X-RAY IDENTIFICATION OF CHLORITE SPECIES*

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ABSTRACT

An x-ray method is developed for identifying chlorite species in fine-grained materials. A survey of the crystal chemistry of chlorites shows that in orthochlorites the principal compositional variables are the Al ions in tetrahedral coordination and the Fe^{2+} ions in octahedral coordination. These can be estimated from the basal (001) spacing and the structure factors of the lower order reflections. The problems which arise with leptochlorites and the applicability of the method to chlorites containing dioctahedral layers are discussed. Four examples are given comparing results obtained by the x-ray method with the results of chemical analysis.

Isomorphous substitution is exceedingly varied in the chlorite group of minerals and various schemes have been suggested for subdivision into species according to chemical composition, notably by Tschermak (1890, 1891), Orcel (1927), Orcel et al. (1950) and Hey (1954). The relations of optical properties to chemical composition have been considered especially by Winchell (1926, 1936) and also by Hey (1954), so that in the absence of chemical knowledge, species can be determined from optical data with a considerable degree of certainty. The development of an x-ray method for species identification is of interest chiefly in relation to materials which are unsuitable for chemical and/or optical study, such as clays, shales and fine-grained materials generally. Eventually, when the x-ray method has been more widely tested, it may have more general applicability for reasons of speed and convenience.

THE NATURE OF THE PROBLEM

Since all members of the chlorite family have the same type of structure (Fig. 1), the identification of particular species must proceed from a consideration of the finer details of the x-ray diagram, namely the precise lattice dimensions and the intensities of reflections (or structure factors). Hitherto, x-ray studies had been concerned only with the lattice dimen-

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sions (Engelhardt (1942), Gruner (1944), Bannister and Whittard (1945), Brindley and MacEwan (1953), Hey (1954)) and not at all with reflected x-ray intensities. With sufficient structure factor data, the problem could be fully solved by standard methods of structure analysis, but the restrictions imposed by the use of the powder method and impure materials make it necessary to consider how much information can be extracted from the available reflections.
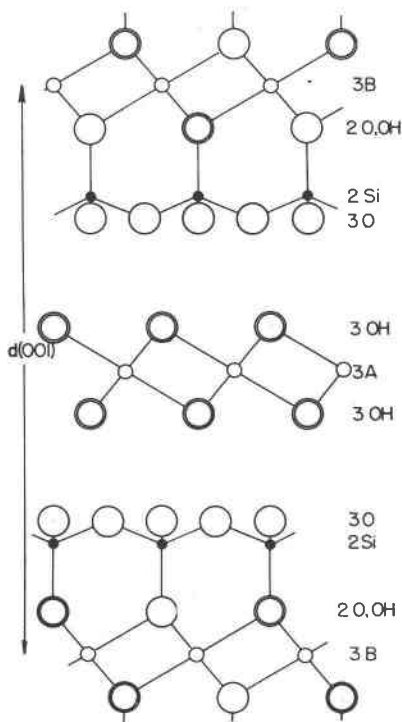

Fig. 1. The chlorite structure projected on 010. In this projection, O and (OH) ions overlap and their distribution in the b direction cannot be shown.

In the following sections we consider the principal compositional parameters of the chlorites and the application of lattice spacing and structure factor measurements to their determination. Finally a number of examples are given comparing results obtained by the x-ray method with those obtained by chemical analysis.
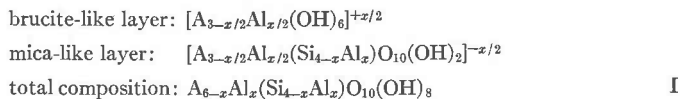
STRUCTURAL CHEMISTRY OF THE CHLORITES

The chlorite field is customarily divided into two broad subdivisions, the *orthochlorites* with compositions ranging between $(Mg, Fe^{2+})_4Al_2(Si_2$-

$Al_2)O_{10}(OH)_8$ and $(Mg, Fe^{2+})_6Si_4O_{10}(OH)_8$ with minor amounts of other elements, and the *leptochlorites* which do not fit into this scheme and are generally richer in trivalent ions, notably Fe^{3+}. In many cases the latter appear to have originated as ferrous orthochlorites and to have been subsequently oxidized (see discussion by Hey, 1954).

The chlorite structure, see Fig. 1, consists of an alternating series of brucite-like hydroxide layers, of general composition $A_3(OH)_6$, and mica-like layers, of general composition $B_3(Si, Al)_4O_{10}(OH)_2$. A and B stand for a variety of ions in octahedral positions which, in the orthochlorites, are mainly divalent. If there are $(Si_{4-x}Al_x)$ atoms in tetrahedral positions, the layer acquires a negative charge $-x$ which is balanced by a corresponding number of trivalent ions in the A and B positions. On a priori grounds it is not evident whether the distribution of cations in the A and B positions is the same, and whether the charge is balanced wholly in the mica-like layer or in both layers.

Case I. Orthochlorites

The simplest situation arises when the A and B sites are occupied by the same distribution of cations, and Al is the only trivalent ion. The compositions and charges of the layers are then as follows:

brucite-like layer: $[A_{3-x/2}Al_{x/2}(OH)_6]^{+x/2}$

mica-like layer: $[A_{3-x/2}Al_{x/2}(Si_{4-x}Al_x)O_{10}(OH)_2]^{-x/2}$

total composition: $A_{6-x}Al_x(Si_{4-x}Al_x)O_{10}(OH)_8$ I

Case II. Orthochlorites containing Mg and Fe^{2+} ions

If, in formula I, A_{6-x} contains y Fe^{2+} ions and the remaining ions are Mg, the formula becomes

$$Mg_{6-x-y}Fe_y^{2+}Al_x(Si_{4-x}Al_x)O_{10}(OH)_8 \qquad II$$

Chlorites satisfying these conditions require the determination of two parameters, x and y.

Case III. Orthochlorites containing Fe^{3+} ions

In orthochlorites, Fe^{3+} is usually a minor constituent and probably occurs wholly in octahedral positions. In the light of recent work by Osthaus (1953) on the crystal chemistry of Fe^{3+} ions in montmorillonites, the possibility cannot be entirely dismissed that Fe^{3+} ions may occupy tetrahedral positions, but if the usual assumption is made that they occupy octahedral positions, then the formula can be written:

$$Mg_{6-x-y}Fe_y^{2+}Fe_z^{3+}Al_{x-z}(Si_{4-x}Al_x)O_{10}(OH)_8 \qquad III$$
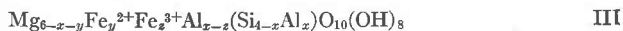
Three variables are required to specify such a chlorite.

Case IV. Leptochlorites

If these are oxidized chlorites (Hey, 1954) formed by a process of the type

$$Fe^{2+} + OH^- \rightarrow Fe^{3+} + O^{2-} + H$$
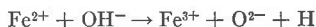
where H leaves the lattice as H_2O by aerial oxidation, then the Fe^{3+} ions are not replacing Al ions in octahedral coordination. The leptochlorite formula can then be written

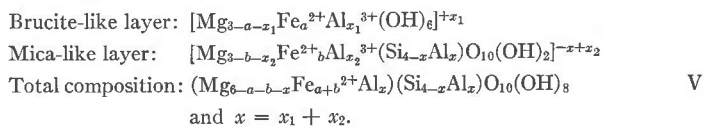$$Mg_{6-x-y}Fe_{y-z}^{2+}Fe_z^{3+}Al_x(Si_{4-x}Al_x)O_{10+x}(OH)_{8-z} \qquad \text{IV}$$
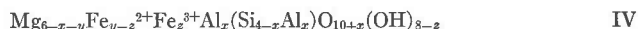
where z is the number of ferrous ions which have oxidized to ferric ions. The formula represents a partially oxidized orthochlorite of type II. When the original mineral already contains some ferric ions, as in formula III, a more complex leptochlorite formula is required.

Case V. Chlorites with unequal distributions of octahedral cations.

A possibility not usually considered, mainly because it is not amenable to bulk chemical analysis, is that the octahedral ions are not distributed equally between the A and B positions. It is conceivable, for example, that the replacement of divalent by trivalent cations required for electrical neutrality may occur wholly or largely within the mica-like layer. Such a structure would have little or no ionic binding force between layers and would be expected to resemble talc as regards mechanical properties.

Another possibility is that a chlorite may be formed from a mica by replacing the interlayer cations by a hydroxide layer carrying the same overall ionic charge. The ions occupying the A and B sites may then be of different compositions. If Fe^{3+} ions are absent, the compositions and charges of the component layers can be expressed as follows:
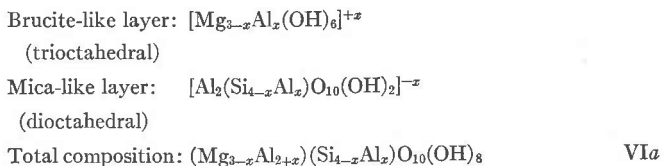
Brucite-like layer: $[Mg_{3-a-x_1}Fe_a^{2+}Al_{x_1}^{3+}(OH)_6]^{+x_1}$

Mica-like layer: $[Mg_{3-b-x_2}Fe_b^{2+}Al_{x_2}^{3+}(Si_{4-x}Al_x)O_{10}(OH)_2]^{-x+x_2}$

Total composition: $(Mg_{6-a-b-x}Fe_{a+b}^{2+}Al_x)(Si_{4-x}Al_x)O_{10}(OH)_8 \qquad \text{V}$

and $x = x_1 + x_2$.

Four parameters, a, b, x_1 and x_2, are required to describe this arrangement. Bulk chemical analysis cannot differentiate case IV from case II; it will determine $(a+b) = y$ and $(x_1+x_2) = x$ but it provides no means of splitting x and y into components for the two layers. In so far as x-ray analysis can solve this problem, it will give information not obtainable by ordinary chemical procedures.
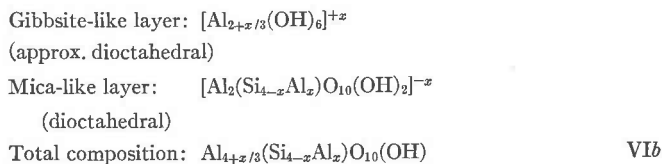
Case VI. Chlorites with dioctahedral layers

A further possibility is that one or both of the octahedral layers in a chlorite structure may be dioctahedral rather than trioctahedral.

Possible combinations are as follows:

Brucite-like layer: $[Mg_{3-x}Al_x(OH)_6]^{+x}$
(trioctahedral)

Mica-like layer: $[Al_2(Si_{4-x}Al_x)O_{10}(OH)_2]^{-x}$
(dioctahedral)

Total composition: $(Mg_{3-x}Al_{2+x})(Si_{4-x}Al_x)O_{10}(OH)_8$ VI*a*

Still another possibility is the double dioctahedral case:

Gibbsite-like layer: $[Al_{2+x/3}(OH)_6]^{+x}$
(approx. dioctahedral)

Mica-like layer: $[Al_2(Si_{4-x}Al_x)O_{10}(OH)_2]^{-x}$
(dioctahedral)

Total composition: $Al_{4+x/3}(Si_{4-x}Al_x)O_{10}(OH)$ VI*b*

Chlorites of these compositions have not yet been discovered, but their possible existence in fine-grained sediments cannot be ignored, and it is worth considering how they might be recognized from *x*-ray data.

X-Ray Evaluation of Chlorite Species

The quantities experimentally determinable are the lattice parameters, $d(001)$ and b, and the reflected intensities (or structure factors). Since chlorites have a well defined layer structure parallel to (001), the basal 00*l* reflections will provide the clearest information on the ionic distribution.

The b parameter

This parameter is best determined from the easily recognized 060 reflection, with d about 1.53–1.54 Å for all trioctahedral layer silicates. The 040 reflection is usually weak and not easily seen in a powder diagram and the 020 reflection is often obscured by the 003 reflection. The main usefulness of the b parameter is that it provides a clear distinction between di- and trioctahedral structures.

Within the trioctahedral group b is not well suited to the recognition of particular species. Engelhardt (1942) and Hey (1954) correlated b with the number of Fe atoms in the chlorite structure, but Brindley and MacEwan (1953, pp. 38–41) have shown that it must be related to all the lattice substitutions. Since AlO_4 tetrahedra are larger than SiO_4 tetrahedra, increasing substitution of Si by Al tends to expand the tetrahedral layers. If Mg ions are regarded as the normal octahedral cations, then replacement of Mg^{2+} (ionic radius, 0.78 Å) by Al^{3+} and Fe^{3+} (ionic radii 0.57 and 0.67 Å respectively) tends to shrink the lattice, and replacement by Fe^{2+} ions (ionic radius, 0.83 Å) to expand it. Since the tetrahedral and octahedral layers are parallel to one another, the actual b

parameter will be the result of a compromise between the two kinds of layers and therefore a function of all the substitutions within the lattice. In so far as Al ions occupy tetrahedral and octahedral positions equally, their overall contribution to an expansion or contraction of the layers may be small and the resultant b value may then be determined principally by the Fe^{2+} substitutions. However, we consider that b is not a useful parameter to use for species determination, and that the Fe content can be more reliably determined from structure factor determinations.

The basal spacing, d(001)

This spacing depends on the compositions of the layers and the bonding forces between them. Gruner (1944) and Bannister and Whittard
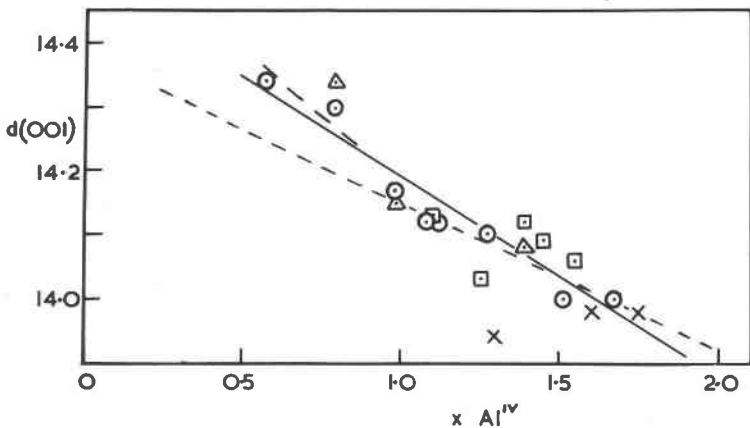

Fig. 2. Basal spacing, $d(001)$, of chlorites plotted against x, the number of Al atoms replacing Si atoms in the formula $(Si, Al)_4$. Experimental observations are as follows: O Bannister and Whittard (1945); × Engelhardt (1942); □ McMurchy (1934); △ Brindley and Ali (See Brindley, 1951). Dashed line shows a relation given by Hey (1954).

(1945) correlated the basal spacing with the replacement of Si by Al, and attributed the variation of $d(001)$ principally to the ionic bonding forces. In orthochlorites satisfying formulae II and III, the ionic bonding forces depend mainly on the layer charges, $\pm x/2$, where x = no. of Al ions in tetrahedral positions. Substitutions within the layer determine their dimensions in the manner already indicated, but if these dimensions remain roughly constant, then $d(001)$ can be correlated with x as a first approximation.

In Fig. 2, observed values of $d(001)$ are plotted against x for a number of analyzed chlorites and the results lie on or near the straight line

$$d(001) = 14.50 - 0.31x.$$

Hey (1954) has given a similar relation with constants 14.38 and -0.23 in the present notation, which is also shown in Fig. 2.

We have examined the scatter of the points in Fig. 2 in relation to the Fe^{2+} and Fe^{3+} contents of the minerals and, in agreement with Hey, find a tendency for Fe-rich chlorites to give low spacings but the observations are too scattered to justify at this stage an attempt to express quantitatively how the mean line of Fig. 2 varies with Fe content.

The intensities of the basal reflections

No quantitative discussion of the basal intensities has previously been given although it is well-known that the (001), (003) and (005) reflections are relatively weak from iron-rich chlorites. This follows directly from the fact that the octahedral layers associated with the A and B cations are separated by a distance of $d(001)/2$, so that the only contributions to the odd orders come from the Si-O hexagonal networks. The octahedral layers make additive contributions to the even orders which are relatively very strong for the iron-rich chlorites. For the same reasons it is seen directly that an unequal distribution of cations between the A and B sites leaves the even order basal reflections unaffected, but has a pronounced effect on the odd orders because the contributions from the octahedral layers no longer cancel out exactly.

The nearly equal scattering factors of Si, Al and Mg, and of Fe, Cr and Mn preclude any distinction between atoms in these groups on the basis of intensity measurements. It should be possible, however, to locate and estimate Fe (and equivalent) atoms in relation to Mg (and equivalent) atoms. Structure factors have been calculated for a range of chlorite compositions using atomic scattering factors given by Bragg and West (1928), with allowance for x-ray dispersion in the case of the Fe atoms. Dispersion lowers the effective atomic scattering factor of Fe by amounts 1.5, 4.4 and 3.0 for Cu, Co and Fe $K\alpha$ radiations respectively. We have used a dispersion correction of 3.0 units which is correct for Fe $K\alpha$ radiation (this is most commonly employed for iron-rich materials) and will not be seriously in error for the other two radiations. The c-parameters for the chlorite structure have been taken from a fourier synthesis for penninite (Brindley and Robinson, 1951, p. 180); the variations of these parameters for other chlorites will have a negligible influence on the lower order structure factors.

RESULTS OF STRUCTURE FACTOR CALCULATIONS

The calculated structure factors, F, tabulated in Tables 1, 2 and 3, correspond to the formulae I–VI previously given. These formulae represent the content of half of a unit cell comprising one chlorite layer. The

signs of F correspond to an origin placed at the center of the mica-like layer.

(a) Orthochlorites without Fe^{3+} ions

Table 1 lists the calculated F values for orthochlorites satisfying formula II and having equal cation distributions in the A and B positions.

TABLE 1(A). STRUCTURE FACTORS, F, FOR ORTHOCHLORITE REFLECTIONS
CALCULATED FOR VARIOUS VALUES OF y IN THE FORMULA:
$$Mg_{6-x-y}Fe_y^{2+}Al_x(Si_{4-x}Al_x)O_{10}(OH)_8$$
ASSUMING A SYMMETRICAL DISTRIBUTION OF THE OCTAHEDRAL CATIONS.
THE VALUES OF F CORRESPOND TO ONE FORMULA UNIT

$00l$ y	001	002	003	004	005	006	007	008
0	22	41	-55	80	55	-18	-40	-11
1	22	51	-55	88	55	-2	-40	-6
2	22	61	-55	96	55	-5	-40	-1
3	22	71	-55	104	55	1	-40	4
4	22	80	-55	111	55	7	-40	9
5	22	90	-55	119	55	13	-40	14
6	22	100	-55	127	55	19	-40	19

(F values for odd orders are independent of y.)

TABLE 1(B). STRUCTURE FACTOR RATIOS

y	$F(002)/F(001)$	$F(002)/F(003)$	$F(004)/F(002)$	$F(004)/F(003)$ $F(004)/F(005)$
0	1.86	0.75	1.95	1.45
1	2.32	0.93	1.73	1.60
2	2.77	1.11	1.57	1.75
3	3.22	1.29	1.46	1.89
4	3.64	1.45	1.39	2.02
5	4.09	1.64	1.32	2.16
6	4.55	1.82	1.27	2.31

F is independent of y (the number of Fe^{2+} ions) for the odd order reflections, but increases with y for the even orders. The parameter y is determined from $|F|$ values measured in arbitrary units by comparing observed and calculated values of the ratios $F(002)/F(001)$, $F(002)/F(003)$, $F(004)/F(002)$, $F(004)/F(003)$ and $F(004)/F(005)$. Although higher orders are included in Table 1, it is seldom they will be available in actual

analyses due to the presence of other reflections, except when pure chlorites are examined.

The accuracy with which y can be determined by this procedure rests on several considerations. On the experimental side, the reflected intensities must be accurately measured and correctly converted to $|F|$ values. This requires careful attention to points of detail to ensure that the experimental conditions presupposed by a theoretical formula are adequately satisfied. On the theoretical side, the calculated values depend on the accuracy of the scattering factors and the state of ionization of the atoms in the structure.

(b) Orthochlorites containing Fe^{3+} ions

Formula III represents the case where the Fe^{3+} ions are wholly in octahedral positions, and the octahedral cations are equally distributed. X-ray intensities do not distinguish between Fe^{2+} and Fe^{3+}, and the use of Table 1 therefore gives $(y+z)$. The parameter x will be obtained from Fig. 1 and this gives the amount of Al in tetrahedral positions. If, however, as in case (a), we take x instead of $(x-z)$ for the octahedral Al, then octahedral Al is over-estimated and the Mg will be under-estimated.

At present there is no obvious way by which the z Fe^{3+} ions in formula III can be determined by x-rays. However, it appears to be the case that Fe^{3+} is usually a small component in orthochlorites so that the errors in Al and Mg may be relatively unimportant.

(c) Leptochlorites containing Fe^{3+} ions

In so far as leptochlorites are oxidized forms of orthochlorites, they are represented by formula IV. The Fe^{3+} ions, being derived from Fe^{2+} ions, are not replacing Al^{3+} ions in octahedral sites as in case (b). The parameter x is determined from $d(001)$ measurements, and the total iron, $Fe_{y-z}^{2+}Fe_z^{3+}$, will be given by use of Table 1. We still cannot determine the parameter z, but this will not introduce errors into the Mg and octahedral Al determinations, as in case (b). In effect, the result yielded by the x-ray method will be the original, unoxidized orthochlorite.

If the leptochlorite is derived from an orthochlorite containing Fe^{3+} ions in its original composition, then the same errors will arise as we have discussed in case (b).

### (d) Chlorites with unequal distributions of octahedral cations

X-ray intensities will distinguish only between Fe (and equivalent) atoms and Mg (and equivalent) atoms. If the octahedral Al ions are unequally distributed in a purely magnesian chlorite, so that the $Al^{VI}:Mg$ ratio differs in the two layers, then x-ray intensity measurements will give

no indication of this situation. Such a distribution would influence the layer charges and presumably also the $d(001)$ spacing. In such circumstances, the use of Fig. 2 and Table 1 to determine x and y may lead to incorrect results.

On the other hand, if the unequal distribution affects the $Fe^{2+}:Mg$ ratio, the structure factors will be sensitive indicators. Since the even order $00l$ reflections depend on the amplitude sum from the octahedral layers and the odd order reflections on the amplitude difference, the even orders will determine the *total* Fe^{2+} and Mg in the octahedral positions, while the odd orders will give the asymmetry in the distribution.

Table 2 gives the results of calculations of the odd-order $00l$ structure factors for a range of asymmetrical distributions of Fe^{2+} ions. Owing to

TABLE 2. STRUCTURE FACTORS OF ODD ORDER $00l$ REFLECTIONS FOR VARIOUS ASYMMETRIC DISTRIBUTIONS OF Fe^{2+} IONS BETWEEN THE A AND B OCTAHEDRAL POSITION IN AN ORTHOCHLORITE OF GENERAL COMPOSITION:

$$Mg_{6-x-y}Fe_y^{2+}Al_x(Si_{4-x}Al_x)O_{10}(OH)_8$$
$$= Fe_y^{2+}(Mg, Al)_{6-y}(Si, Al)_4O_{10}(OH)_8$$
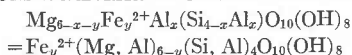
Distribution of Fe^{2+} ions			Structure factor, F			
Fe^{2+} ions in mica-like layer	Fe^{2+} ions in brucite-like layer	Excess Fe in mica-like layer	001	003	005	007
$y/2+\frac{1}{2}$	$y/2-\frac{1}{2}$	1.0	34	-45	62	-34
$y/2+\frac{1}{4}$	$y/2-\frac{1}{4}$	0.5	28	-50	58	-37
$y/2$	$y/2$	0	22	-55	55	-40
$y/2-\frac{1}{4}$	$y/2+\frac{1}{4}$	-0.5	16	-60	51	-43
$y/2-\frac{1}{2}$	$y/2+\frac{1}{2}$	-1.0	12	-64	48	-46

the relatively large scattering factor of the Fe atom compared with those of Mg and Al, any asymmetry in the iron distribution has a very marked effect on the structure factors. Moreover, Table 2 shows that as Fe atoms are transferred from the mica-like layer to the brucite-like layer, $|F|$ diminishes for the 001 and 005 reflections, but increases for the 003 and 007 reflections.

(e) Chlorites with dioctahedral layers

Table 3 lists the calculated results for two of these structures. A double dioctahedral structure (formula VIb, and No. 2 in Table 3) gives the same odd-order scattering factors as the symmetrical trioctahedral orthochlorites, (c. f. Tables 1 and 2). The even order scattering factors, particularly those for 002 and 004, bear a different ratio to each other and to the odd orders as compared with the orthochlorite data in Table 2.

Thus $F(004)/F(002)$ is about 3.0 as compared with ratios ranging from about 1.2 to 2.0 in Table 2, the (001) and (002) reflections are more nearly equal and (003) is relatively large as compared with the orthochlorite data.

A structure which is trioctahedral in the brucite-like layer and dioctahedral in the mica-like layer, (formula VIa and No. 1 in Table 3) is characterized by a (003) reflection which is relatively strong compared with the (001) and (002) reflections. In this respect it resembles an orthochlorite with an asymmetric distribution of octahedral cations and a preponderance of Fe in the brucite-like layers, (c.f. Tables 1 and 2).

It will probably always be difficult to decide with certainty purely from x-ray intensity data if a chlorite-type mineral has one or both octahedral layers of the dioctahedral type. When such a question arises, useful auxiliary information will be provided by the b parameter. For dioctahedral layer minerals, b is usually of the order of 8.85–9.00 Å

TABLE 3. STRUCTURE FACTORS FOR CHLORITES CONTAINING DIOCTAHEDRAL LAYERS

(1) Trioctahedral brucite layer, dioctahedral mica layer, formula VIa.

(2) Dioctahedral gibbsite layer, dioctahedral mica layer, formula VIb.

00l	001	002	003	004	005	006	007	008
(1)	12	31	−65	71	46	−25	−47	−17
(2)	22	21	−55	62	55	−33	−40	−24

and for trioctahedral minerals is distinctly larger, and of the order of 9.2–9.3 Å.

A SUMMARY OF THE PROCEDURE FOR DETERMINING CHLORITE SPECIES FROM X-RAY DATA

The spacings and reflected intensities of the first five basal 00l reflections must be accurately measured. The 060 reflection should be recorded to confirm if the mineral is trioctahedral. Care must be taken to use a valid formula for converting reflected intensities to structure factors. Geiger counter diffractometers will be found more accurate and convenient for obtaining the required data but particular care must be exercised in deriving the structure factors, (see notes in appendix).

The basal parameter $d(001)$ in conjunction with Figure 2 gives x, the number of tetrahedral Al ions, which is also the number of octahedral Al ions except when Fe^{3+} ions substitute for Al in octahedral sites.

We have seen that $F(001)$, $F(003)$ and $F(005)$ vary with the asymmetry

of distribution of Fe ions. For *symmetrical* distributions, these structure factors are independent of Fe content and good agreement should be obtained between the observed values and the calculated values in Table 1. If good agreement is not obtained, and provided the experimental data are reliable, then the distribution may be *asymmetrical;* the asymmetry can be considered in the light of the data given in Table 2.

When the experimental evidence points to a symmetrical distribution, then the first five 00*l* structure factors can be used in conjunction with Table 1 to determine the y parameter, i.e., the number of Fe atoms. When there is doubt about the octahedral cations being symmetrically distributed, then the ratio $F(004)/F(002)$ gives a value for y which is independent of any asymmetry.

EXAMPLES OF THE APPLICATION OF THE METHOD

A detailed account will be given of the application of the foregoing methods to the identification of a chlorite supplied by the Sierra Talc

TABLE 4. EXPERIMENTAL DATA FOR THE IDENTIFICATION OF A CHLORITE

00l	$d(00l)$	$d(001)$	I (integrated)	F (relative values)
001	14.1 (4)	14.1 (4)	318	9.7_2
002	7.08	14.16	360	20.8_4
003	4.720	14.16	259	26.8_1
004	3.541	14.16	285	38.1_5
005	2.836	14.18	$77\frac{1}{2}$	25.30
007	2.023	14.16	—	—
00, 10	1.417	14.17	—	—
00, 11	1.288	14.17	—	—
	Mean	14.16_5		

and Clay Co. with the kind assistance of Professor J. A. Pask. The material was an almost pure chlorite and more basal reflections were recorded than would usually be possible with less pure material. The identification, however, has been based essentially on the first five orders. The experimental data are given in Table 4. The mean basal spacing, $14.16_5 \pm 0.00_5$ Å, would not be materially changed by using the first five orders only. Using Fig. 2, we obtain

$$x = 1.09 \pm 0.05$$

The uncertainty in x, 0.05, is based primarily on an estimated uncertainty in the position of the line in Fig. 2. An uncertainty of ± 0.01 Å in $d(001)$ has a relatively small effect on x.

We consider next the values of $|F|$ for (001), (003) and (005), and obtain the following ratios:

|	$|F|$ (001)	$|F|$ (003)	$|F|$ (005)
Experimental ratio:	0.362	1	0.94_3
Calculated ratio, assuming symmetrical distribution of octahedral cations, (Table 1)	0.40	1	1.00
Calculated ratio, assuming an excess of Fe atoms in mica layer of -0.2, (using Table 2)	0.35	1	0.94

The agreement between the observed ratios and those calculated on the assumption of a symmetrical distribution of octahedral cations is quite close and it is scarcely worth while to consider an asymmetrical distribution. Nevertheless, reference to Table 2 shows that the slightly lower observed ratios are consistent with slightly less Fe in the mica layer than in the brucite layer. In fact, by transferring as little as 0.1 Fe from the mica to the brucite layer we obtain complete agreement with the observed values. This asymmetry is so small that we hesitate to claim it as a real deviation from a symmetrical distribution.

Neglecting this small asymmetry and using the full range of experimental data up to (005) in conjunction with Table 1, we obtain the following values for y:

	$F(002)/$ $F(001)$	$F(002)/$ $F(003)$	$F(004)/$ $F(002)$	$F(004)/$ $F(003)$	$F(004)/$ $F(005)$
Experimental	2.14	0.78	1.83	1.42	1.51
y (Table 1)	0.61	0.33	0.55	-0.20	0.40

Mean y (excluding $F(004)/F(003)$) $= 0.47 \pm 0.11$ or 0.5 ± 0.1

Using formula II, we express the structure formula as:

$$Mg_{4.4}Fe_{0.5}{}^{2+}Al_{1.1}(Si_{2.9}Al_{1.1})O_{10}(OH)_8$$
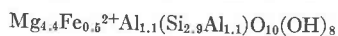
From the chemical analysis given by Pask and Warner (1954) (see analysis A in Table 1 of their paper), the following formula is calculated:

$$Mg_{4.29}Fe_{0.14}{}^{2+}Al_{1.52}(Si_{3.06}Al_{0.94})O_{10.46}(OH)_{7.54}.$$

The agreement is very good as regards the tetrahedral Al and the Mg, but less good as regards the Fe^{2+} and Al in octahedral coordination. Similar tests have been applied to three other chlorites namely:

Penninite, from Binnental (Switzerland), supplied by F. A. Bannister (British Museum), analyzed by R. F. Youell (University of Leeds).

Prochlorite, from Salcombe, Devon (England), supplied by C. E. Tilley (University of Cambridge), analyzed by H. C. G. Vincent. (*Geol. Mag.*, **75**, p. 503, 1938).

Daphnite, from Cornwall (England), supplied and analyzed by J. S. Webb.

The results of these four tests are indicated in Fig. 3, which shows on a triangular diagram the total octahedral compositions as calculated from the chemical analyses (black circles) and as derived from the x-ray data (shaded circles). The diagram is divided into areas according to
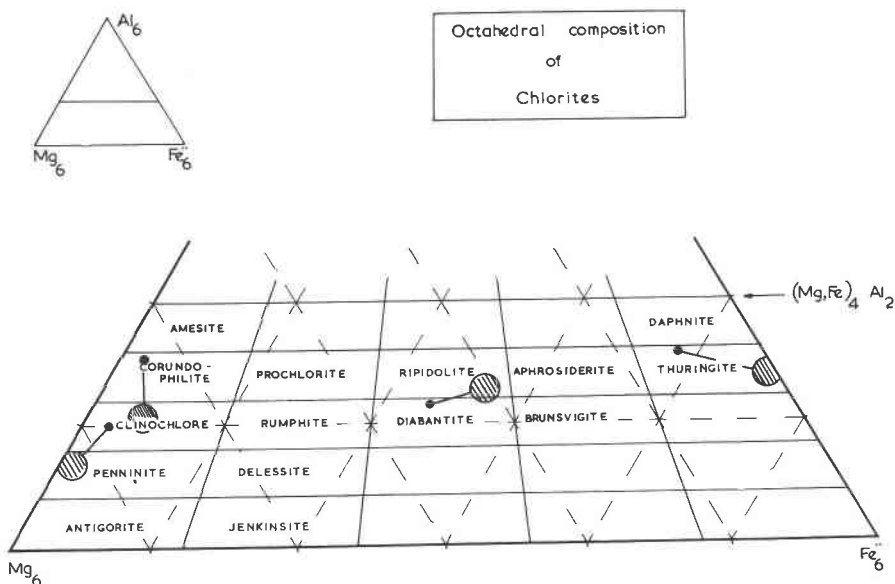

FIG. 3. A comparison of the octahedral compositions of four chlorites determined from chemical analyses (small black circles) and from x-ray data (large shaded circles). To avoid confusion, corresponding circles are joined.

Winchell's classification to show the general distribution of species names.

These results suggest that the identification of chlorite species from x-ray data can be carried out with a moderate degree of success.

REFERENCES

BANNISTER, F. A., AND WHITTARD, W. F. (1945), *Mineral. Mag.*, **27**, 99–111.

BRAGG, W. L., AND WEST, J. (1928), *Z. Krist.*, **69**, 118–148.

BRINDLEY, G. W., AND MACEWAN, D. M. C. (1953), Structural aspects of the mineralogy of clays and related silicates: in *Ceramics—a symposium*, pp. 15–59, published by British Ceramic Society.

BRINDLEY, G. W., AND ROBINSON, K. (1951), The Chlorite Minerals, Ch. VI of *X-ray Identification and Crystal Structures of Clay Minerals*, published by the Mineralogical Society (London).

ENGELHARDT, W. VON (1942), *Z. Krist.*, **104**, 142–159.

GRUNER, J. W. (1944), *Am. Mineral.*, **29**, 422–430.

HEY, M. H. (1954), *Mineral. Mag.*, **30**, 277–292.

McMURCHY, R. C. (1934), *Z. Krist.*, **88**, 420–432.

ORCEL, J. (1927), *Bull. Soc. Franç. Min.*, **50**, 75–454.

ORCEL, J., CAILLÈRE, S., AND HÉNIN, S. (1950), *Mineral. Mag.*, **29**, 329–340.

OSTHAUS, B. B. (1953), Abstracts of Second Conference on Clays and Clay Minerals, Columbia (Miss.), p. 12. See also "Clays and Clay Minerals," *Nat. Acad. Sci.*, Washington (1954), pp. 404–417.

PASK, J. A., AND WARNER, M. F. (1954), *J. Am. Ceramic Soc.*, **37**, 118–128.

TSCHERMAK, G. (1890), *Sitzungsber. Akad. Wiss. Wien, Cl. Mat.-Nat.*, **99**, abt. 1, 174–268.

TSCHERMAK, G. (1891), *Ibid.*, **100**, abt. 1, 29–107.

WINCHELL, A. N. (1926), *Am. J. Sci.*, **11**, 283–300.

WINCHELL, A. N. (1936), *Am. Mineral.*, **21**, 642–651.

APPENDIX

Conversion of reflected energy, E, to $|F|^2$ for different experimental arrangements

The increasing use by non-specialists of x-ray methods of identifying minerals, particularly by counter diffractometer methods, may justify the following notes. The basic formula (see, for example, James (1948), pp. 41–51) expresses the energy dE reflected by a small volume dv of non-absorbing crystal as it rotates within a beam of unpolarized x-rays of intensity I_0 per unit cross-section as

$$dE = \text{Const.} \, I_0 |F|^2 \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) dv \qquad (1)$$

Single crystals and oriented powder particles

With micaceous minerals such as chlorites the particles may be well oriented with their basal planes parallel to a glass slide. Reflection from these planes will then be equivalent to reflection from an extended crystal face provided the orientation is sufficiently good.

Case I. The incident x-ray beam falls wholly on an extended crystal face or an area of oriented powder particles

Integration of equation (1), taking account of absorption in the specimen and assuming it to be sufficiently thick to transmit a negligible

portion of the radiation, leads to the expression

$$E = \text{Const.} \frac{I_0 S_0}{2\mu} \mid F \mid^2 \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) \tag{2}$$

where $\mu =$ linear absorption coefficient and $S_0 =$ cross-section of the incident beam where it falls on the specimen.

Case II. The crystal or oriented powder specimen lies within the x-ray beam

In mineral identification work a situation often arises where the individual crystal or oriented powder specimen lies wholly within the x-ray beam so that the fraction of the beam which can be reflected depends on the angular setting of the specimen within the beam. If the specimen area is A, it intercepts an area $A \sin \theta$ of the beam and provided the beam is of uniform intensity the result is equivalent to equation (2) with $A \sin \theta$ in place of S_0. The reflected energy is given by

$$E = \text{Const.} \frac{I_0 A}{2\mu} \mid F \mid^2 \sin \theta \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) \tag{3}$$

It is assumed that the areal dimensions are large compared with the thickness so that "edge" effects are negligible.

Cases I and II combined

With counter diffractometers, it often happens that the amount of material available or that the size of the crystal flake is such that the incident radiation falls wholly on the specimen only when θ is greater than a certain value. If W is the width of the specimen, δ the divergence of the radiation, and R the spectrometer radius, then the limiting condition is $R\delta = W \sin \theta$. Equation (3) is appropriate when $\sin \theta < R\delta/W$, and equation (2) when $\theta > R\delta/W$.

Powdered specimens with random orientation

For a small volume dv of randomly oriented powder particles having negligible absorption, the equation analogous to (1) is

$$dE = \text{Constant } p I_0 \mid F \mid^2 \cos \theta \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) dv \tag{4}$$

where p is the multiplicity factor for the reflecting planes concerned, and dE is the energy per unit time in the whole diffracted halo.

Case III. Counter diffractometer technique with a large area of randomly oriented powder particles

By integration of equation (4) for a "thick" block of powder, assuming that the radiation falls wholly on the specimen and that the window

of the Geiger counter accepts a fixed length out of each diffracted halo, we obtain

$$E = \text{Const. } pI_0S_0 |F|^2 \left(\frac{1 + \cos^2 2\theta}{\sin\theta \sin 2\theta}\right) \tag{5}$$

Case IV. Counter spectrometer technique with small area of randomly oriented powder particles

A specimen of area A intercepts an area $A \sin\theta$ of the incident beam, so that $A \sin\theta$ replaces S_0 in equation (5) and we have

$$E = \text{Const. } I_0A |F|^2 \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta}\right) \tag{6}$$

Powdered specimens with partial orientation

A situation which is not amenable to precise calculation arises with imperfectly oriented powder specimens. Comparison of equations (2) and (5) relating to "large" specimens, with equations (3) and (6) relating to "small" specimens, shows that in passing from fully oriented reflecting planes to randomly oriented crystallites an additional factor of $1/\sin\theta$ is introduced into the expressions for E. For a given set of reflecting planes $\sin\theta$ is proportional to n, the order of the reflection in the Bragg equation. Thus for the two reflections (001) and (002), the ratio of their angular functions changes by a factor 2/1 depending on whether we assume a fully ordered or fully disordered arrangement of the reflecting particles. For higher orders, the ratio depends less critically on which formula is used. In the identification of chlorites, however, and in all similar problems, the lower orders are likely to be the most useful and therefore the question of orientation is an important one.

When dealing with flakey powders, such as commonly occur with micaceous minerals, it is recommended that identification procedures which involve intensity measurements should be carried out with (i) aggregate specimens oriented as well as possible by careful sedimentation, and (ii) powder specimens prepared with a minimum of orientation, e.g., by filling the specimen holder from the back rather than from the front surface.

Other difficulties

Under this heading brief reference may be made to other difficulties inherent in the precise interpretation of x-ray intensities. When single crystals and mineral flakes rather than fine powders are used, extinction effects may modify the reflected intensities, especially of strong, low-order reflections. When composite specimens containing several crystalline components are used, questions of differential absorption arise par-

ticularly when the absorption coefficients of the components are very different. These difficulties are minimized by using fine powders. The formulae given for E refer to the total reflected energy whereas experimentally the peak intensity is often measured. The two are proportional for peaks of constant width. The present application is concerned mainly with low-order reflections of which the widths will be largely constant.

Other techniques

These notes have been written mainly in relation to Geiger counter diffractometer technique. When photographic technique is used, equation (3) is still valid for a small flake of crystal or a thin fragment of well-oriented powder rotated within an x-ray beam. For stationary powder blocks and powder rods, equations (5) and (6) are not valid and formulae (see James, 1948) must be used containing the appropriate absorption factors.

REFERENCE

JAMES, R. W. (1948), The Optical Principles of the Diffraction of X-Rays. G. Bell and Sons, London.

Manuscript received Jan. 21, 1955.