The effect of isomorphous substitutions on the intensities of (00l) reflections of mica- and chlorite-type structures.

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Introduction.

A WIDELY used method of quantitative analysis in clay mineralogy is the comparison of the intensities of X-ray reflections from a so-called standard mineral with the unknown. In the clay minerals where isomorphous substitution is frequent the term 'mineral' generally covers a range of compositions and what is meant by such a term is a group of closely similar minerals. The so-called standard mineral is any member of a group which the particular worker may have in a pure or almost pure condition. If the standard mineral and the mineral in the unknown give different intensities for an equal volume of material the results will be inaccurate. It is therefore essential if we are to evaluate the standard-mineral method to see what sort of errors are involved in assuming all the members of a group have the same X-ray intensities. In this paper the effects of preferred orientation and absorption of X-rays in the specimen have been ignored, but, in a final analysis, these effects, too, would have to be taken into account.

The majority of clay minerals have layer structures and the different groups of clay minerals are readily characterized by their different layer thicknesses. In these layer structures the a and b axes are perpendicular and lie in the plane of the layers so the low order (00l) reflections are commonly used for both qualitative and quantitative mineralogical analysis. All the 2:1-type clay minerals either are, or can be converted into, mica-type and chlorite-type structures without alteration of the fundamental silicate layer. The montmorillonite and the vermiculite minerals, which can be regarded as expanded mica structures, can be collapsed by heating to give (00l) reflections in similar positions to the mica reflections. The intensities of the (00l) reflections from such heated specimens will depend on the nature and amount of the interlayer

material and on the constitution of the silicate layer as do those of the micas (see below). Thus calculations for mica-type and chlorite-type structures can be applied to the great majority of 2:1-type clay minerals.

THEORY.

The intensity of a reflection from a fine powder (as defined by Brindley, 1945) recorded on a cylindrical film by the Debye-Scherrer method is given by

$$\frac{P}{I_0} = \frac{pl}{8\pi r \sin \theta} QVA\Psi, \tag{1}$$

where P is the energy diffracted into length l of a Debye-Scherrer halo by the set of planes (hkl), (hkl), and $(\bar{h}\bar{k}\bar{l})$ being considered as different sets. I_0 is the energy per unit area in the incident beam, r is the distance from specimen to film, p is the multiplicity factor for the set of planes considered, V is the volume of crystal powder irradiated of the substance giving the reflection, A is a factor for absorption in the specimen, Ψ is a factor for preferred orientation in the specimen.

$$Q = \frac{N^2\lambda^3}{\sin 2\theta} |F|^2 \left(\frac{e^2}{mc^2}\right)^2 \frac{1+\cos^2 2\theta}{2} \tag{2}$$

where the symbols have their usual significance (James, 1950), in particular N is the number of unit cells per unit volume and F is the structure factor per unit cell. In the clay minerals a more appropriate unit is the unit layer and in this paper all F values are calculated for this unit and so N becomes the number of unit layers per unit volume.

For a given reflection from a given mineral group with a given λ equations (1) and (2) show that intensity is proportional to F^2. For clay mineral layer structures with a plane of symmetry parallel to the layers, if the origin of co-ordinates is taken at the plane of symmetry and the summation is made over half the unit layer, the expression for $F(00l)$ becomes

$$F(00l) = 2 \sum f_a \cos 2\pi lz, \tag{3}$$

where f_a is the atomic scattering factor of atom type a for the radiation used and z is the fractional co-ordinate of the atom.

From equations (1), (2), and (3) it is apparent that within a mineral group the most important factor in changing low angle $(00l)$ intensities will be isomorphous substitutions, for atomic co-ordinates do not vary

much within a group and small variations in them do not affect the intensities of low-angle reflections appreciably.

In the subsequent sections, tables of F values for basal reflections are given for micas and chlorites of different chemical compositions. The results are given as F's rather than in the form of intensities for a particular experimental method as F values can be converted to intensities for different experimental arrangements by using the appropriate equations (James, 1950).
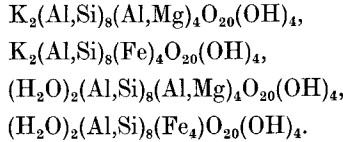
APPLICATION TO THE MICA GROUP.

The clay minerals are composed of a framework of O and OH ions, the interstices of which may be filled with Si, Al, Mg, Fe, and K ions. Within a mineral group, if we treat O and OH together, the anion framework is constant and its scattering power for X-rays can be taken as that of the oxygens. Si, Al, and Mg have very similar atomic scattering factors (f_a's) at low angles of diffraction and this allows them to be treated together in a structural position where any two occur together, and in such cases the atomic scattering factor of the major occupant has been used for all such atoms in that position. For example, all tetrahedral atoms have been treated as Si, for Si is always the major occupant of these positions; in dioctahedral micas where the octahedral positions are largely filled with Al with slight replacement of Al by Mg and Fe, the atomic scattering factor for Al has been used for (Al, Mg), and the Fe atoms are treated separately.

In the mica structure we can have isomorphous substitution of Al for Si in tetrahedral positions, and Al, Mg, and Fe can all occur in octahedral positions. Of these the substitution of Fe is the only one which appreciably affects low-order $(00l)$ intensities. The cation population of the interlayer position can also vary. There is less K in illites than in the true micas and it seems a fair assumption that the K-vacant positions in illites are occupied by H_2O or $(H_3O)^+$. If the K-vacant positions are indeed vacant in illites then the change in the intensities compared to true micas will be even greater than for a structure with H_2O or $(H_3O)^+$ in the interlayer positions, for the total scattering power of the atoms in the interlayer position will be changed even more.

Using the atomic co-ordinates given by Jackson and West (1930) for muscovite, the atomic scattering factors for atoms in silicates given by Bragg and West (1928), and taking the plane of the octahedral ions as origin, $F(00l)$ per unit layer ($9 \times 5 \times 10$ Å. approximately) has been

calculated for reflections at 10 Å., 5 Å., and 3·3 Å. for dioctahedral micas whose composition lies within the limits,

$$K_2(Al,Si)_8(Al,Mg)_4O_{20}(OH)_4,$$
$$K_2(Al,Si)_8(Fe)_4O_{20}(OH)_4,$$
$$(H_2O)_2(Al,Si)_8(Al,Mg)_4O_{20}(OH)_4,$$
$$(H_2O)_2(Al,Si)_8(Fe_4)O_{20}(OH)_4.$$

A similar range is covered for trioctahedral micas.

TABLE I. Contributions of various parts of mica layer to the F's of $(00l)$ reflections.

Section of structure.	Composition.	Contribution for $9 \times 5 \times 10$ Å.^{3}:		
		to F (10 Å.).	to F (5 Å.).	to F (3·3 Å.).
Skeleton	$(Si,Al)_8O_{20}(OH)_4$ (invariant)	17	$\overline{120}$	74
Interlayer	2·0 K —	$\overline{37}$	34	$\overline{30}$
	1·5 K 0·5 H_2O	$\overline{32}$	30	$\overline{26}$
	1·0 K 1·0 H_2O	$\overline{27}$	25	$\overline{22}$
	0·5 K 1·5 H_2O	$\overline{23}$	21	$\overline{18}$
	— 2·0 H_2O	$\overline{18}$	16	$\overline{14}$

Octahedral		Normal.	Anoma-lous.	Normal.	Anoma-lous.	Normal.	Anoma-lous.
4Al	...	45	45	42	42	39	39
3Al1Fe	...	58	54	54	51	50	46
2Al2Fe	...	71	64	66	59	60	52
1Al3Fe	...	85	73	78	67	71	59
4Fe	...	98	82	90	75	81	66
6Mg	...	68	68	62	62	56	56
5Mg1Fe	...	81	78	75	71	67	63
4Mg2Fe	...	94	87	87	79	78	70
3Mg3Fe	...	107	96	99	87	89	77
2Mg4Fe	...	120	105	111	96	100	84
1Mg5Fe	...	133	114	123	104	111	91
6Fe	...	146	123	136	112	122	98

The results are in table I. They are given as contributions of various parts of the mica structure to $F(00l)$ per unit layer. The invariant skeleton consists of the tetrahedral cations and the oxygen framework. The interlayer and the octahedral contributions are given for different atomic populations of these positions. The octahedral contributions are given under two headings, normal and anomalous. This is necessary because the atomic scattering factor of Fe is reduced when Co-$K\alpha$ radiation is used owing to anomalous dispersion. The F value for a basal reflection of a particular mica is given by the sum of the appropriate contributions obtained from table I.

For example, for the 5 Å. reflection from a mica of composition $(K_{1\cdot5}(H_2O)_{0\cdot5})(Al_3Fe_1)(Al,Si)_8O_{20}(OH)_4$:

(a) with Cu-$K\alpha$ radiation

$$F(5) = F(5)(\text{skeleton}) + F(5)(Al_3Fe_1) + F(5)(K_{1\cdot5}(H_2O)_{0\cdot5})$$
$$= \overline{120} + 54 + 30 = \overline{36};$$

(b) with Co-$K\alpha$ radiation

$$F(5) = \overline{120} + 51 + 30 = \overline{39}.$$

For compositions intermediate between those given in table I interpolation gives accurate values for F.

APPLICATION TO THE CHLORITE GROUP.

For the calculations on this group the same curves of atomic scattering factor were used as before and corrections for anomalous dispersion of Co-$K\alpha$ radiation by Fe were made. The atomic co-ordinates used were those given by Norrish (1952) which are closely similar to those given by Brindley and Robinson (1951). The plane of the mica layer octahedral cation sheet which is a symmetry plane was taken as the origin of co-ordinates.

The chlorite structure consists of a regular interleaving of mica-type and brucite-type layers. There are therefore two kinds of octahedral sites per unit layer and in both of these Fe may replace (Mg,Al). The calculations in this paper deal only with chlorites where both octahedral layers are trioctahedral. The replacement of (Mg,Al) by Fe is the only isomorphous replacement commonly encountered which would change the intensities of the low-order basal reflections. For a given Fe content the octahedral atoms can be arranged in different ways between the two types of octahedral site so both number and arrangement of Fe atoms affect intensities.

The F values per unit layer for (00l) reflections at 14 Å., 7 Å., 4·7 Å., and 3·5 Å. have been calculated for chlorites whose chemical composition lies in the range

$$[(Mg,Al)_{12}][(Si,Al)_8]O_{20}(OH)_{16}$$

and $\qquad [(Mg,Al)_4Fe_8][(Si,Al)_8]O_{20}(OH)_{16}$
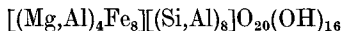
for both symmetrical and asymmetrical arrangements of the octahedral ions.

For chlorite structures the intensities of the basal reflections at 7 Å. and 3·5 Å. are dependent on the Fe content but independent of its

arrangement. Values for $F(7)$ and $F(3.5)$ are given in table II for the range of chemical composition previously indicated at intervals of 1 Fe

TABLE II. F (7 Å.) and F (3.5 Å.) for (00l) reflections of chlorite-type structures for a unit layer.

Octahedral atoms (per unit layer).			F (7 Å.)		F (3.5 Å.)	
			Normal.	Anomalous.	Normal.	Anomalous.
12Mg	...	...	95	95	150	150
11Mg1Fe...	...	...	108	104	161	157
10Mg2Fe...	...	...	120	113	172	165
9Mg3Fe ...	...	...	133	122	184	172
8Mg4Fe ...	...	...	146	130	195	179
7Mg5Fe ...	...	...	159	139	206	186
6Mg6Fe ...	...	...	172	148	217	193
5Mg7Fe ...	...	...	184	157	228	201
4Mg8Fe ...	...	...	197	166	239	208

atom per unit layer. The F's for basal reflections at 14 Å. and 4.7 Å. depend on the difference in scattering power between the occupants of the two types of octahedral sites. Table III gives the values for $F(14)$

TABLE III. F (14 Å.) and F (4.7 Å.) for (00l) reflections of chlorite-type structures for a unit layer.

Content of mica octa-hedral sheet less content of brucite octahedral sheet.			F (14 Å.)		F (4.7 Å.)	
			Normal.	Anomalous.	Normal.	Anomalous.
6Mg–6Fe...	...	...	$\overline{29}$	$\overline{29}$	$\overline{196}$	$\overline{196}$
5Mg–5Fe...	...	...	$\overline{16}$	$\overline{18}$	$\overline{184}$	$\overline{188}$
4Mg–4Fe...	...	...	$\overline{2}$	$\overline{6}$	$\overline{172}$	$\overline{180}$
3Mg–3Fe...	...	...	11	5	$\overline{160}$	$\overline{172}$
2Mg–2Fe...	...	...	24	17	$\overline{148}$	$\overline{164}$
1Mg–1Fe...	...	...	38	28	$\overline{136}$	$\overline{156}$
0Mg–0Fe...	...	...	51	40	$\overline{124}$	$\overline{147}$
1Fe–1Mg...	...	...	65	51	$\overline{112}$	$\overline{139}$
2Fe–2Mg...	...	...	78	63	$\overline{100}$	$\overline{131}$
3Fe–3Mg...	...	...	91	74	$\overline{88}$	$\overline{123}$
4Fe–4Mg...	...	...	105	86	$\overline{76}$	$\overline{115}$
5Fe–5Mg...	...	...	118	97	$\overline{64}$	$\overline{107}$
6Fe–6Mg...	...	...	132	109	$\overline{52}$	$\overline{99}$

and $F(4.7)$ for the possible differences in scattering power between the two types of site, the difference in scattering power being reckoned as mica octahedral contribution less brucite octahedral contribution.

To obtain the F values for a chlorite of a particular composition, the $F(7)$ and $F(3.5)$ values are obtained from table II. There are usually several possible arrangements of the octahedral atoms and so several

possible values for $F(14)$ and $F(4.7)$ can be obtained from table III corresponding to the possible arrangements.

For example, to obtain the F values for a chlorite (for Cu-$K\alpha$) which contains 2 Fe atoms per unit layer, i.e. $[(Mg,Al)_{10}Fe_2][(Al,Si)_8]O_{20}(OH)_{16}$, from table III $F(7) = 120$ and $F(3.5) = 172$. With 2 Fe atoms per unit layer the possible $F(14)$ and $F(4.7)$ are obtained as shown in table IV.

TABLE IV. Possible F (14 Å.) and F (4.7 Å.) values for (00l) reflections of a chlorite structure of composition $(Mg_{10}Fe_2)(SiAl)_8O_{20}(OH)_{16}$ per unit layer.

| Possible arrangements. | | | From table III. | |
Mica.	Brucite.	Difference.	F (14 Å.)	F (4.7 Å.)
6Mg	4Mg,2Fe	2Mg–2Fe	24	$\overline{148}$
5Mg,1Fe	5Mg,1Fe	0Mg–0Fe	51	$\overline{124}$
4Mg,2Fe	6Mg	2Fe–2Mg	78	$\overline{100}$

The converse of the above method can also be applied. From the ratio $F(7)/F(3.5)$ the Fe content of a chlorite can be obtained and from the ratio $F(14)/F(4.7)$ it may be possible to decide how the atoms are arranged.

DISCUSSION.

There are four points which should be brought to notice:

(1) If the intensities of an unknown mica or chlorite after correction for absorption, orientation, &c., do not fit the calculated data, then either its chemical composition lies outside the range for which calculations have been made or the atomic co-ordinates are significantly different from those used here and the reason for the discrepancy should first be sought in them.

(2) F values for micas and chlorites apply to the stated unit volumes and therefore their F's are not directly comparable.

(3) In connexion with quantitative analysis by the standard-mineral method the data in tables II, III, and IV show that appreciable changes in F and hence in intensities occur in both micas and chlorites owing to isomorphous substitution. This effect is illustrated in table V, which gives the relative intensities of Debye-Scherrer reflections with Cu-$K\alpha$

TABLE V. Relative intensities of (00l) reflections for equal volumes of different mica-type minerals.

Mineral.	Structural formula.	Relative intensities of (00l) reflections.		
		10 Å.	5 Å.	3.3 Å.
Muscovite	$K_2(Al_4)(Si,Al)_8O_{20}(OH)_4$	1.0	0.7	1.2
Phlogopite	$K_2(Mg_6)(Si,Al)_8O_{20}(OH)_4$	3.6	0.2	1.7
Illite	$K_1(H_2O)_1(Al_4)(Si,Al)_8O_{20}(OH)_4$	1.9	1.0	1.4

for equal volumes of three minerals of mica structural type (ideal formulae). The results show that large errors can occur in the standard-mineral method unless great care is taken to match the standard mineral and the mineral in the unknown. It is also of interest that the integrated intensity of the 10 Å. reflection from an illite should be greater than that of muscovite if the illite specimen is totally composed of crystalline material.

(4) The calculations suggest a possible alternative to the standard-mineral method of quantitative analysis. For this the preferred orientation factor Ψ, the absorption factor A, and the relative integrated intensities have to be measured for $(00l)$ reflections. This involves extra work but in the standard-mineral method A and Ψ are usually ignored, the assumption being that both factors are the same in the standard and the unknown or that the factors are negligible, and it is further assumed that peak intensities are proportional to integrated intensities in both the standard and the unknown. There is no great difficulty in evaluating all of these. The absorption factor can be calculated from the chemical composition of the unknown mixture, the preferred orientation of the specimen can be measured in several ways (e.g. Brindley, 1953), and the relative integrated intensities can be obtained by detailed photometry of line profiles or more directly using diffractometers.

The problem of finding the percentage of mica (say) in a mixture consists in evaluating equation (1) for V_{mica}. Assuming absorption and preferred orientation factors have already been obtained, the unknown factors in equation (1) applied to mica reflections are P/I_0, F^2, and V_{mica}.

(i) *To obtain the F^2 values for the particular mica in the mixture.*—If the absolute intensities of the $(00l)$ reflections, say $1, 2, 3$, &c., of the mica in the unknown are P_1/I_0, P_2/I_0, P_3/I_0, &c., then their integrated relative intensities on a Debye-Scherrer powder pattern are P_1, P_2, P_3, &c.

From equation (1)

$$\frac{P_1}{P_2} = \frac{F_1^2 \Psi_1 A_1 \Xi_1}{F_2^2 \Psi_2 A_2 \Xi_2}, \qquad (4)$$

where Ξ is the combined cone size and polarization factor for a randomly oriented powder and is equal to

$$\frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta}$$

and Ψ, A, F, and P have the same meaning as in equation (1). From the photograph we obtain the ratios P_1/P_2, P_2/P_3, &c., and Ψ_1, Ψ_2, A_1, A_2,

Ξ_1, Ξ_2 can all be obtained. Hence using equation (4) we obtain the ratio F_1^2/F_2^2 and similarly F_2^2/F_3^2, &c. Consideration of the (060) spacing of the mica along with the best fit of observed and calculated values of the ratios F_1^2/F_2^2, &c., gives the F^2 values of the particular mica in the mixture.

(ii) To obtain P/I_0.—P/I_0 is the absolute intensity of a reflection. With photographic methods, to evaluate P/I_0 a known volume of an internal standard,[1] e.g. sodium chloride whose absolute intensities are known, is mixed with the unknown powder. Comparison of the integrated relative intensities of the sodium chloride reflections with their known absolute intensities gives the factor to apply to the integrated relative intensities of the mica reflections to put them on an absolute scale. With spectrometers absolute intensities can be determined directly without using an internal standard by monitoring both incident and reflected beams.

Having obtained two of the three unknowns in equation (1) substitution gives V_{mica}, and the proportion of mica in the mixture can then be obtained.

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[1] Care must be taken that both the unknown and the internal standard satisfy the conditions specified by Brindley (1945) for a fine powder.