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ESTIMATION OF HEAVY ATOM CONTENT AND DISTRIBUTION IN CHLORITE USING CORRECTED X-RAY POWDER DIFFRACTION INTENSITIES

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Abstract—The heavy atom content and distribution in chlorite were estimated using the relative intensities of basal X-ray powder diffraction (XRD) peaks. For these peaks to be meaningful, however, corrections had to be made for the effects of sample thickness, sample length, and preferred orientation of the mineral grains, all of which are 2θ dependent. The effects of sample thickness were corrected for by a simple formula. The effects of sample length were accounted for by using rectangular samples and by ensuring that the sample intersected the X-ray beam through the range of diffraction angles of interest. Preferred orientation of mineral grains were either measured directly or estimated. Estimated values were quicker and easier to obtain and were within 5% of measured values. A comparison of the compositional parameters of chlorite estimated before correcting for these sample effects with those estimated after the corrections had been applied indicate that the uncorrected values differed from the corrected values by as much as 55% of the latter values. Mounts of a single sample prepared by different filter-membrane peel and porous-plate techniques yielded widely different compositions until the measurements were corrected for sample effects. Analyses in triplicate indicated that the XRD intensity ratio 003/001 is preferred for calculating heavy atom distributions and abundances in chlorite because of the relative strength of the 001 peak.

Key Words—Chlorite, Heavy atoms, Intensity measurements, Sample preparation, X-ray powder diffraction.

INTRODUCTION

Several X-ray powder diffraction (XRD) techniques are available to estimate the total octahedral heavy element (Fe, Cr, and Mn) content of chlorite and the distribution of heavy elements between the two octahedral sheets of the mineral (cf. Brown and Brindley, 1984, 342–346). These techniques involve comparing the intensities of the basal series of XRD peaks of chlorite measured in a random powder mount. For oriented clay mounts analyzed with a flat-specimen diffractometer, the preferred orientation of crystallites in the sample will significantly affect measured intensity, as will other sample parameters, such as length and effective thickness.

The effects of these three sample parameters (length, thickness, and preferred orientation) are 2θ dependent, and if their respective contributions to diffraction intensity are not taken into account, a comparison of the intensity of peaks separated by more than a few degrees 2θ may produce spurious results. Correction for sample thickness involves measuring the average mass absorption coefficient of the sample and the weight of clay per unit area and calculating the resultant intensity loss at high diffraction angles. Details of this procedure are outlined in Johnsson and Reynolds (1986).

Intensity variations due to sample length may be avoided by using an incident-beam slit assembly having an angular divergence small enough to ensure that the entire X-ray beam intersects the sample length at low diffraction angles. Circular samples prepared by the filter-membrane peel method (Drever, 1973) may have large intensity losses at low diffraction angles, even if the beam divergence is nominally small enough to intersect the entire sample length. This intensity loss is quantifiable, and may be corrected for either by a modification of the filter-membrane peel apparatus or by a calculation.

The effect of preferred orientation on measured intensity is also quantifiable, and if a sample is well-oriented, the degree of preferred orientation can be measured directly (Reynolds, 1986). If a sample is not well oriented, the degree of preferred orientation can be estimated based on the assumption that the intensities of certain diffraction peaks are proportional to $1/(\sigma^*)^2$, where σ^* is the standard deviation of a Gaussian crystallite orientation distribution.

This paper discusses methods for correcting for sample parameters, such as length and preferred orientation, in chlorite-rich samples, and presents results that illustrate the dangers of calculating octahedral heavy element concentrations from XRD intensity measurements that have not been corrected.

SAMPLE LENGTH CORRECTION

The loss of diffracted beam intensity at low 2θ angles due to insufficient sample length is a crucial factor to

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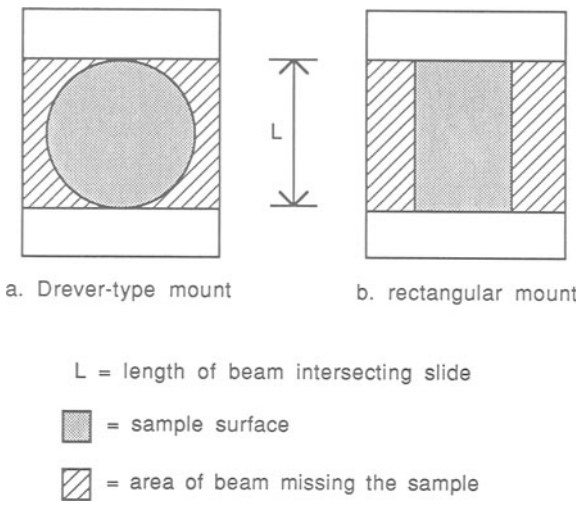


Figure 1. Difference in geometry between circular and rectangular sample mounts: (a) circular mount (Drever, 1973); (b) rectangular mount (Pollastro, 1982, and this study).

be considered before intensity comparisons can be made. Although the loss of intensity can be calculated and a correction factor applied, the correction algorithm for a circular sample of nonuniform length [the normal Drever-type mount (Drever, 1973)] is more complex and difficult to apply than that for a rectangular sample of uniform length. The difference is demonstrated diagrammatically in Figure 1. A modification of Drever's (1973) filter-membrane peel technique was used to prepare mounts of several samples in this study. The modification, based in part on the recommendations of Pollastro (1982) and K. Tellier (Dept. of Earth Sciences, Dartmouth College, Hanover, New Hampshire, personal communication, 1987) is the same basic technique described by Drever (1973), but involves the use of a rectangular column as a sample reservoir rather than a cylinder. The resultant clay film is in the shape of a rectangle of uniform length. The sample length correction based on the geometry of the clay film can be calculated by trigonometry and easily applied or avoided completely if the angular divergence of the X-ray beam is constrained to be small enough so that the entire beam contacts the sample in the 2θ range of interest.

ESTIMATION OF PREFERRED ORIENTATION

To compare directly the intensity of peaks occurring over a range of diffraction angles in a non-random sample, corrections must be made for the effects of preferred orientation. The procedure outlined below calculates the Lorentz-polarization factor (LP) for a sample of known preferred orientation, removes the influence of LP from the measured intensity of each diffraction peak, and substitutes a random powder LP, thereby producing a set of basal peak intensities corrected to approximate a random powder.

The calculation of LP for a peak at a given diffraction angle requires that σ^* for that sample be known. The value of σ^* is estimated here using the approximation of Reynolds (1986) that the intensity of diffraction peaks at moderate diffraction angles ($\sim 25°2\theta$) is proportional to $1/(\sigma^*)^2$. The intensity of the illite 003 peak at $26.6°2\theta$ (CuKα) was chosen by Reynolds as a standard in the relationship

$$\sigma^* = \sqrt{\frac{K * Q.R.I.}{I(003)}\left(\frac{45}{\mu^*}\right)},$$

in which K is an empirical constant equal to 30.1, I(003) is the integrated intensity of the illite 003 peak, 45 is the mass absorption coefficient of a monomineralic illite sample, and μ^* is the average mass absorption coefficient of the sample. Q.R.I. is the quartz reference intensity measured with the same instrumental parameters as the measurement of the sample. It consists of the peak height in counts/s of the quartz peak at $26.65°2\theta$.

If a sample is not monomineralic illite, the denominator of this relationship must be modified to include the intensity of a peak for each constituent phase, corrected for the abundance of that phase in the sample. For clays, such as kaolinite and smectite, the measured intensity can be divided by a factor which relates the intensity of the selected peak of each mineral to the intensity of the illite 003 peak (Reynolds, 1980). The correction is not as straightforward for a mineral such as chlorite, however, because variations in octahedral heavy atom content will cause the intensity of the 004 peak (which is in the proper 2θ range) to change independent of its abundance in the sample. The intensities of the 001 and 003 chlorite peaks, however, can be used to make the appropriate correction by the procedure outlined below.

The intensity of the even-order chlorite peaks are controlled by the total number of octahedral heavy atoms in the mineral. The intensity of the odd-order peaks are controlled by the distribution of octahedral heavy atoms in the mineral. The sum of the structure factors of the 001 and 003 peaks, however, is nearly a constant over the range of octahedral heavy atom distribution values commonly encountered in chlorites. The reason for this is demonstrated in the calculation of the structure factor. The structure factor is the amplitude of scattering from a crystal in the diffracting condition and is expressed as:

$$|F(00l)| = \sum_j n_j f_j \cos[2\pi l z_j / d(001)],$$

where j = the type of atom, n_j = the number of j-type atoms in the layer, f_j = the scattering power of j-type atoms at the diffraction angle, and the cosine term is

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Table 1. Heavy atom content of chlorites estimated from corrected diffraction intensities.

Sample	Sample type[1]	Measured σ^*	Estimated σ^*	D[2]	FDI[3]	Total heavy atoms
V-507	plate	8.8	8.75	0.01	0.503	1.81
	filter	10.6	10.8	0.10	0.527	1.75
38G-1	plate	20.7	21.0	0.60	0.689	1.59
B-1	filter	22.3	21.1	0.23	1.00	0.23

σ^* = standard deviation of a Gaussian crystallite orientation distribution.
[1] plate = porous plate (Kinter and Diamond, 1956); filter = 47-mm filter-membrane peel (Drever, 1973).
[2] D = number of heavy atoms in silicate layer minus the number of heavy atoms in the hydroxide layer (Petruk, 1964).
[3] FDI = number of heavy atoms in the silicate layer divided by the total number of octahedral heavy atoms (Walker, 1987).

the expression of the phase angle of the scattered radiation in which l = the order of the reflection and z_j = the distance of the atom from the origin of the calculation measured along the normal to the (001) plane. The calculation is one-dimensional because only the 00l reflections are of interest. One of the octahedral layers is customarily taken as the origin of a structure factor calculation for the chlorite basal diffraction series. The selection makes the unit cell centro-symmetric if it is projected onto the z-axis and thereby simplifies the calculation.

The relative intensity of the odd-order peaks is controlled by the sign of the cosine terms in the structure factor equation; that is, if the term representing the octahedral layer at the origin of the calculation is positive (cos = 1), the term representing the octahedral layer at the end of the calculation is negative (cos = −1). As the distribution of octahedral heavy atoms changes, the two octahedral terms will change equally and in opposite directions. Because the absolute scattering power of a layer is determined by the number of electrons in that layer, electrons subtracted from one octahedral layer are, in essence, added to the other octahedral layer. The sum of the scattering powers of the two layers, therefore, will remain a constant, except for small differences due to changes in the scattering power of an atom with diffraction angle. The use of a composite peak, therefore, provides an intensity reference that is independent of the iron content or of the distribution of iron between the silicate and hydroxide layers.

To calculate the intensity of a 001-003 composite chlorite peak, the individual intensities of the 001 and 003 peaks must be divided by a calculated LP (assuming $\sigma^* = 12$) to yield the structure amplitude or $|F_{00l}|^2$ (because intensity $\propto |F_{00l}|^2 LP$). The square roots of these structure amplitudes must be added and the sum squared, resulting in $|F_{00l}|^2$ for a composite (001 + 003) peak.

To be used in the calculation of σ^*, $|F_{00l}|^2$ must be multiplied by a mineral intensity factor (MIF) relating the intrinsic intensity of the chlorite composite peak to the intensity of the illite 003 peak. The MIF is determined by calculating the structure amplitudes of both the chlorite composite peak and the illite 003 peak, assuming that σ^* is equal to a constant (here, $\sigma^* = 12$). $|F_{00l}|^2$ for the chlorite composite peak is divided by the illite $|F_{003}|^2$ to yield an MIF = 2.8 for chlorite. If $|F_{00l}|^2$ for the chlorite composite peak in a sample with a different σ^* is divided by this MIF, the intensity of the composite peak can be directly compared to the intensity of the illite 003 reflection from the sample. The value, therefore, is a measure of the abundance of chlorite relative to illite in the sample. The theory can be extended to include the effects of other minerals present in the sample (Reynolds, 1986).

These calculations are easily performed on a microcomputer, and by assuming an initial value for σ^* (usually 12), σ^* for any sample can be quickly determined iteratively, and the proper LP for each peak can be calculated. Diffraction intensities corrected in this way approximate random powder values, and intensity ratios calculated from them can be compared directly to tabulated values, such as those given in Brown and Brindley (1984).

PRACTICAL APPLICATION

Three chlorite-rich samples were analyzed to test the application of the corrections described above: sample V-507 was separated from a shale collected in western New York State; sample 38G-1 formed during the hydrothermal alteration of andesitic host rock in the Fresnillo mining district in Mexico; and sample B-1 was separated from a limestone in the Bertie Formation of eastern New York State. The degree of preferred orientation (σ^*) was measured directly using the procedure of Reynolds (1986) and calculated by the method outlined above. The results are compared in Table 1, and it can be seen that estimates of the degree of preferred orientation do indeed closely approximate measured values.

Estimation of the distribution of octahedral heavy atoms in chlorite using peak intensity ratios was proposed by Petruk (1964), who introduced the concept of "symmetry" of octahedral heavy atom substitution, symbolized by D (equal to the number of octahedral heavy atoms in the silicate layer minus the number in the hydroxide layer). In a study of Fe-rich chlorite (2.00–5.5 Fe atoms per 6 octahedral sites) from several slate terranes, Walker (1987) suggested that the param-

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Table 2. Uncorrected and corrected compositional data for selected chlorites.

Parameter measured	Sample[1]	I_u[2]	$I_{c(\sigma^*)}$[3]	I_c[4]	Difference	Proportion of corrected value (%)
FDI	V-507 (p)	0.778	0.503		0.275	55
	V-507 (f)	0.481	0.527	0.524	0.043	8
	38G-1 (p)	0.570	0.689		0.156	21
	38G-1 (f)	0.726		0.625	0.101	16
	B-1 (f)	1.00	1.00		0.00	0
Total heavy atoms	V-507 (p)	2.70	1.81		0.89	49
	V-507 (f)	1.98	1.75	2.10	0.12	6
	38G-1 (p)	1.90	1.57		0.6	21
	38G-1 (f)	1.44		1.30	0.14	11
	B-1 (f)	0.33	0.23		0.10	43

[1] (p) = porous plate sample; (f) = filter peel sample (see footnote to Table 1).
[2] I_u = uncorrected diffraction intensity.
[3] $I_{c(\sigma^*)}$ = intensity corrected for effects of preferred orientation.
[4] I_c = intensity corrected for effects of sample length, thickness, and preferred orientation.

eter FDI (Fe distribution index), which is the ratio of the number of octahedral heavy atoms in the silicate layer to the total number of octahedral heavy atoms in the mineral, was more useful as a petrogenetic indicator than D because it does not depend as strongly on the total octahedral heavy atom content of the mineral.

Table 1 lists compositional information calculated for four samples prepared from the three different chlorites. Sample V-507 was prepared by both the filter-membrane peel technique (Drever, 1973) and the porous-plate technique (Kinter and Diamond, 1956) to check the reproducibility of the chlorite composition estimates after correction for preferred orientation. The dependence of the parameter D on the total octahedral heavy atom content can be appreciated by comparing D for samples V-507 and B-1. Both are less than 0.25, yet the physical significance of the value is different, a difference which is reflected in the parameter FDI. In sample V-507, the octahedral heavy atoms are nearly equally distributed (FDI = ~0.5), whereas in sample B-1, all the octahedral heavy atoms occur in the silicate layer (FDI = 1.0).

The importance of correcting XRD analyses for the effects of sample length, thickness, and preferred orientation is demonstrated in Table 2, in which FDI and total octahedral heavy atoms are calculated from uncorrected diffraction intensities (second column) and from intensities corrected for thickness and preferred orientation (third column), and for sample length along with thickness and orientation (fourth column). The fifth column shows the magnitude of the difference between the uncorrected values and those corrected for length, thickness, and orientation, and the sixth column gives the percentage of the corrected value represented by that difference. Differences between corrected and uncorrected values range from 0 to 55% of the corrected value, and do not vary systematically. The lack of systematic variation reflects the complex interaction between length, thickness, and preferred orientation, each of which most strongly affects diffraction intensities within a different angular range.

Brown and Brindley (1984) gave two different tables for determining the distribution of octahedral heavy atoms and the total octahedral heavy atom content, one utilizing the 005 peak and one utilizing the 001 peak. They suggested that by using both methods, a more accurate representation of the octahedral heavy atom distribution in a chlorite may be achieved. The differences between the two methods can be evaluated by performing analyses on one sample prepared three times by identical techniques. Table 3 presents the results of an analysis of a sample (FRL-15) performed in this fashion.

Differences between those values in Table 3 calculated for FDI and total octahedral heavy atoms using the 001 peak and those calculated using the 005 peak are large. Values calculated with the ratio that uses the 005 peak of chlorite (indicated by a 5 in parentheses) are more variable than those calculated using the 001 peak (indicated by a 1 in parentheses). This variability is probably due to the intrinsic weakness of the 005 peak and attendant difficulties in measuring its intensity with accuracy. Octahedral heavy atom parameters calculated from the 003/001 intensity ratio are assumed, therefore, to be closer to the actual value than those calculated using the 005 peak, because the 001 peak is stronger than the 005 peak and has no interferences in this sample. Calculation of octahedral heavy atom distributions and abundances by this method is the only way short of a structure refinement to determine these values for chlorite; hence, an independent check of these results was not possible.

A computer program (MIF*) was developed to calculate the distribution and total numbers of octahedral heavy atoms in chlorite according to the above principles. The program corrected integrated areas of diffraction peaks for the effects of sample thickness and preferred orientation and calculated intensity ratios which were compared to the tabulated values of Brown

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Table 3. Comparison of results of using two different intensity ratios to calculate compositional parameters.[1]

Parameter	Replicate		Corrected data
FDI (5)[2]	a		0.689
	b		0.639
	c		0.686
		average (S.D.)	0.671 (0.28)
FDI (1)[3]	a		0.634
	b		0.636
	c		0.664
		average (S.D.)	0.64 (0.16)
Total heavy atoms (5)[2]	a		2.80
	b		3.09
	c		3.00
		average (S.D.)	3.00 (0.15)
Total heavy atoms (1)[3]	a		3.00
	b		3.05
	c		3.03
		average (S.D.)	3.03 (0.02)

[1] Sample FRL-15. Slate from the Seboomook Formation, Aroostook County, Maine (Walker, 1987).

[2] (5) = parameter calculated using the 003/005 peak intensity ratio.

[3] (1) = parameter calculated using the 003/001 peak intensity ratio.

and Brindley (1984) to determine the distribution and total number of octahedral heavy atoms. The program also tested the reported 2θ values of the basal series peaks for rationality, and corrected for sample displacement errors which affect the peak positions. The program was written in True BASIC and was designed to run on the Apple Macintosh computer. Copies of the program are available from the first author.

SUMMARY AND CONCLUSIONS

This study has demonstrated that:

1. Sample length errors can be eliminated by using rectangular samples whose length ensures that the sample intersects the entire X-ray beam length through the range of diffraction angles of interest.

2. σ^* can be estimated and used to correct intensity data gathered from oriented mounts to approximate random powder intensity data.

3. The intensity of the chlorite 001 peak can only be used if σ^* is measured or estimated, and if corrections are made to account for the steep rise in the Lorentz polarization factor at low diffraction angles.

4. If sample parameters such as length, thickness, and preferred orientation are not considered, results can be widely divergent.

5. Analyses in triplicate indicate that the ratio 003/001 is preferred for calculating octahedral heavy atom distributions and abundances because of the relative strength of the 001 peak and the lack of interfering peaks.

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