SEMI-QUANTITATIVE ANALYSIS OF CHLORITES BY X-RAY DIFFRACTION

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ABSTRACT

The determination of the chemical composition of chlorites, using the ratio of structure factors for the 002 and 004 reflections, is unreliable because of the small change in the ratio with composition. By using the rapidly changing ratio F_{003}/F_{001}, a factor may be computed which relates theoretical structure factors to the structure factors calculated from a diffractogram. By determining the theoretical value of F_{002}, the composition of the chlorite is determined. Sample thickness, detector error, time constant, and sample size must all be controlled for the successful application of this technique. In particular, the relationship between sample size and divergence slit size has a most important effect on x-ray intensities. The method is accurate to within 13 per cent of the composition of the chlorite octahedral sheets.

INTRODUCTION

Determination of the chemical composition of chlorites by x-ray diffraction is the subject of several papers (Brown, 1955; Brindley and Gillery, 1956; Petruck, 1959). The method is to calculate a structure factor from the intensity of each peak on a diffractogram. The ratio of F_{004} and F_{002} [structure factor for the (004) peak and structure factor for the (002) peak] can then be compared with the computed ratio for theoretical chlorite compositions. If the F_{004}/F_{002} ratios are the same, then the chlorite has the same composition as the theoretical chlorite. Table 1 is a list of structure factors for chlorites computed by Brown (1955, p. 662). It lists structure factors for the first four basal reflections from chlorites of various compositions in the isomorphic series $(MgFe)_{12}(SiAl)_8O_{20}(OH)_{16}$.

THEORY

The intensity of an x-ray peak is related to the structure factor of this peak by the equation:

$$I = K(j) \frac{1}{V^2} (A\theta) \left| F \right|^2 \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \tag{1}$$

where I = the integrated intensity of the diffraction line, K = a constant which depends upon certain physical constants and the geometry of the difffractometer (Cullity, 1956, p. 389), j = the multiplicity factor, V = volume of the unit cell, $A\theta$ = the absorption factor, F = the structure factor, θ = the Bragg diffraction angle.

The absorption factor ($A\theta$) depends only on the linear absorption coefficient of the sample if a diffractometer is used. The structure factor F

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TABLE 1. STRUCTURE FACTORS FOR F_{002} (7 Å) AND F_{004} (3.5 Å) OF CHLORITE
MINERALS FOR CuKα RADIATION[1]

Octahedral atoms per unit layer		F_{002}	F_{004}
12 Mg	0 Fe	95	150
11 Mg	1 Fe	108	161
10 Mg	2 Fe	120	172
9 Mg	3 Fe	133	184
8 Mg	4 Fe	146	195
7 Mg	5 Fe	159	206
6 Mg	6 Fe	172	217
5 Mg	7 Fe	184	228
4 Mg	8 Fe	197	239

Structure factors for F_{001} (14 Å) and F_{003} (4.17 Å) of chlorite minerals for CuKα
radiation, together with the ratio F_{0c3}/F_{001} for various asymmetric cation
distributions

Excess Fe in the talc layer per 12 octahedral positions	F_{001}	F_{003}	F_{003}/F_{001}
+3 atoms	91	− 88	0.97
+2 atoms	78	−100	1.28
+1 atom	65	−112	1.72
0	51	−124	2.43
−1 atom	38	−136	3.58
−2 atoms	24	−148	6.17
−3 atoms	11	−160	14.5

[1] Adapted from Brown (1955).

should include a correction for temperature at large values of θ. An empirical temperature correction is included in the structure factors listed in Table 1. The Lorentz and polarization factors are combined in the

$$\left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}\right)$$

term which is appropriate for random powder samples. The analogous form for diffraction from a single crystal is

$$\left(\frac{1 + \cos^2 2\theta}{\sin 2\theta}\right).$$

A detailed discussion of each of the terms in equation (1) is found in (Cullity, 1956 and Klug and Alexander, 1954).

A structure factor expresses the amplitude of diffracted x-radiation to be expected from a crystal because of the scattering of x-ray waves by atoms lying in different positions in the unit cell. The atomic scattering

factors of silicon, aluminum and magnesium are about the same. Therefore, structure factors (and intensities) are unaffected by substitution of aluminum for silicon in the tetrahedral sheets of chlorite or aluminum for magnesium in octahedral sheets. Atomic scattering factors for iron, manganese, chromium and titanium are similar, and x-ray intensities are unaffected by their mutual substitution in the octahedral sheets. The atomic scattering factors for the iron-manganese-chromium-titanium group are about twice as large as those for the silicon-aluminum-magnesium group, and x-ray intensities will distinguish one group from the other. Therefore, the chemical composition of chlorites determined from x-ray intensities is $Fe+Mn+Cr+Ti:Mg+Al$. The $Si:Al$ ratio in the tetrahedral sheets may be determined by the precise measurement of the basal spacing of the chlorite cell (Brindley and Gillery, 1956). A general formula for chlorite can then be written: $(MgAl)_{12-x}(FeMnCrTi)_x$ $(Si_{8-y}Al_y)O_{20}(OH)_{16}$ where the variables x and y may be obtained by rapid x-ray methods.

In a consideration of only the $(00l)$ reflections from a chlorite, the constant K, multiplicity factor (j), absorption coefficient ($A\theta$), and volume of the unit cell V may be ignored as they are constant. Equation (1) then becomes:

$$I = |F|^2(L.P.). \qquad (2)$$

Using the diffractometer technique, the intensity (I) of a peak may be measured in counts per second. The combined Lorentz-polarization factor (L.P.) can be computed for the diffraction angle at which the peak occurs. Thus, the value of $|F|$ may be determined for every peak provided certain experimental conditions are met. A ratio of $|F|$ values may then be used to determine the composition of the chlorite.

TEST OF ORIGINAL METHOD

In order to test the practicality of using structure factors for semi-quantitative chemical analyses, several chlorites whose compositions were known from wet chemical analyses were x-rayed. The compositions were computed from the F_{004}/F_{002} ratio by the method proposed by Brown (1955), Brindley and Gillery (1956) and Petruck (1959). Results for a few samples were close to the wet analyses. But for most samples the computed composition differed greatly from the wet analysis, and some computed compositions exceeded the possible contents of the chlorite unit cell. Therefore, the method was rejected as unreliable under the experimental conditions used.

Examination of Table 1 readily indicates the reason for these unreliable results. Although the theoretical values of the (002) and (004) struc-

ture factors increase rapidly with increasing iron, their ratio varies only from 1.58 to 1.21. The precision of the x-ray diffraction techniques used are too low, at present, to accurately subdivide such a small range.

The large change in the theoretical value of F_{002} or F_{004} with composition would be adequate for determining the composition of a chlorite if the absolute value could be calculated from the x-ray diffractogram. Unfortunately, the value calculated for a structure factor from intensity measurements bears no obvious relation to the theoretical values in Table 1. If it did, one would only have to compare the structure factor with Table 1 to get the composition of the chlorite. It is only by comparing a ratio of two calculated factors with a ratio of two theoretical factors that the chlorite composition may be determined.

The Proposed Method

The theoretical values of F_{001} and F_{003} change in opposite directions and therefore their ratio changes rapidly. But Table 1 shows that this does not depend upon total composition but only on the distribution of cations among the two different octahedral sheets in chlorites. By comparing the ratio F_{003}/F_{001} calculated from a diffractogram, with the ratio F_{003}/F_{001} for theoretical structure factors, the exact asymmetry of the chlorite may be determined by interpolation. This asymmetry can exist only for specific theoretical values of F_{001} and F_{003}. These theoretical values of F_{001} and F_{003} can be read from Table 1, interpolating if necessary. When F_{001} (theoretical) and F_{003} (theoretical) are known for the chlorite sample, a factor relating calculated F's to theoretical F's can be calculated:

$$\frac{F_{001}(\text{theoretical})}{F_{001}(\text{calculated})} = \qquad (3)$$

$$\frac{F_{003}(\text{theoretical})}{F_{003}(\text{calculated})} = \qquad (4)$$

Equations (3) and (4) should yield approximately the same numerical factor. Multiplication of F_{002} calculated from the diffractogram by the average of equations (3) and (4) yields the theoretical F_{002} for the chlorite sample. Comparison of the theoretical F_{002} with Table 1, with interpolation if necessary, gives the composition of the chlorite.

An example may clarify the calculations. Using the intensities scaled from a diffractogram and equation (2), F_{001} is calculated to be 0.430 and F_{003} is calculated to be 0.740. The ratio F_{003}/F_{001} is 1.72, and comparison with Table 1 shows that this corresponds exactly to an asymmetry of one excess iron atom in the talc layer of the chlorite. If the F_{003}/F_{001} ratio had not corresponded to a whole number of atoms asymmetry, interpolation in Table 1 would give the exact asymmetry. Table 1 shows that the

theoretical structure factors for the chlorite studied are $F_{001} = 65$ and $F_{003} = -112$. F_{001} (theoretical) divided by F_{001} (calculated) (65/0.430) equals 151. For the 003 reflection, equation (4) gives a factor of -152. Signs may be ignored as it is the absolute value of the structure factor that is given by equations (1) and (2). We have determined that the theoretical structure factors for this particular chlorite are 151.5 times as large as the structure factors that we calculate from the diffractogram. F_{002} calculated from the diffractogram is 0.920. Multiplying this by 151.5 the result is 139.5 for the value of F_{002} theoretical. Comparison with Table 1 shows that an F_{002} of 139.5 corresponds to a chlorite composition of between three and four iron atoms per 12 octahedral positions. Interpolation indicates that the composition of the chlorite is exactly 3.5 Fe/12.

The x-ray determination of the octahedral sheet composition of seven wet analyzed chlorites and per cent error is tabulated in Table 2.

EXPERIMENTAL CONDITIONS

Sample preparation

Certain conditions are necessary for the successful application of this x-ray technique. Any method of sample preparation is sufficient which results in detection of the (001), (002) and (003) diffraction peaks. Sedimentation of the finely ground sample on a glass slide, using a polar liquid such as water or alcohol, results in enhancement of the basal reflections and suppression of all others.

In order to achieve maximum diffracted intensity, the thickness of the sample must exceed a certain minimum (Alexander and Klug, 1948) according to the equation:

$$t \geqq \frac{3.2}{\mu} \frac{\rho}{\rho'} \sin \theta \qquad (5)$$

where μ is the linear absorption coefficient of the solid sample material per centimeter, ρ is the density of the solid sample material, and ρ' is the density of the sample powder including interstices.

Using CuK α radiation, a minimum thickness of 0.09 mm satisfies equation (5) for a pure magnesium chlorite up to a 2θ angle of 18.8° (003). The substitution of one iron atom for magnesium decreases the minimum thickness to 0.046 mm, and a pure iron chlorite requires a thickness of only 0.016 mm.

Intensity measurements

Intensity may be measured on diffractograms as counts per second of the top of the peak above background level. Peak height measurements

TABLE 2

Chlorite	Fe+Mn+Cr+Ti per 12 octahedral cations		% error of 12 positions
	Wet analysis	Proposed x-ray method	
F-149	8.22	8.84	5.17
F-147	7.72	6.24	12.3
A-20	6.04	6.16	1.0
A-45	4.24	3.62	5.17
A-35	3.64	2.08	13.0
A-41	1.42	2.00	4.84
A-25	0.68	0.76	0.67

Sources of Chlorites

F-149: Daphnite, (Lake View Lodge, Perseverance Gold Mine), Kalgoorlie, Western Australia. Analyst: Le Mesurier.

F-147: Daphnite, (Santa Claus Gold Mine), Randalls, Central Division, Western Australia. Analyst: Simpson.

A-20: Ripidolite, one-half mile north of Bull Hill, Castledon area, Vermont. Analyst: P. J. Byler.

A-45: Ripidolite, (Budo Mine?) Shiono-machi, Niigata pref., Japan. Source: Sudo; Analyst: unknown.

A-35: (Hitachi Mine), Ibaragi pref., Japan. Analyst: H. Sato.

A-41: Roxbury, Conn. Analyst: J. Ito.

A-25: Clinochlore, West Town, Chester Co., Pa. Analyst: J. Ito.

are directly proportional to the integrated intensity (I), referred to in equations (1) and (2), if the width of the measured peaks is the same. This condition is satisfied for diffraction from (00l) planes of the same mineral.

Detector error

Geiger-Muller tubes become inefficient detectors of x-ray photons at high rates of arrival, and a correction for the so-called "dead time" is necessary for all peaks greater than about 100 c.p.s. The correction takes the form:

$$N_t = \frac{N_o}{1 - N_o K \tau} \qquad (6)$$

where N_t = the true peak height in counts per second, N_o = the observed peak height in counts per second, K = a constant having the value 1.7 or 3.4 for full-wave or half-wave rectification, respectively, of the x-ray source, τ = the resolving time of the Geiger tube which is generally about 1.5×10^{-4} seconds (Klug and Alexander, 1954). A graph of N_o versus N_t may be plotted in order to speed up calculations.

Time constant

The pulse-averaging circuit (as represented by the time constant control) and the scanning speed of the goniometer affect peak intensity. A large time constant tends to smooth out the random fluctuations in energy received by averaging over a period of time. But this time lag also reduces the peak height from its true value. High scanning speeds increase this peak reduction error. A practical solution is to keep the product of the scanning speed (deg/min) multiplied by the time constant (sec) at one or two, at which values the peak distortion is small (Parrish, 1960).

Sample size

An important consideration in diffractometer technique is the effect of the divergence slit size and the sample size on the intensity of peaks. The divergence slit controls the area of the sample that is irradiated by x-rays. The narrower the slit the smaller the area of sample irradiated and the lower the intensity of all peaks. As long as all of the energy in the x-ray beam falls on the sample, the intensity of one diffraction peak may be compared with another. But at low angles of θ part of the x-ray beam will pass above and below the sample, thus irradiating the sample with less energy and reducing peak heights from their true value. This problem may be solved by choosing a narrower divergence slit. But this will decrease the intensity of all peaks by reducing the amount of energy reaching the sample. Alternatively, the sample length can be increased so that it will completely intercept the x-ray beam at a particular angle θ. The relationship is:

$$L = \frac{\gamma}{57.3} \frac{R}{\sin \theta} \tag{7}$$

where L = the length of the sample surface in centimeters, γ = the angular aperture of the divergence slit in degrees, R = the goniometer radius in centimeters, θ = the angle between the x-ray beam and the sample.

The chlorite samples used in this study were sedimented to completely cover a standard glass slide of 4.6 cm length. Solution of equation (7) indicates a minimum 2θ angle of 7.4° for a one degree divergence slit and a goniometer radius of 17.0 centimeters. For CuK α radiation, the 14 Å (001) chlorite peak at $2\theta = 6.3°$ requires a sample length of 5.4 centimeters. Assuming that the energy is uniformly distributed throughout the x-ray beam, chlorite (001) peak heights have been increased by 15 per cent

$$\left(\frac{4.6 \text{ cm.}}{5.4 \text{ cm.}} = 0.85 \right)$$

to make them comparable to peaks received at angles greater than 7.4°.

Lorentz factor

The proper Lorentz factor to use in equations (1) and (2) is determined by whether the sample is a single crystal or a random powder. In the usual case of an oriented aggregate of mineral grains, the proper factor to use is not immediately obvious.

Fortunately, the composition of chlorites as determined by the proposed method varies only slightly when the two different Lorentz factors are used. However, the asymmetry of cation distribution does show a pronounced change. Use of the Lorentz random powder factor tends to report a symmetric cation distribution for the seven chlorites in Table 2. These chlorites are all of high temperature origin, and it is assumed that their structures would approach symmetric cation distribution in the high thermal energy environment. For this reason, the Lorentz random powder factor is probably closer to the true correction factor for oriented aggregates.

ADVANTAGES OF THE METHOD

1. The method is rapid for a scan of only 14 degrees 2θ is required.
2. As little as 15 milligrams of sample on half a glass slide, will give accurate results.
3. Compositional results (though not sensitivity of detection) are independent of orientation.
4. The method can be used on any mixture which does not contain other minerals yielding peaks corresponding to 14, 7, or 4.7 Å.
5. If the composition of a chlorite is known, then the presence of a septechlorite may be inferred.
6. The composition determined as Fe-equivalent versus Mg-equivalent is a parameter of significance in studies of ore deposition, metamorphism, and diagenesis.
7. The method can be extended to other mineral groups. The chief requirement is that ratios of F's be taken from reflections which change in opposite direction with change in composition.

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