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IDENTIFICATION OF CLAY MINERALS BY SINGLE CRYSTAL ELECTRON DIFFRACTION*

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ABSTRACT

Procedures for identifying clay minerals by means of single crystal electron diffraction patterns obtained with electron microscope-electron diffraction equipment without tilt adjustment of the crystals, are examined critically. In a few special but highly important cases, E.D. patterns and micrographs are characteristic of particular minerals. Generally, clays and related layer silicates give closely similar hexagonal patterns. It is shown that identification is not feasible from observations of intensity distributions nor on the basis of angular relations, but partial identification is possible from accurate measurements of b parameters. By using aluminum metal as an internal standard, parameters accurate to 0.2% are obtained.

INTRODUCTION

Although electron microscopy has been applied extensively to morphological studies of clay minerals, electron diffraction is seldom used as a general tool, probably because x -ray powder techniques provide adequate identification procedures. In particular centers of research, electron diffraction studies of minerals, including clay minerals, have been undertaken and references to this work will be made later. In the field of clay mineralogy, electron diffraction and particularly single crystal diffraction has important advantages over other methods of investigation, as the following examples illustrate:

(a) In all cases where the identity of an individual clay crystal is important, electron diffraction provides the only method for its identification. For example, in the synthesis of clay minerals from gels the development of crystalline forms can be observed microscopically at a stage much earlier than crystalline products can be detected by x -rays (Gastuche and De Kimpe, 1959).

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(b) Correlation of crystal growth and morphology with crystal structure for micron-sized particles can be studied by combined electron microscopy and electron diffraction. Such information is very rarely accessible to x -ray study.

(c) In studying the thermal decomposition reactions of fine-grained minerals, E.D. patterns may supply clear information when x -ray powder diffraction yields poor and inconclusive results. Studies of partially crystallized phases often yield clearer results by electron diffraction than by x -ray powder diffraction. An early study of this type was made by Eitel *et al.* (1944), and the work of Roy *et al.* (1955) on metakaolin, and of Brindley and Choe (1961) on the decomposition products of alumina hydrates provides further illustrations.

(d) Crystal structure analysis from single crystal E.D. patterns has been developed particularly by Cowley and by Russian workers. The following papers may be cited as being representative of work in this area: Cowley (1953), Cowley and Rees (1958), Pinsker (1949, 53), Vainshtein (1956), Pinsker and Vainshtein (1957, 58), Zviagin (1957, 58), Popov and Zviagin (1958, 60), Zviagin (1960), Zviagin and Mishchenko (1960).

(e) A further application of single crystal E.D. methods to clay mineral study lies in the identification of minor impurities. Contaminants present to the extent of about 1% or less will seldom be recognized in x -ray powder diagrams. If the impurities have a distinctive appearance in the electron microscope, then identification by electron diffraction may be possible. Even when impurities are present in clays to a considerably greater extent than 1%, they may still escape detection in x -ray identification. Probably as much as 10% of halloysite, or even a higher percentage, in the presence of kaolinite could escape detection by x -ray methods because of the similarity and overlapping of the patterns but electron microscope and diffraction techniques would give a clear identification, (See Brindley and Comer, 1956).

In view of the numerous potential applications of electron diffraction to the study of clay mineral crystals, an investigation was undertaken of methods for identifying single crystals of clay minerals by means of E.D. patterns. The results show that although there are considerable difficulties arising from the structural similarities of many of the clay minerals, certain features of the patterns permit a partial identification.

EXPERIMENTAL PROCEDURES

Since it will usually be desirable to examine the morphology of clay particles and to select particular crystals for diffraction study, an instrument which combines the possibilities of electron microscopy with

selected area diffraction will generally be preferred. On the other hand, instruments designed primarily as diffraction cameras with little or no provision for use as microscopes may have advantages for tilting and adjusting the crystals under examination, but it is a serious disadvantage if the individual crystal cannot be selected visually. These techniques have been discussed recently by Ross and Christ (1958) and by Ross (1959) in relation to mineral studies.

In the present investigation, an R.C.A. electron microscope, type EMU-2D, fitted with a diaphragm for selected area study, has been employed. There was no provision for precise orientational adjustment of the crystals, which were examined in the orientation they adopted on the stage of the instrument, *i.e.*, essentially normal to the electron beam. The recorded patterns are 5×5 cm. in size and can be measured to give lattice spacings accurate to about 0.2% from single crystal spot patterns when an internal calibration standard is employed.

Specimen preparation is essentially the same as for the electron microscopy of clays, but to obtain isolated crystals it is desirable to have well dispersed samples somewhat more dilute than those generally used for microscopy. Aluminum metal has been used as an internal standard; 2.4 mg. of pure aluminum is evaporated under vacuum on to the sample mounted on a collodion film at a distance of about 10–11 cm. The estimated thickness of the metal is about 60 Å. The resulting photographs show a spot pattern from the clay crystal with a superimposed ring pattern from the aluminum. The patterns are measured directly after enlargement to about 50×50 cms. by projection. The positions of individual spots cannot be fixed directly with any accuracy, but when the entire network of spots is carefully ruled out, the pattern can be measured accurately and (with certain reservations discussed later) spacings can be obtained to within 0.2%.

IDENTIFICATION PROCEDURES

(a) *Clay minerals giving easily recognized E.D. patterns*

A few clay minerals give patterns which are immediately diagnostic. Halloysite has a characteristic tubular or rolled sheet morphology and the E.D. pattern often resembles an *x*-ray rotation diagram. These patterns have been discussed by Honjo *et al.* (1954). However, it appears that hexagonal spot patterns may also be obtained from halloysite, possibly from fractured tubes or from thin portions of tubes lying more or less normal to the electron beam. Sepiolite has a fibrous morphology and its E.D. pattern differs from those of other clay minerals (Brindley, 1959). An unusual E.D. pattern for a chlorite has been reported by Eckhardt (1958), but most chlorites appear to give hexagonal spot pat-

terns (c.f. Figure 2). Antigorite is platy or lath-like, and single crystal patterns are characterized by a long a parameter ranging from about 33 to 43 Å; for some crystals values of 90–110 Å have been obtained. These features of antigorite are easily recognized in single crystal E.D. patterns, but are not easily recognized by x -ray powder diagrams, (Zussman, Brindley, and Comer, 1957). Such highly characteristic E.D. patterns, which are recognizable at sight, are notable exceptions to the results obtained generally for clay minerals.

(b) *Identification based on diffracted intensities*

Different clay minerals, having different crystal structures, would be expected to give characteristic distributions of diffracted intensities. In fact, most clay minerals and related layer lattice silicates give very similar hexagonal spot patterns with the experimental conditions employed. Figures 1 and 2 show some typical results.

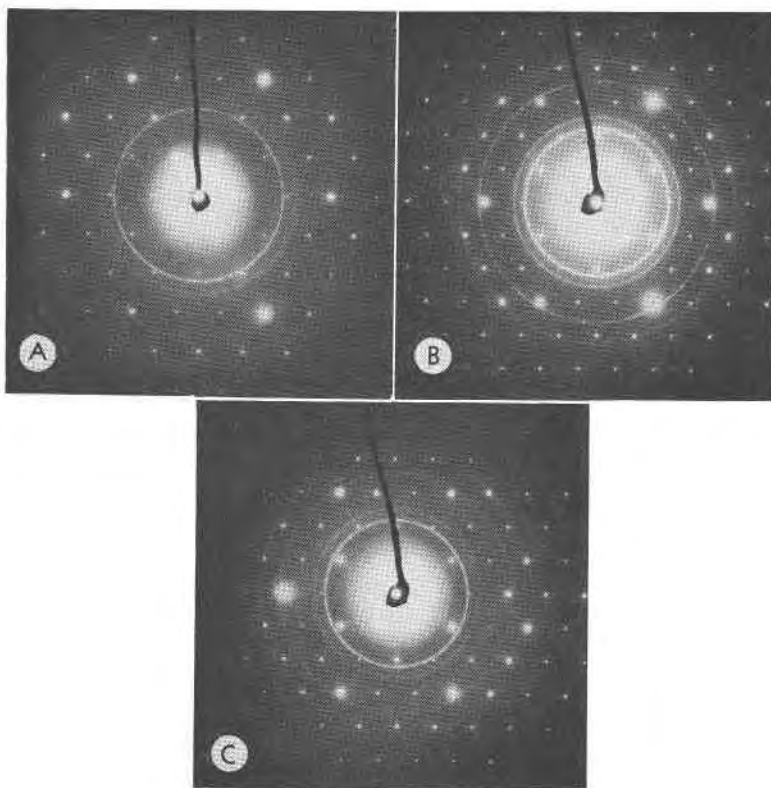


FIG. 1. Single crystal electron diffraction diagrams of (a) kaolinite, (b) dickite, (c) nacrite, with calibration rings from aluminum metal.

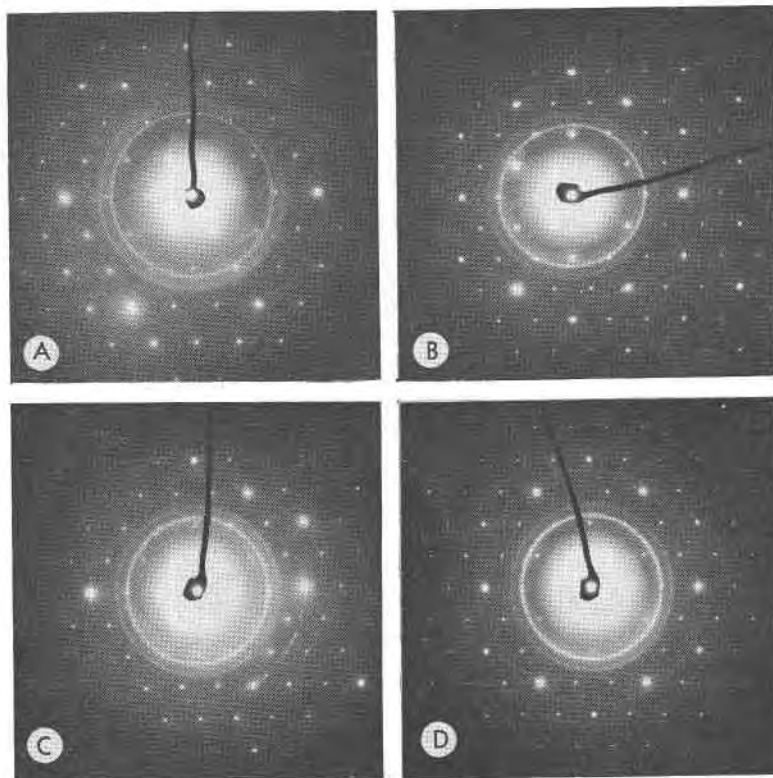


FIG. 2. Single crystal electron diffraction diagrams of (a) muscovite, (b) biotite, (c) clinoclchlore, (d) daphnite, with calibration rings from aluminum metal.

This lack of discrimination calls for careful consideration. In the first place, the orientation of the crystals excludes the basal reflections which are important in x -ray identification. Secondly, the $(hk0)$ reflections are essentially similar for the various layer silicates because of structural similarities, particularly in projections on the basal plane. Such variations as occur in figures 1 and 2 are largely erratic from one crystal to another of the same mineral and may arise from uncontrollable variations of thickness, tilt, mosaic character, or similar variables.

It is evident that if a monoclinic crystal (most clay minerals are monoclinic or approximately monoclinic) lies with (001) on the collodion substrate, then the a^*b^* reciprocal net is not parallel with the plane of the photograph, and a series of Laue zones rather than a continuous spot pattern will be produced. In the present experiments, such zonal patterns have been seen for dickite crystals prior to grinding the material. Generally, however, zonal patterns have not been observed and one is led to

consider a diffusion of the reciprocal lattice points parallel to c^* , such that the recorded diagrams do not show strictly ($hk0$) reflections but intersections of the Ewald sphere with (hk) lines.

Diffusion parallel to c^* due to extreme thinness of the crystals is unlikely even though very thin crystals tend to be selected preferentially. X-ray powder diagrams do not show greatly broadened ($00l$) lines. Diffusion may arise from stacking faults parallel to (001) and undoubtedly the prevalence of such faults in layer silicates must have an important influence on the E.D. patterns of most clay minerals. Another source of diffusion parallel to c^* has been suggested by Cowley (1960) who considers that if the structural layers have appreciable curvature, the electron scattering from the component sheets of atoms will be incoherent, *i.e.*, the diffraction process will be essentially two-dimensional in character.

It has to be recognized, however, that three-dimensional diffraction data are obtainable from layer silicate minerals, including clay minerals. The "texture method" used particularly by many Russian workers, which utilizes a large number of crystals oriented with respect to the substrate but disoriented in the plane of the substrate, gives three-dimensional data from which structure analyses have been made, and by this technique it should be possible to distinguish and identify clay minerals. It is not, however, a single crystal method, and it requires equipment in which tilting of the specimen can be made. Oberlin (1957) and Oberlin and Tchoubar (1959) reported a close agreement between observed and calculated electron diffraction intensities for single crystals of kaolinite, but it is not clear how crystals were selected or adjusted with exactly the required orientation to record correctly the ($hk0$) zone of reflections.

It must be concluded that most clay crystals give rise to sufficient diffusion of the $hk0$ diffractions parallel to c^* so that hexagonal spot patterns can be obtained from crystals lying flat on the substrate and without precise tilt adjustment. Under these conditions, identification on the basis of electron diffraction intensity distributions is not generally feasible.

(c) Identification on the basis of the β -angle

A second potential method of identification rests on a determination of the β -angle for those clay minerals which are monoclinic or approximately monoclinic. This method also requires a true recording of the a^*b^* reciprocal net, and from the discussion in the previous section it seems unlikely that these conditions can be readily satisfied. However, the method deserves brief consideration.

For a monoclinic structure,

$$a^* = 1/d(100) = 1/(a \sin \beta)$$

$$b^* = 1/d(010) = 1/b$$

and the reciprocal axial ratio is given by

$$a^*/b^* = b/(a \sin \beta)$$

For the layer lattice silicates, the crystal axial ratio b/a is always very close to $\sqrt{3}$ and therefore one can write

$$a^*/b^* = \sqrt{3}/\sin \beta$$

An important consequence of this result is that the true a^*b^* reciprocal net is not precisely hexagonal. As is well-known, an hexagonal array can be represented by a centered rectangular cell with axial ratio *exactly* equal to $\sqrt{3}$.

Kaolinite is a good example to consider, for although not strictly monoclinic, since $\alpha = 91.6^\circ$, it has a β -angle of 104.8° which is larger than that for any other clay mineral. The calculated value of a^*/b^* is 1.797. A series of careful measurements have been made on ten well-defined single crystal diagrams of kaolinite, which yielded an axial ratio of $1.734_5 \pm 0.001_6$. A similar result was obtained previously by Gastuche and De Kimpe (1959), though with less precision because they did not use an internal standard. Such a standard is desirable even for ratio determinations in order to correct for any optical or electron-optical aberrations.

This result provides further evidence that the E.D. patterns do not record the true a^*b^* reciprocal net under the conditions of the experiment. The observed pattern can be considered as a projection of the true a^*b^* net made possible by the diffusion of the reciprocal lattice nodes parallel to c^* . The recorded parameters are therefore $a^* \cos(\beta - 90^\circ)$, and b^* , and their ratio is given by

$$\frac{a^* \cos(\beta - 90^\circ)}{b^*} = \frac{b}{a} \simeq \sqrt{3}$$

This agrees exactly with the experimental results for kaolinite.

It is evident that, under the conditions employed, the β -angle cannot be determined and that clay mineral identification on this basis is not feasible.

(d) Identification on the basis of the b -parameter

Values of the b parameter of a number of clays and related minerals are listed in Table I. They fall into several groups. The dioctahedral minerals generally have smaller b parameters than the trioctahedral minerals, but the extent of ionic substitution in the lattice also determines the precise parameter values.

Among the *dioctahedral* minerals, the 1:1 kaolin minerals have $b = 8.95$ Å with little or no variation in the value.

For the 2:1 minerals, the smallest b parameters are shown by those minerals with mainly Al ions in the octahedral positions. Montmoril-

TABLE I. VALUES OF b -PARAMETERS FOR CLAYS AND RELATED LAYER SILICATE MINERALS FROM X-RAY DATA

		$b(\text{\AA})$
1. <i>Diocahedral minerals</i>		
1:1 type	Kaolin minerals	8.95
2:1 type	Montmorillonite } Beidellite }	8.95-9.00
	Muscovite	9.00-9.02
	Glauconite	9.07-9.12
	Nontronite	9.13
2. <i>Triocahedral minerals</i>		
1:1 type	Serpentine minerals	9.20-9.26
	Amesite	9.19
	Chamosite (ferrous)	9.33-9.38
	Cronstedtite	9.52
	Greenalite	9.61
2:1 type	Phlogopite	9.20-9.23
	Biotite	9.25
	Hectorite	9.09
2:2 type	Chlorites	9.20-9.35

lonites and beidellites have $b \approx 8.95-9.00 \text{ \AA}$ and muscovite and similar micas have $b \approx 9.00-9.02 \text{ \AA}$. Substitution of iron and magnesium for aluminum leads to larger values of b , approximately $9.07-9.12 \text{ \AA}$ for glauconites (Warshaw, 1957) and about 9.13 \AA for nontronite. Very approximately, the b parameter, in \AA , appears to be related to composition by the equation:

$$b = 9.00 + 0.06_y$$

where y is the number of Fe+Mg ions replacing 2 Al ions in octahedral positions.

Among the *trioctahedral* minerals, the 1:1 serpentine minerals have values of b in the range $9.20-9.26 \text{ \AA}$. Chamosite with an octahedral cation population approximately $(\text{Fe}_{1.8}^{2+} \text{Mg}_{0.2} \text{Al}_{0.8})$ has $b \approx 9.33-9.38 \text{ \AA}$, but in the oxidized ferric form, $b \approx 9.10 \text{ \AA}$. Amesite, with approximately $(\text{Mg}_2 \text{Al})$ in octahedral positions, has $b \approx 9.19 \text{ \AA}$. The mineral greenalite with approximate octahedral composition $(\text{Fe}_{2.3}^{2+} \text{Fe}_{0.5}^{3+})$ has $b \approx 9.61 \text{ \AA}$ and cronstedtite with octahedral cation composition $(\text{Fe}_2^{2+} \text{Fe}^{3+})$ and tetrahedral cation composition $(\text{Si} \text{Fe}^{3+})$ has $b \approx 9.52 \text{ \AA}$, (Steadman and Youell, 1957, 1958).

Among the 2:1 mica-type minerals, phlogopite has $b \approx 9.20-9.23 \text{ \AA}$ (Smith and Yoder, 1956), biotite has $b \approx 9.25 \text{ \AA}$ (Walker, 1949). Hectorite, with octahedral cation composition approximately $(\text{Mg}_{2.7} \text{Li}_{0.3})$ has $b \approx 9.09 \text{ \AA}$.

Among the chlorites, the b parameters range from about 9.20–9.35 Å and this variation has been studied several times in relation to (Fe, Mn) substitution. The results can be represented by the following relations:

$$b = 9.21 + 0.032(\text{Fe}) \dots \text{(based on data by Engelhardt, 1942)}$$

$$b = 9.202 + 0.028(\text{Fe, total}) + 0.047(\text{Mn}) \dots \text{(Hey, 1954)}$$

$$b = 9.210 + 0.037(\text{Fe}^{2+}, \text{Mn}) \dots \text{(based on data by Shirozu, 1958)}$$

The variation with Fe content (number of Fe ions replacing Mg in octahedral positions) is considerably less than in the 2:1 minerals where Al is the replaced cation.

It is obvious that on the basis of b parameter measurements alone, the identification of clay minerals is restricted in scope. However, it can be expected that E.D. techniques will be applied to problems of a more specialized kind than those to which x -ray diffraction is routinely applied. Also, electron diffraction will not be applied except in conjunction with electron microscopy. In special circumstances, accurate b parameter measurements in conjunction with electron microscope observations can be expected to be a very useful identification aid.

The following results will show the degree of accuracy which can be achieved by using an internal calibration standard and an instrument of the electron microscope type.

EXPERIMENTAL RESULTS

An R.C.A. electron microscope, type EMU-2D, has been used to measure the b parameters of typical clay minerals, with thin vaporized layers of aluminum metal as an internal calibration for all E.D. patterns.

The results obtained are given in Table II. For each mineral, the arithmetic mean value and the mean deviation are given. Each individual observation is believed to be accurate to 0.2–0.3%; the mean deviations

TABLE II. SINGLE CRYSTAL ELECTRON DIFFRACTION MEASUREMENTS OF b PARAMETERS OF SOME CLAYS AND LAYER SILICATE MINERALS

Mineral	Patterns measured	$b(\text{Å})$
Kaolinite	10	8.946 ± 0.008
Dickite	12	8.945 ± 0.014
Nacrite	14	8.935 ± 0.010
Muscovite	10	9.000 ± 0.009
Biotite	5	9.240 ± 0.007
Chlorite	5	9.200 ± 0.007
Clinocllore	5	9.207 ± 0.027
Corundophilite	5	9.180 ± 0.017
Daphnite	5	9.240 ± 0.060

are slightly better than 0.2% in most cases, but for daphnite, a chlorite, the results are somewhat poorer. The variation of the results for the last-named mineral may represent a real variation among the crystals examined; three mica crystals were measured from this sample.

It is evident from this tabulation, and from the data in Table I, that it is quite practicable to distinguish the following mineral groups: (1) the kaolin minerals, (2) muscovite and similar minerals, (3) the ferro-magnesian layer silicates. Within the latter group, however, distinction of particular minerals is not possible without additional information.

SUMMARY AND CONCLUSIONS

Single-crystal electron diffraction has many applications within the field of clay mineralogy if a satisfactory identification procedure can be developed. Apart from the special, but very important, cases in which the E.D. patterns are highly characteristic of individual minerals or varieties, the majority of clay minerals have similar structures and give similar E.D. patterns when the crystal lies flat on a substrate without precise orientational adjustment; this limitation is inherent in many types of equipment designed primarily for electron microscopy. It is shown that identification on the basis of characteristic intensity distributions or on the basis of the β -angle, is not generally feasible with such instruments. From accurate measurements of b parameters, using aluminum metal as an internal standard, it is possible to obtain at least partial identification of clays and related layer lattice silicates. The variation of b with iron content in minerals is discussed.

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