-ray powder analysis are often inadequate for clay-mineral work since they cannot be used for spacings as large as 17.7Å (the minimum requirement for clay-mineral analysis) while air scattering of the incident X-ray beam and sometimes also scattering by faulty collimation restricts still further the measurement of long spacings.

The use of powder layers in preference to rods or tubes of powder is recommended by some workers. MacEwan (1946) describes the use of a thin powder layer set edge-wise to the X-ray beam, and which may be given a small

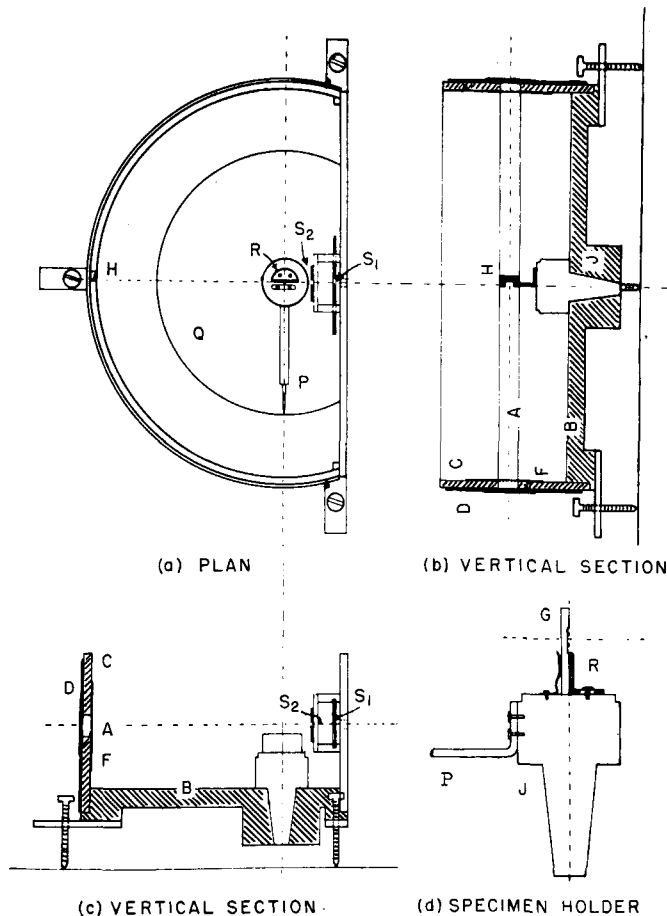


FIGURE 1. Semi-focusing powder camera for clay mineral analysis (Brindley and Robinson). This consists of a brass cylinder, C, soldered to a massive base, B, having additional thickness at the centre to take the conical joint, J, within which rests the specimen holder. The outer wall of the cylinder and the conical joint are accurately co-axial. The powder is pressed into a shallow cavity in a small glass plate, G, which is held by a spring against the vertical face of the right-angled piece, R. This vertical surface is adjusted to lie accurately on the axis of the camera, so that the powder surface is automatically set on the axis. A fine slit, S_1 , allows an X-ray beam having a divergence of about $\frac{1}{2}^\circ$ to fall on the powder surface; S_2 is a trimming slit. The film is held on the outer surface of C by a slightly stretched, black rubber band, D. The reflected X-rays reach the film through the aperture, A, and to avoid weakening thereby the cylinder C, a stop, H, is inserted having knife-edges which cut into the direct beam above and below the equatorial plane. The film holder is made light-tight by thin aluminium foil, F, or thin nickel foil when $\text{CuK}\alpha$ radiation is employed. The angular setting of the powder surface is determined by a pointer, P, moving over a graduated scale, Q. Diagrams (a), (b) and (c) are drawn on the same scale, the external diameter of the cylinder C being 20.0 cm; diagram (d) is on twice this scale.

angular oscillation. The present writer has employed for many years flat powder layers set at an appropriate angle to the incident X-ray beam, a method which gives partial focusing of the reflected beams over a useful range of angles. Figure 1 shows the type of camera used by Brindley and Robinson (1946) in their study of the structure of kaolinite. With the powder plate set at an angle $\alpha \approx 3^\circ$ to the incident X-ray beam and with $\text{CuK}\alpha$ radiation, spacings ranging from about 4\AA to 20\AA , or beyond, can be sharply recorded; with $\alpha \approx 9^\circ$ or 12° , a range from about 7\AA down to about 1.5\AA is obtained.

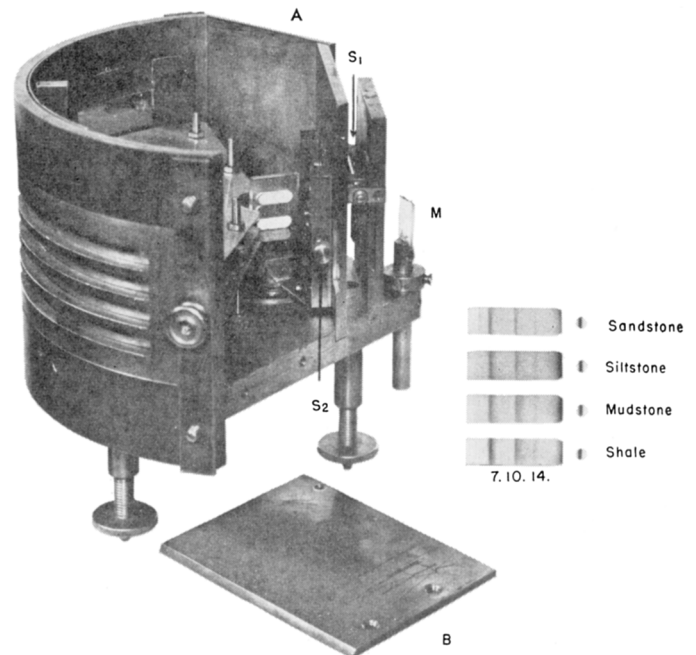


FIGURE 2. Semi-focusing, multi-exposure camera for clay mineral analysis (Brindley and Crooke). This camera takes four powder specimens which are tightly pressed into cavities in perspex or glass holders, preferably from the back surface to minimize orientation of flaky minerals in the front surface. The reflections from the four powders are separated by three aluminium baffles and are recorded on a film held on the outer surface of the camera by a black rubber band. Four X-ray beams are selected by a slit system at S_1 and trimmed by adjustable knife edges at S_2 . M is a lithium fluoride monochromator.

The camera is of massive construction so that the side plates, A and B, can be removed without disturbing the curvature of the film mount.

The powder diagrams show the 7, 10, and 14\AA lines from kaolin, mica, and chlorite components, and illustrate the results obtained when the camera is set to focus in the range from $5\text{-}20\text{\AA}$.

The increasing diffuseness of the mica line in passing from the sandstone to the shale is readily seen.

Figure 2 shows a camera designed and used by Brindley and Crooke, with which four powders can be examined simultaneously and separately. The principle is closely similar to that discussed by de Wolff (1948), but is modified so that surface reflection rather than transmission recording is obtained.

Since clay minerals give few, if any, reflections at $2\theta > 90^\circ$, it is unnecessary to extend the recording range far beyond this angle. By cutting off the higher angles, as in the cameras shown in figures 1 and 2, it is possible to use large-diameter instruments (20 cm diameter is used by the writer) and at the same time place the specimen relatively close to the X-ray source. This arrangement, combined with the use of surface reflection and partial focusing, enables high resolution diagrams to be obtained without excessively long exposure times.

The spectrometer also uses flat powder layers with the additional advantage that the reflections are always recorded under conditions of sharp focusing. The amount of powder required by the spectrometer is considerable, especially if the material has to be hand-picked under a microscope and further purified by sedimentation or other methods. With photographic recording, layers of smaller extent suffice; the writer commonly employs a

powder cavity of about 5 by 3 by 0.5 mm but when little material is available, a thin layer about 5 by 1 mm (or even smaller dimensions) on a glass plate may be used.

White Radiation Effects and Use of Monochromators. Clearer powder diagrams are obtained by using crystal-monochromatized radiation in preference to filtered radiation. Curved crystal monochromators, usually of quartz, combined with cameras of a focusing type give sharply focused patterns against a low background intensity. Plane monochromators may be used with powder specimens, of flat or rod type, mounted at the centre of a circular camera. For clay-mineral investigations, synthetic lithium fluoride is probably the most generally suitable monochromator. It is a very strong reflector and is completely stable under atmospheric conditions.

The writer has found when using filtered radiation that the peak of the white radiation reflected from the very strong (10.1) quartz reflection appears in a position corresponding to $\text{CuK}\alpha$ radiation reflected from a spacing of about 11 to 12 Å. In consequence, clay materials containing appreciable quartz can produce this spurious reflection in the region where basal reflections from clay minerals are found. Such anomalies are eliminated by using crystal-monochromatized radiation.

It is necessary to remember, however that many crystal monochromators reflect not only the characteristic wavelength λ from the X-ray tube, but also the harmonics of wavelengths $\lambda/2$, $\lambda/3$, . . . in the second, third, and higher orders, which are selected by the monochromator from the general radiation. The following may be cited as an illustration of what may happen. The writer, examining strong basal reflections from a chlorite using a lithium fluoride monochromator set for $\text{CuK}\alpha$ radiation, recorded additional weak reflections apparently corresponding to odd orders of a 28 Å spacing. No trace of these reflections was obtained with the usual filtered radiation. It eventually became apparent that these additional reflections were due to $\lambda(\text{CuK}\alpha)/2$ radiation. Such effects are largely eliminated by using fluorite or diamond as a monochromator since the second and higher order reflections from these crystals are of negligible intensity compared with the first orders.

DIFFERENTIATION OF CHEMICAL SPECIES

Use of Spacing and Intensity Measurements. This is the most difficult phase in the identification of minerals by means of X-rays, but under favourable circumstances considerable progress can be made. The problem to be considered is how the X-ray diagram of a particular mineral structure varies with its composition. It has already been stated that it is principally the sizes and the scattering powers of the atoms which are involved, and that lattice dimensions and reflected intensities are the observable parameters. This means that atoms of similar atomic number, and therefore with similar scattering factors, must be differentiated primarily by dimensional considerations, and atoms of different electronic contents but similar sizes must be differentiated by intensity considerations. Thus in ferro-magnesian minerals, the Fe:Mg ratio will often be determined more sensitively by intensity observations than by spacing measurements, though both may be useful. On the other

hand, the replacement of Si by Al in tetrahedral coordination and of Al by Mg in octahedral coordination cannot be ascertained by intensity measurements, but some progress can be made by using dimensional arguments. These concepts have been partially applied to the montmorillonoids by MacEwan (1951), to the micas by Brown (1951), and to the chlorites by von Engelhardt (1942), and Bannister and Whittard (1945).

A more systematic approach to the problem is required, however, and a first step in this direction has been made by Brindley and MacEwan (1953) in which formulae are derived relating layer dimensions, more particularly the b_0 -parameter, to the substitutions of atoms in tetrahedral and octahedral positions. A brief survey is given in the preceding paper by the writer in this symposium, *Structural Mineralogy of Clays*. The formulae are general and are intended to be applicable to all layer silicates. Comparison of observed parameters with calculated values shows a close over-all agreement, but some exceptions occur, notably among the micas. This leads to the question whether the interlayer cations, which have been omitted from these calculations, may play an appreciable part in determining the layer parameters.

The relations between lattice parameters and composition given by MacEwan, Brown, von Engelhardt, and Bannister and Whittard, were each obtained on the basis of a more restricted argument and therefore may be more exactly applicable within the domain considered by each of them.

Di- and Tri-octahedral Minerals. An early attempt to identify chemical species by X-ray diffraction was made by Nagelschmidt (1937) who showed that the (060) spacing of dioctahedral micas was about 1.50 Å and of trioctahedral micas about 1.53 to 1.55 Å. This important distinction has been confirmed by much subsequent work both with the micas and with other mineral groups, and constitutes the first stage in attempting to identify a particular chemical species.

Kaolin-type Minerals. This term covers all minerals with the same kind of layer structure, namely, the kaolin minerals proper, the serpentine minerals, chamosite, amesite, etc.

Among these minerals, the problem of identification is relatively simple because isomorphous substitution of atoms occurs to only a small extent. Thus the kaolin minerals proper have essentially aluminum atoms and the serpentine minerals essentially magnesium atoms in octahedral positions. Chamosite appears to be the only widely occurring ferrous iron member; its composition is slightly more variable. Other kaolin-type minerals such as amesite, cronstedtite, garnierite, and greenalite are relatively rare. The powder diagrams are sufficiently distinct for there to be little real difficulty in making a broad separation.

Micas, Chlorites and Montmorillonoids. Among these minerals extensive isomorphous substitution of atoms occurs and the designation of the chemical species depends principally on the nature and extent of the substitutions. In addition to the work already cited on the recognition of these mineral species by lattice spacing and intensity measurements, a short account may be given of a critical test carried out by F. H. Gillery in the writer's labora-

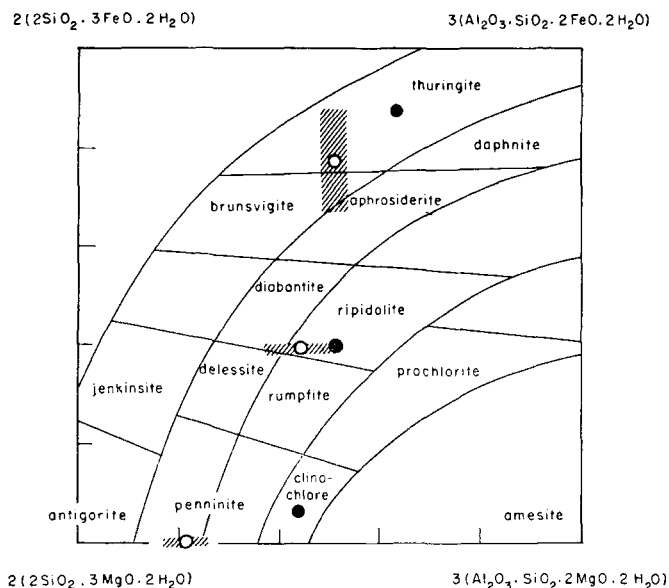


FIGURE 3. X-ray identification of chlorite species. Black circles represent the chemical analyses of three chlorites, and the open circles their evaluation by purely X-ray methods; the shaded areas indicate the estimated uncertainties in the X-ray evaluations. (Brindley and Gillery)

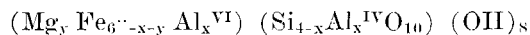
tory to identify unspecified chlorites solely by X-ray analysis.

A Detailed Test of Chlorite Identification by X-rays. The following methods and assumptions were used:

(i) The octahedral positions were assumed to be fully occupied and the distribution of atoms to be the same in the two octahedral layers of the chlorite structure. The intensities of the first five basal reflections were then calculated with the assumption that Al and Si in tetrahedral positions scatter equally, that Mg and Al in octahedral positions scatter equally, and similarly Fe and Cr. The basal intensities can then be used to determine the ratio of the heavily scattering atoms (mainly Fe) to the lightly scattering atoms (mainly Mg and Al) in the octahedral positions.

(ii) The proportion of Al to Si in tetrahedral positions was determined from the curve relating basal spacing to this ratio (Bannister and Whittard, 1945; Brindley and Robinson, 1951).

A simplified general formula for chlorites can be written:



An important assumption here is that the iron is wholly ferrous, which is largely true for many chlorites. On this basis, x can be found from the basal spacing curve and the ratio of Fe^{2+} to $(\text{Mg} + \text{Al}^{\text{VI}})$, viz. $(6-x-y)/(x+y)$, from the basal intensities. Thus x and y can both be evaluated. If Al_x^{VI} is partially replaced by Fe^{3+} , an additional variable is introduced which cannot be evaluated at present purely from X-ray data.

In figure 3 are shown the final results obtained for three chlorites. Using the well-known diagram of Winchell (1936) showing the compositional and optical ranges of members of the chlorite group, the X-ray esti-

mation of three chlorites is indicated by shaded areas and their chemical compositions by closed circles. The agreement is sufficiently good to show the potentialities of the X-ray method. It is evident that the Fe^{2+}/Mg ratio has been determined more reliably than the $\text{Al}^{\text{VI}}/\text{Si}$ ratio. This is not surprising, because the basal spacing will probably depend partly on the substitutions in the octahedral layers. It should be observed, however, that x determines not only the $\text{Al}^{\text{VI}}/\text{Si}$ ratio but also the resultant charges in the layers and this may well be the dominant factor in determining the basal spacing of a chlorite.

The results shown in figure 3 justify a restrained optimism as regards the evaluation of the chemical species of a layer mineral purely by X-ray methods. The main requirement is the accurate determination of the basal spacing and basal intensities and this implies that these reflections shall not be masked by reflections from other minerals in a mixture. Herein lies the main experimental difficulty. In the case of a mica, the 10\AA and 5\AA reflections are unlikely to be masked, but in the case of a chlorite the 7\AA and 3.5\AA reflections correspond very closely with reflections from kaolin-type minerals, a point which has already been discussed above. The kaolin reflections can be suppressed by heating the material to about 450° to 550°C ., but such treatment may modify the chlorite intensities and vitiate their use for determining the Fe/Mg ratio.

The writer has recently encountered the problem of determining the nature of a chlorite which is very fine grained, particle size 1 micron or less, which appears to be closely intergrown with a kaolin mineral. It has not been possible so far to separate these minerals and the identity of the chlorite remains unknown.

IDENTIFICATION OF MINERAL VARIETIES

Structural varieties of each chemical species differ principally in the stacking sequence of the layers. Such differences influence the finer points of the X-ray diffraction diagrams. Their recognition turns on the number and kind of components in a material. The varieties of some chemical species are more easily recognized than those of other species.

Thus the kaolin varieties, kaolinite, dickite, nacrite, halloysite, and the characteristically disordered form of kaolin mineral found in fireclays, are relatively easy to recognize, provided the powder diagram is not too heavily overcrowded with other reflections. The writer has been able to recognize kaolinite and dickite together when quartz was the only contaminant. A small percentage of halloysite along with kaolinite would not be easily detected. The extent of the disorder in a kaolinite would not be easily estimated in the presence of mica, quartz, feldspars, and possibly other impurities.

The structural varieties of the micas have been studied especially by Hendricks and Jefferson (1939) using single crystals. The characteristics of these varieties are not easily seen in powder diagrams, but Grim and Bradley (1951) have shown that if mica is the dominant mineral in a sample, then there are characteristic lines in the powder diagrams which enable some varieties, at least, to be recognized. This calls for careful and detailed study.

The structural varieties of chlorites have been studied so far only by single-crystal methods (Brindley, Oughton, and Robinson, 1950) and it is doubtful if powder diagrams will yield sufficient detail for their recognition in a finely divided form. It is, however, certain that if chlorites are ground to a fine powder mechanically, then the distortions introduced will make it impossible to recognize the original structural variety.

RECOGNITION OF DISORDERED LAYER SEQUENCES

Ordered and disordered layer sequences occur in all the structural sub-groups and give rise to characteristic diffraction effects; the more pronounced the disorder, the more prominent are the effects which are produced. In powder diagrams, asymmetrical bands of scattered X-ray intensity are obtained in place of symmetrical lines. The bands usually correspond to a group of lines rather than to a single line, but the position of a maximum intensity near the low-angle limit of a band (the most noticeable feature and the one which is usually measured and recorded in tables of lattice spacings), corresponds closely with a particular line in the diffraction pattern of the ordered mineral.

The most pronounced effects due to disordered layer sequences arise with minerals such as halloysite and montmorillonite where the layers appear to be displaced parallel to both the a - and the b -axis so that the only reflections obtained, other than the basal $(00l)$ reflections, are the two-dimensional (hk) bands. The positions of maximum intensity near the low-angle limits can be indexed approximately as $(hk0)$ and the entire sequence of reflections then appears to correspond to an orthorhombic or orthohexagonal cell. This, however, is an incorrect description of the lattice. The band of intensity extending to higher angles from each $(hk0)$ position corresponds closely to an (hkl) sequence with the h and k indices having fixed integral values and l taking values extending continuously from $l = 0$. The reason why the position of maximum intensity corresponds only approximately with an $(hk0)$ designation depends partly on the variation of structure factor with angle and partly on the fact that each angular position in a band recorded in a powder diagram corresponds to a small range of l values.

Theoretical treatments of diffraction by small, two-dimensional crystal lattices have been given by Warren (1941), by Wilson (1949), and by Brindley and Méring (1951). By making certain reasonable assumptions, Warren was able to arrive at explicit formulae for the distribution of intensity in the diffraction bands which Brindley and Robinson (1948) have shown give good agreement with observed data for halloysite. Brindley and Méring analysed the problem in rather more detail but the final conclusions were that Warren's approximations were, in most cases, amply good enough.

There is more difficulty in recognizing the one-dimensional disorder which often takes the form of layer displacements parallel to the b -axis by amounts of $nb_o/3$. Displacements by this simple fraction of a unit cell side occur in the kaolin- and chlorite-type structures because, in the hydroxyl sheets of these layers, the (OH) radicals are situated at intervals of $b_o/3$ parallel to the b -axis and in consequence a displacement by $nb_o/3$

introduces no change in near-neighbour relations between adjacent layers.

Two effects follow from the random b -axis displacement of layers. In the first place, reflections with $k = 0, 3, 6 \dots$ remain unaffected, but reflections of type (hkl) with $k \neq 3n$ disappear. The two-dimensional regularity of the layers remains, however, so that bands, similar to those produced by halloysite and montmorillonite, occur when $k \neq 3n$. These bands are usually much weaker than the strong (hkl) reflections with $k = 3n$ and in consequence are not easily seen. The strongest band produced by all layers of the type found in clay minerals is the $(02, 11, 1\bar{1})l$ band, the three components of which completely overlap. The maximum of this band corresponds closely with a lattice spacing of $b_o/2$ and occurs therefore at about $d = 4.5 - 4.6 \text{ \AA}$. This type of disorder is recognized partly by the smaller number of reflections as compared with a fully ordered mineral, namely those with $k = 3n$, and partly by the very characteristic intensity profile of the $(02, 11, 1\bar{1})l$ band.

Very little quantitative work has yet been done on the determination of the degree of disorder. The kind of effects to be expected with increasing disorder are (i) a fading out and a broadening of the (hkl) reflections with $k \neq 3n$, (ii) the development of the 02 band, with a modulation of the intensity distribution corresponding to the partial order in the structure.

In practice, with a range of kaolin minerals, for example, it is possible to place them in a sequence of increasing disorder, but a more detailed analysis of this question still requires to be developed.

SUMMARY

This contribution has endeavoured to outline the principles of X-ray identification of clay minerals without reproducing lists of spacing data, which can be found elsewhere. The identification problem has been broken down into stages corresponding with the classification of clay minerals described in the previous paper *Structural Mineralogy of Clays* contributed by the writer to this symposium. It is shown that the basal reflections are largely sufficient to determine the structural group and sub-group of a clay mineral. The determination of chemical species is inherently more difficult to carry through by purely X-ray methods. From an X-ray and structural standpoint, atoms differ in size and in scattering power. Therefore in determining chemical species, attention must be paid to details of lattice spacings and diffracted intensities. A critical test of the identification of three chlorites is described and it is concluded that in favourable cases the possibility of identifying species by X-ray analysis can be regarded with restrained optimism. The problems of recognizing structural varieties are briefly outlined and the potentialities indicated. Sometimes the recognition of a particular structural variety determines at the same time the chemical species.

Disorder in clay minerals is of two kinds, namely disorder due to mixed-layer sequences and disorder due to layer displacements. The characteristic diffraction phenomena arising from these disorders are discussed and the possibilities of studying them in detail are considered.

Questions of X-ray technique are treated briefly with special reference to the measurement of long spacings

and elimination of spurious effects arising from the use of filtered radiation and of certain crystal monochromators.

ACKNOWLEDGMENTS

Finally I wish to record my deep appreciation of the invitation to attend the First National Conference on Clays in the United States, and my pleasure at the opportunities it has provided of visiting many people and laboratories in this country. I wish also to express my best wishes for the success of the Clay Minerals Group which has been initiated at this Conference, and the hope that despite the distance separating Europe and America, there will be useful collaboration between the newly founded United States group and the groups now actively functioning in Belgium, Britain, France, and Sweden.

DISCUSSION

T. F. Buehrer:

How accurately can one determine the proportion of the various minerals present in a colloidal clay of a soil, and by what factors would such estimates be complicated?

G. W. Brindley:

The method for quantitative mineralogical analysis by means of X-rays is the well known one of adding a standardizing substance in known proportion and comparing the ratios of the intensities of diffraction lines from the different minerals with the intensities of lines from the standard substance. The choice of standard substance depends to some extent on the problems to be undertaken; the diffraction pattern of the standard should interfere as little as possible with those of the components to be measured. In the case of clay-mineral mixtures, it is not easy to find a standard which meets this requirement satisfactorily, but the writer and R. H. Crooke in work not yet fully published have found ferric ammonium sulfate to be a useful substance.

The accuracy obtainable is usually not very high but the use of self-recording counter spectrometers in place of photographic techniques increases considerably both the accuracy and the convenience of the X-ray method.

The principle of the method is to compare suitable reflections from a range of minerals such as kaolinite, mica, montmorillonite, chlorite, etc., with a suitable reflection or reflections from the standard substance in binary mixtures of known proportions. In a multi-component mixture, the intensity ratios will be related in the same way to the composition ratios provided the particle sizes of all the components are sufficiently fine. This proviso raises difficult problems both theoretically and experimentally if the particles are so coarse that they absorb individually an appreciable percentage of the incident X-radiation. This, however, is not likely to arise with the clay fraction of a soil.

A more serious difficulty arises in connection with the standard intensity ratios. Such ratios can, of course, be established for particular specimens of kaolinite, mica, montmorillonite, etc., in relation to a chosen standard. The question is whether the minerals to be estimated reflect X-rays exactly as the kaolinite, etc., used in making up the standardizing mixtures. This depends on the "crystallinity" of the minerals involved and also on their precise chemical composition.

A further source of uncertainty arises from the easy orientation of flaky minerals. The most convenient reflections for intensity measurements are often the basal, 001, reflections and these are the reflections most susceptible to orientation effects.

The second part of Dr. Buehrer's question is therefore more easily answered than the first part. The accuracy obtainable depends so much on circumstances that a simple, direct answer is scarcely possible. I could, however, hazard a guess that a crystalline component present to the extent of 50 percent by weight in a mixture might well be estimated to within ± 5 percent, i.e., an accuracy of 10 percent in the determined value. But a component present to the extent of only 5 percent might be estimated with an uncertainty of $\pm 2\frac{1}{2}$ percent, i.e., about 50 percent in the determined value.

I feel that X-ray methods for quantitative determinations should be applied with considerable circumspection and that it is a wise precaution always to vary as widely as possible the experimental

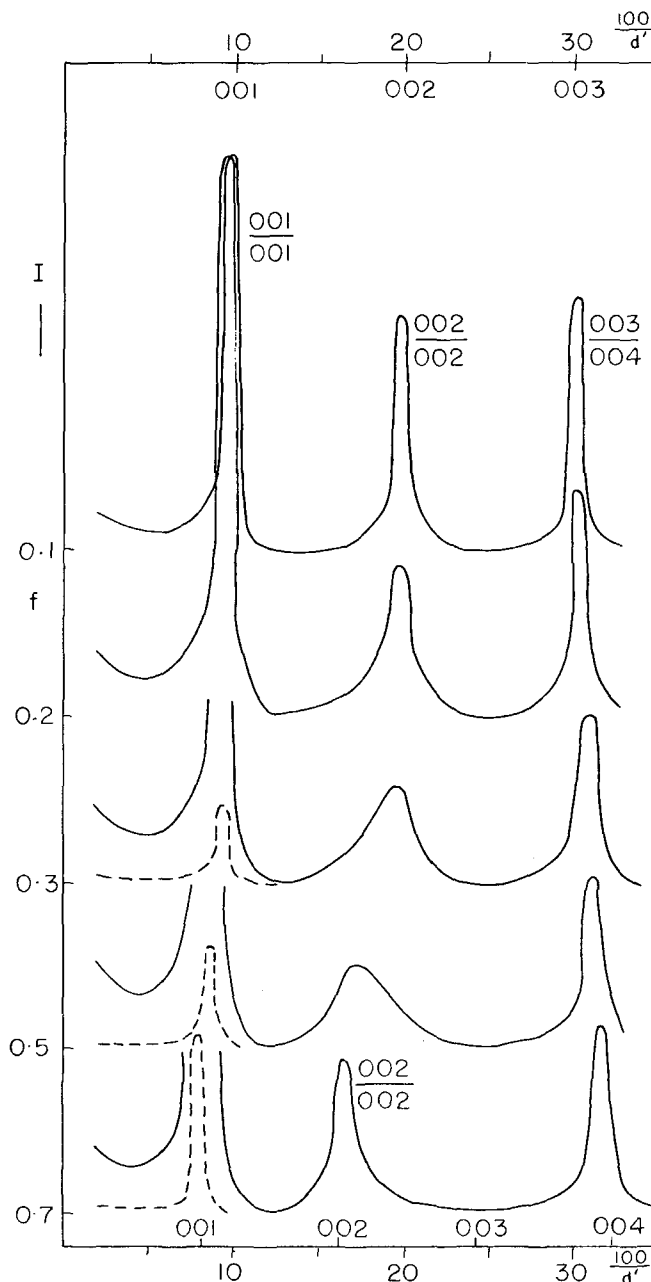


FIGURE 4. Ten-Å and 12.4Å spacings: dioctahedral mica layers. From Brown and MacEwan 1951.

conditions, in order that the many elusive factors which may influence intensity measurements can be given an opportunity to reveal themselves. Measurements carried out with small variation of the experimental conditions may show a high degree of consistency among themselves that is quite misleading as regards the accuracy of the determination.

M. E. King:

Another factor beside orientation, which introduces uncertainties in estimating a given crystalline component in a mixture, is the presence of substances which highly absorb X-rays, such as calcite. In one sample X-ray analysis indicated that quartz was present in an amount of about 15 to 20 percent, whereas microscopical analysis indicated about 60 to 65 percent quartz. After the calcite was removed, the results obtained by means of X-rays and microscope were in agreement.

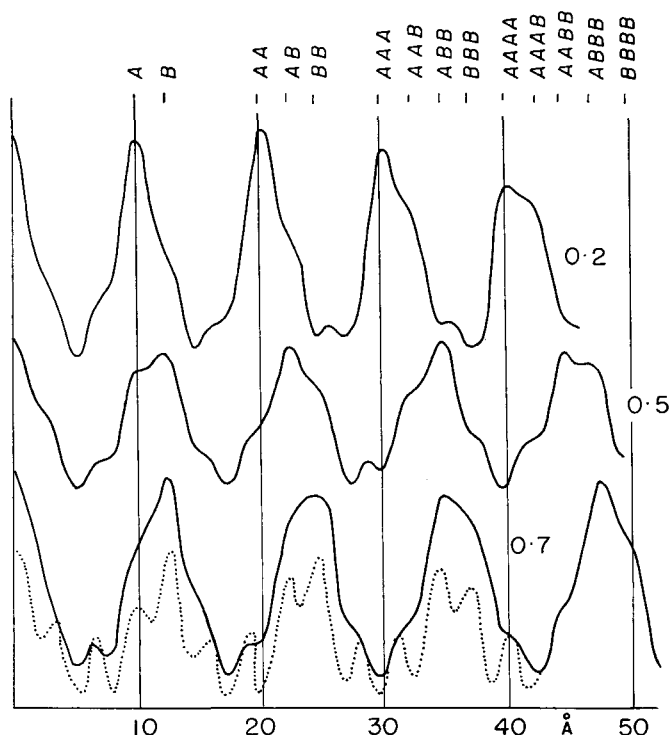


FIGURE 5. Calculated series for mixtures of 10Å and 12.4Å spacings with mica-type layers. The number attached to each curve gives the proportion of the higher spacing. The ordinates of these curves are proportional to the probability of finding a layer at a given distance from any layer chosen as origin: the (arbitrary) zero level is not shown. The letters indicate the significance of the peaks, *A* meaning a 10Å spacing, and *B* a 12.4Å spacing; thus *AAB* is a peak which arises from two spacings of the first type plus one of the second (in any order). The meaning of the dotted curve is explained in the text. From MacEwan, *Nature*, v. 171.

G. W. Brindley:

The effect of strongly absorbing constituents in a composite powder is quite complex and has been discussed by several writers (Brindley, 1945; Wolf, 1937; Wilchinsky, 1951). Mention may also be made of the effect of an amorphous skin on crystalline particles. Such a skin diminishes the reflected intensity both by its non-crystalline character and by its absorption. Such an effect has been demonstrated quantitatively by Nagelschmidt et al. (1952).

D. M. C. MacEwan:

A problem which quite commonly turns up in dealing with X-ray diffraction by clay minerals is that of random interstratification. This consists in the interleaving of different layers, in a manner which may be either regular or random. The layers may be either of different structural types, e.g., kaolinite and montmorillonite, or may consist of layers of the same structural type, but with different thicknesses of interlamellar material, water or organic molecules—e.g., partially hydrated halloysite (Brindley and Goodyear 1948), partially expanded montmorillonite, chlorite, and swelling chlorite (Stephen and MacEwan 1951).

The basal series of reflections from such material may contain broad bands, but quite often it consists of lines which are not very noticeably less sharp than those from other fine-grained material, but which do not form a rational series of orders, i.e., a series with spacings in the ratios $1: \frac{1}{2}: \frac{1}{3}: \dots$. Whenever such an irrational series is present, we may suspect random interstratification.

We are then confronted with the problem of finding out what such a non-rational series of lines means. Sometimes they may be modified, e.g., by removing water, or by saturating the material with glycerol or glycol; and the modifications in the pattern of lines may give us a clue to what was originally present. This cannot always be done however, nor is it always sufficient to give us

the clue we were seeking. Ideally, we want some direct method of proceeding from the measured spacings and their intensities to the types of layers present and their proportions.

In the case where the silicate layers present are of similar nature, and are separated by interlamellar material of relatively small scattering power, the problem simplifies itself into the determination of the inter-layer spacings present, and the proportions in which they are present. This can be done, as Mering (1949) has pointed out, by calculating the Fourier transform of a modified curve of scattered intensity from the base, as a function of reciprocal spacing (or, nearly, of angle).

Unfortunately, this curve is very difficult to obtain in practice, because the scattered intensity is very low in certain regions, and is liable to be interfered with by non-basal reflections from the same mineral, and by reflections from other minerals. We have found that, where the pattern is one of fairly sharp discrete lines, quite a lot of information can be obtained by calculating the much simpler function:

$$\sum_r \frac{I_r}{\Theta |F_l|^2} \cos 2\pi \mu_r R,$$

where I_r = integrated intensity of r th line; F_l = scattering function for a single layer (this is a function of μ); μ_r = reciprocal spacing corresponding to r th line; R = interlayer separation in Å.

This is a very simple summation, having only as many terms as there are lines. The resulting function of R , when plotted, should show peaks corresponding to the interlayer distances present, their heights giving the proportions in which they occur. The function may be regarded either as a simplified Fourier transform, or as a Patterson function with non-rational indices, i.e., with infinite unit cell.

Often, owing to the paucity of observations, the series is arbitrarily cut off at a certain term. This gives rise to diffraction, i.e., to spurious peaks, as with an ordinary Patterson summation, and the remedy is the same, to smooth the series by arbitrarily reducing the higher-order terms, i.e., by multiplying the intensities by a function which diminishes with increasing μ . This broadens the peaks, making exact spacing measurements difficult, so it may be convenient to calculate both the smoothed and the unsmoothed series. The second will give the accurate spacing values, and any peaks not common to the two series will be rejected. There are other refinements and snags, which cannot be described in detail here.

Figures 4 and 5 show what can be done, even with very restricted information. Figure 4 gives the diffraction to be expected from mixed-layer structures containing mica-type layers with separations of 10 and 12.4Å, in the proportions shown. These curves are calculated by Brown and MacEwan (1950), and do not go beyond $\mu = 35$, i.e., $d = 2.8$ Å (μ being arbitrarily defined as $100/d$), there being only three peaks in this region, one of them rather diffuse. Figure 5 shows the smoothed summation from these three peaks. For comparison, an unsmoothed summation corresponding to the last of the three curves is also shown, in dotted line.

It is easy to see that the initial portion of the summations gives us very adequate information about the spacings present, and their proportions. Taking the $f = 0.7$ curves as an example, we see from the dotted curve that the spacings present are 10 Å at 12.4 Å. The heights of these peaks are in the ratio of 34:66, which is near enough to the true value of 30:70. There is some difficulty in determining the true zero level from which to measure these heights, but this cannot be discussed in detail here. Comparison of the dotted and full curves shows that peaks at 4 Å, 6.5 Å, 15.5 Å and 19 Å, may be rejected as being the result of diffraction. Thus only these two spacings are present.

The other peaks at larger values of R result from second nearest neighbors, third nearest neighbors, etc., and from them we may, in principle, determine whether the mixture of layers is completely random, ordered, or partially ordered. Thus, if we had a regular alternation of layers, *ABAB* . . . , we should get a large *AB* peak, but no *AA* and no *BB*. If we had a complete segregation of the two types, we should get *AA* and *BB*, but no *AB*. A little consideration will show that, with a completely random mixture of layers, we would expect the heights of *AA*, *AB*, and *BB* to be in the ratio 9:42:49 with 30 percent *A*. This is clearly very close to what is found, so we may say that the mixture is essentially a random one, and this of course is the correct answer.

These summations are very sensitive to the value of μr but are relatively little affected even by quite large changes in $[I_r / F_l]^2$. Thus we may expect that they will give the correct answer even when there is some uncertainty about the nature of the layers, and therefore about the values of F_l .

H. F. Coffey:

When is orientation of clay particles in a sample desirable and when is it not?

G. W. Brindley:

Orientation is desirable when you want to bring out the basal reflections, particularly those at higher angles, so that they can be differentiated with certainty from other reflections. On the other hand if you want to compare the intensities of the reflections in order to check on a structure analysis, then, of course, you wish to measure the intensities without the complications introduced by orientation. In a recent structure analysis of amesite (Brindley et al. 1951) both single-crystal and powder analyses were employed. In order to interpret the powder intensities it was necessary to incorporate an orientation factor.

T. F. Bates:

I believe that electron diffraction will very soon be an important means of studying the clay minerals, particularly the diffraction from single crystals. This can be done by using the Philips electron microscope, the new electron diffraction attachment RCA instrument, or possibly by micro-manipulation and hand-picking some of these tiny microscopically visible crystals and placing them in the RCA electron-diffraction unit so that one knows that he deals with a single crystal.

D. M. C. MacEwan:

The electron-diffraction patterns of highly oriented and extremely thin films of clay with the electron beam passing normally through them are particularly useful. Such a pattern includes only the (hk) or the ($hk0$) lines. If X-rays give diffuse (hk) bands, then electron diffraction will give sharp lines, because with electron diffraction only the initial part of the band is observed. If X-rays give a series of lines with ($hk0$), (hkl), and others, then, in general, electron diffraction will only give the ($hk0$). That means that the pattern is very much simpler than an X-ray pattern. It will be easy to pick out materials of different chemical compositions in a mixture. For the majority of the clay minerals the lines are in a perfect hexagonal pattern, and they can be indexed with hexagonal indices; that is true even if the materials themselves are not hexagonal in symmetry, as of course they generally are not. With nontronite and montmorillonite or nontronite and mica, one gets a complete series of hexagonal lines from each and the lines can easily be separated out into the two separate series. For certain mixtures, such as nontronite and pyrophyllite, an X-ray pattern is much more complicated. Electron diffraction, however, has the disadvantage that the basal reflections are very difficult to observe; they tend to be very diffuse, usually they are completely collapsed. Montmorillonite, e.g., gives 9.6 Å and is indistinguishable from pyrophyllite in that range.

G. W. Brindley:

The fact that the electron diffraction picture shows a hexagonal pattern of spots for montmorillonite and similar crystals has in the past led people to conclude that the crystals are well ordered and are giving three-dimensional diffraction effects. This, of course, is not the case. The explanation is most easily given in terms of the reciprocal lattice. The reciprocal lattice of a single sheet of atoms consists of continuous lines rather than of discrete spots as for well-ordered crystals. The intersection of these continuous lines with the Ewald sphere (or plane) of reflection gives rise to the spots seen in the electron diffraction picture. If one could turn the crystal around and view the reciprocal lattice at a more suitable angle, then the continuous nature of the diffraction would be revealed with electrons just as it is revealed with X-rays. Some of the photographs taken by Finch have in fact shown this (MacEwan and Finch 1950).

W. F. Bradley:

The technique of tilting clay slides for electron diffraction, so that the sphere of diffraction cuts an inclined section in reciprocal space was illustrated by Hendricks in his early work (Hendricks and Ross 1938).

G. W. Brindley:

If one could follow the fluctuation of density along the diffraction lines in reciprocal space, then one would know there was some degree of order in the way in which the plates were stacked.

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