Clays and Clay Minerals, Vol. 40, No. 3, 262–267, 1992.

RANDOMLY INTERSTRATIFIED SERPENTINE/CHLORITE: ITS DETECTION AND QUANTIFICATION BY POWDER X-RAY DIFFRACTION METHODS

R. C. REYNOLDS, JR.,[1] M. P. DISTEFANO,[2] AND R. W. LAHANN[2]

[1] Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755

[2] Exploration Research Division, Conoco Inc., P.O. Box 1267
Ponca City, Oklahoma 74603

Abstract—X-ray diffraction studies of the pore-lining chloritic mineral from the Tuscaloosa Formation disclose a marked pattern of odd-order line broadening for the 001 to the 00,16 reflections. The odd-order peaks are approximately twice as broad as the even orders after correction for instrumental broadening effects. These results are consistent with a randomly interstratified 7-Å/14-Å structure, which is most likely serpentine/chlorite. Quantitative analysis of line broadening and model calculations indicate that the serpentine/chlorite contains 7% serpentine layers.

A simplified method is proposed for quantifying randomly interstratified serpentine/chlorite. Residual line broadening (β_r) is obtained from the half-height widths of uncorrected diffraction profiles for the 004 and 005 "chlorite" reflections by means of the following:

$$\beta_r = (\beta_{005}^{1.25} - \beta_{004}^{1.25})^{\frac{1}{1.25}}.$$

Percent serpentine in the random interstratification is computed from the empirical expression

$$\%S = -0.51 + 24.27\beta_r,$$

which is valid from about 1 to 20 percent serpentine.

Key Words—Interstratification, Mixed-layered, Serpentine/chlorite, Tuscaloosa, X-ray diffraction line broadening.

INTRODUCTION

A powder X-ray diffraction study of pore-lining chlorites in sandstones disclosed that the chloritic mineral from the Tuscaloosa Formation (Louisiana) has a rational basal diffraction pattern with odd-order reflections approximately twice as broad as even orders. This X-ray diffraction phenomenon is caused, in our opinion, by diffraction from a randomly interstratified structure that contains small amounts of a layer type whose $d(001)$ is very close to one-half (7.1 Å) of the nominal chlorite value (14.2 Å). The Tuscaloosa "chlorite," therefore, is not a simple chlorite, but is most likely a randomly interstratified serpentine/chlorite.

Ahn and Peacor (1985) showed high resolution transmission electron microscope lattice fringe images of chlorites from Gulf Coast shales that contain some 7-Å layers. Dean (1983) noted a chlorite with odd-order (00*l*) diffraction line broadening for a few reflections and concluded that it is a serpentine/chlorite. Brindley and Gillery (1954) described a randomly interstratified kaolinite/chlorite which Bailey (1969) later suggested was probably serpentine/chlorite. Walker and Thompson (1990) and Moore and Hughes (1990, 1991) found examples of chloritic minerals with odd-order line broadening. They ascribed the peak broadening to interlayered serpentine.

The purpose of this paper is to (1) establish the structure of the Tuscaloosa chloritic mineral because it is an example of a poorly documented mixed-layered mineral that may be more common in sedimentary rocks than previously supposed, and (2) develop an analytical rationale for dealing with interstratification that is manifested only by line broadening.

EXPERIMENTAL

Sample

The samples of Tuscaloosa Formation studied consist of extremely friable, pale tan, fine to medium-grained sandstone. Scanning electron microscope photographs portray the chloritic mineral as isopachous grain coatings which form microrosettes. Partially decomposed rock fragments among the framework grains are chloritized. The porosity due to the lack of cement, as seen in thin section, is remarkable for a rock of this age and depth of burial.

Sample preparation

An iron mortar was used to gently crush 10 g of rock which was then suspended in 200 ml of distilled water and stirred at high speed in an industrial grade Waring blender. The suspension was irradiated for 3 min at approximately 100 acoustical watts in a horn-type ultrasonic generator and then centrifuged repeatedly in

Copyright © 1992, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1992.0400302 Published online by Cambridge University Press

changes of distilled water to the point of incipient dispersion. Sodium pyrophosphate was added (0.005 M) to promote final dispersion and the suspension was centrifuged to yield the <2 μm fraction e.s.d.

Preliminary X-ray work on <2 μm oriented aggregates disclosed that odd-order line broadening was most pronounced in the coarser sizes of the <2 μm fraction, so the 2–0.5 μm fraction was separated by repeated centrifuging and used for further studies. The particle size effect might be a manifestation of fine-grained chlorite from the matrix which does not exhibit odd-order line broadening, although no experiments were conducted to pursue this idea.

The chloritic mineral has similar diffraction characteristics over the interval of 12,495 to 12,504 ft from a single core. Five core chip samples from this interval were combined to produce a composite sample of sufficient size for further study. An oriented powder aggregate, 2.5 × 4.5 cm, was made of the 2–0.5 μm composite by the centrifuged porous plate method which produces well-oriented and infinitely-thick samples.

Neither treatment by ethylene glycol vapor (12 hr at 60°C) nor heating (375°C for one hr) produced any changes in the diffraction pattern. Therefore, diffraction data were obtained from an air-dried preparation.

X-ray diffraction methods

X-ray diffraction data were obtained using a Siemens D-500 diffractometer with a graphite monochrometer and Cu radiation (40 kV and 30 mA). Diffraction profiles were recorded from $2\theta = 2°$ to $2\theta = 130°$ at 2θ increments of 0.02° for broad peaks and 0.01° for others. A 0.05° aperture slit was used throughout, and divergence slits of 0.3°, 1°, and 3° were employed depending on 2θ. The same peak was measured from adjacent 2θ ranges to allow normalization of the intensities to a common base. Two Soller slits were used for all peaks below 40° 2θ because peak profile distortion due to axial divergence is severe at low diffraction angles, and this effect is minimized by better Soller slit collimation. Measuring the standard deviation of the orientation function gave $\sigma^* = 9.3°$. The appropriate Lorentz factor was computed for both one and two Soller slits in place (Reynolds, 1986), and the intensities of the low-angle peaks that were measured with both Soller slits in place were then adjusted to the Lorentz effects appropriate for one slit.

Accurate values for line breadths require that the instrument signature be deconvolved from peak profiles. Fluorite, ground under acetone to minimize lattice strains, served to map the instrumental signature at different diffraction angles. These data were recorded using instrumental parameters identical to those used for the sample. The fluorite peaks served as blanks to provide the diffraction character of a perfectly crystalline substance. Deconvolving their diffraction profiles from the experimental peaks produced a shape that would be produced by a perfect optical device, that is, one with no distortions.

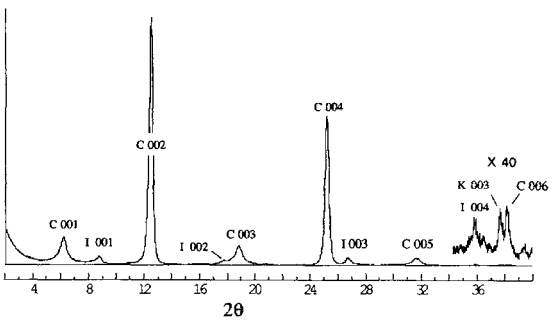


Figure 1. Basal diffraction pattern from the Tuscaloosa serpentine/chlorite oriented aggregate. C is chlorite, I is illite, and K is kaolinite. The inset diffraction pattern near 36° 2θ is the original pattern multiplied by an intensity factor of 40.

The instrumental signature changes with diffraction angle for several reasons, the most important of which is the Kα1-Kα2 separation. Synthetic pseudovoigt profiles were fit to the different fluorite peaks, and the mathematical parameters derived from these were used to calculate instrumental signatures at the diffraction angles of the chloritic mineral peaks.

Ergun's method of iterative folding (Ergun, 1968) was used to deconvolve the instrumental signature from each of the mineral reflections to extract the pure diffraction line shape. Although the Tuscaloosa chloritic mineral was not identified, Reynolds (1989) provided an example of the observed and calculated instrumental signature along with the experimental, deconvolved, and least-squares fit of the deconvolved 00,14 reflection of this mineral. Values for the chloritic mineral peak widths at half-maximum (β, in units of degrees 2θ) were obtained from the least-squares fitted profile for each reflection. The accuracy of this procedure was tested by application to sixteen reflections (l = 1 to 16) from a "normal" chlorite from the Norphlett Formation. The standard deviation of the β values, corrected for the angle-dependent particle-size effect of $1/\cos\theta$, was $\pm 0.02°$ 2θ.

RESULTS

Figure 1 shows a diffractogram of the 2-0.5 μm fraction. The aggregate is highly oriented as indicated by the intense 00l pattern and the absence of the 020 reflection near 19.6° 2θ. Small amounts of illite and kaolinite are present. Odd-order line broadening is not very apparent at this scale, but Figure 2 displays it better. The raw odd-order peak widths are approximately twice as broad as the even ones. The high-Fe content of the chlorite causes the intense even- and weak odd-order reflections.

Table 1 lists the diffraction data from the oriented aggregate. Values for the peak centroid (Klug and Alexander, 1974) of the raw data are given with derived

https://doi.org/10.1346/CCMN.1992.0400302 Published online by Cambridge University Press

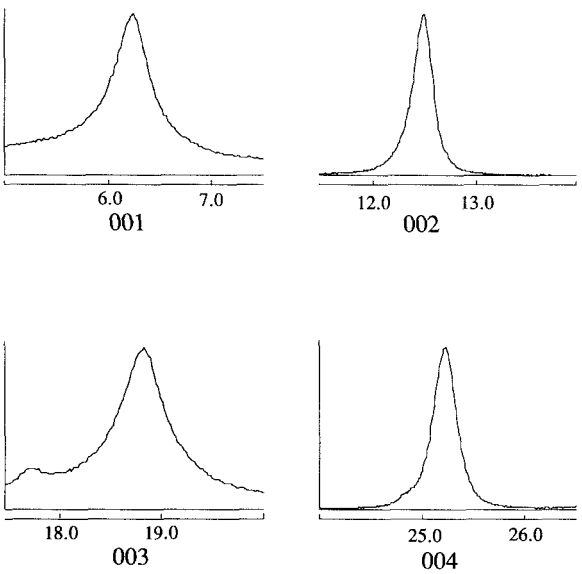


Figure 2. Uncorrected diffraction profiles for the 001, 002, 003, and 004 "chlorite" reflections (Tuscaloosa serpentine/chlorite) normalized to identical peak heights.

Table 1. X-ray diffraction data from an oriented aggregate ($\sigma^* = 9.3°$) of the Tuscaloosa chloritic mineral.

Reflection	d[1]	Intensity[2]	β[3]
1	14.15	6500	0.39
2	7.04	20,500	0.19
3	4.70	4050	0.51
4	3.525	14,400	0.21
5	2.825	1330	0.51
6	2.353	95	0.25
7[4]	2.023	350	0.49
8	1.763	45	
9	1.568	55	0.52
10	1.412	545	0.30
11		N.D.	
12	1.177	265	0.37
13		N.D.	
14	1.0083	180	0.44
15		N.D.	
16	0.8818	230	0.62

Mean $d(001)$ = 14.11 Å. Coefficient of variability = 0.12 percent.

[1] From the raw data peak centroid using CuKα = 1.5418 Å.

[2] Integrated pure diffraction peak intensity (relative units) normalized to a 3° divergence slit and no incident beam Soller slit.

[3] Instrument-corrected width at half maximum height, not corrected for particle-size effects.

[4] Illite 005 reflection extracted by peak stripping.

N.D. means not detected.

d values. Intensities were measured from integrated, deconvolved profiles, and have been adjusted to a common base with a geometry consisting of the divergence slit = 3°, detector slit = 0.05°, and no primary beam Soller slit (one Soller slit used). The low value for the coefficient of variability is noteworthy. No evidence of reflection position irrationality is evident; thus the mineral is not mixed-layered by at least one operational definition.

INTERPRETATIONS

Odd-order 00l line broadening and mixed-layering in serpentine/chlorite

The Scherrer equation that relates optical coherent domain size to peak breadth is given by

$$\beta = \frac{K\lambda}{D \cos \theta}. \quad (1)$$

β is the width of the diffraction profile measured at half-height and expressed in radians. K is a constant near unity, λ is the wavelength, and θ is the diffraction angle. D depicts the thickness of the domain in Å, measured in a direction normal to the diffracting planes, that produces the peak whose breadth is β. Breadth is inversely proportional to cos θ, consequently, the effects of particle size can be removed for analysis of line broadening by multiplying all of the deconvolved line breadths by cos θ.

Figure 3 shows the experimental data plotted as corrected line-breadth (β) *vs* diffraction order for the 001 to the 00,16 reflections. The striking feature of the data is the systematic difference in β between odd and even order reflections. This is precisely what is expected from a random interstratification of a minor component whose $d(001)$ is nearly one-half that of the major constituent, in this case, the interstratification of small amounts of 7-Å layers with large amounts of a 14-Å type. Phase coincidence exists between even-order reflections from the 14-Å layers (or stacks of layers) and the superimposed 00l reflections from the 7-Å type. Destructive phase interference occurs between the two layer types at the diffraction angles of odd-order 14-Å

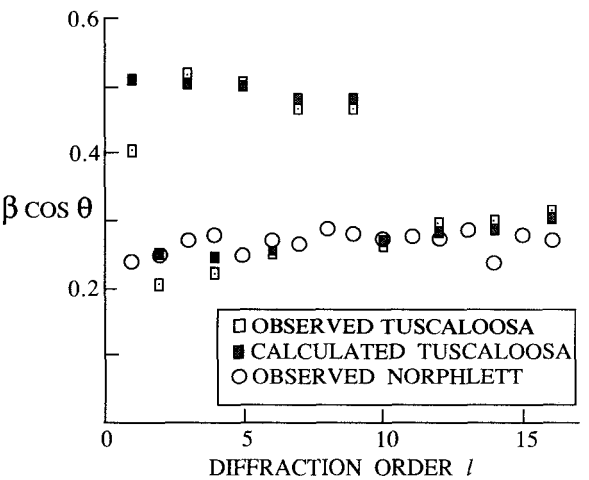


Figure 3. Comparison between calculated peak breadths and experimental results corrected for instrumental distortion. Calculated and experimental breadths have been multiplied by cos θ to eliminate angle-dependent particle size effects.

https://doi.org/10.1346/CCMN.1992.0400302 Published online by Cambridge University Press

periodicities, and at these same angles phase effects eliminate constructive interference from within stacks of 7-Å layers. For odd-order chlorite diffraction angles, significant measurable diffraction arises only from within the uninterrupted sequences of 14-Å layers. In short, the odd orders behave like diffraction from a thin chlorite crystal, whereas the even orders resemble those from a thick one (see Eq. 1). These effects produce odd-order line broadening.

Line-breadth data for the Norphlett chlorite are included in Figure 3. This mineral displays no evidence of odd-order line broadening. Its nearly invariant β values demonstrate that the structural differences between the Tuscaloosa and Norphlett chloritic minerals can be confidently distinguished by the sensitivity of the methods used here.

Peak breadths for a model Tuscaloosa chloritic mineral were generated (Figure 3) by the computer program NEWMOD (Reynolds, 1985). The model structure assumed random interstratification of 7 percent serpentine [$d(001)$ = 7.2 Å] and 93 percent trioctahedral chlorite [$d(001)$ = 14.11 Å] containing 3.34 atoms of Fe per six octahedral positions, symmetrically distributed between the two octahedral sheets.

Line breadths for both odd and even diffraction orders change in different directions with respect to 2θ because the correct ratio of the two $d(001)$ values is not exactly 2:1. The $d(001)$ value for chlorite was obtained directly from the diffraction data (Table 1), and a value of 7.2 Å was assigned to the serpentine component by trial and error model calculations. A value of 7.2 Å reproduces the slopes shown by β *vs* l relationships for both the odd- and the even-order diffraction sequences shown by Figure 3.

Calculated diffraction profiles were based on a defect-broadening model in which the broadening coefficient, δ, denotes the mean defect-free distance, that is, the mean length of X-ray coherence along the Z direction (Ergun, 1970). The most realistic profile shapes and breadths were achieved for δ = 10 unit cells and maximum N = 50 unit cells. Figure 4 shows the instrument-corrected profiles for the 005 and 00,14 reflections superimposed on profiles calculated by NEWMOD using these parameters. The overall agreement is excellent except that the tail ends of the experimental 00,14 peak are somewhat abbreviated. The deconvolution procedure commonly produces ripples adjacent to the peak, and the amplitude of these increases as the deconvolved function becomes more weighty. The raw 00,14 profile is badly distorted by CuKα1-CuKα2 separation; therefore, diminished intensity on the flanks of this peak is most likely caused by the less than robust mathematical conditioning of the deconvolution process.

Agreement between calculated and experimental results (Figures 3 and 4) indicates the essential validity of the model structure. However, there are problems

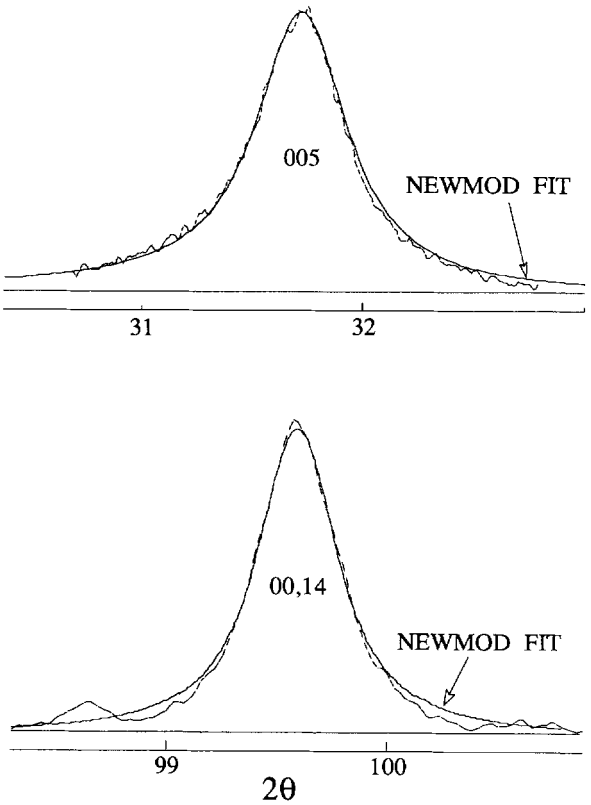


Figure 4. Peak shape comparisons between deconvolved Tuscaloosa serpentine/chlorite experimental profiles and the profiles produced by NEWMOD assuming (1) a mean defect-free distance of 10 unit cells and a maximum crystal thickness of 50 unit cells, (2) $d(001)$ chlorite = 14.11 Å and $d(001)$ serpentine = 7.2 Å, and (3) 7 percent randomly interstratified serpentine.

with the observed and calculated line breadths at low diffraction angles, particularly for the 001 reflection. This anomaly is probably caused by inaccuracies in the instrumental signature below 25° 2θ. No line-shape calibration standard is presently available for peaks below this angle, so the experimental data were deconvolved using extrapolations of the instrumental signature parameters measured at higher angles. Line shape at low angles is distorted by flat-specimen effects and axial-divergence which is significant even with two Soller slits in place (Klug and Alexander, 1974), and these may not have been correctly incorporated in the instrumental correction. For unexplained reasons, the discrepancies are much greater for the Tuscaloosa mineral than for the Norphlett chlorite. Such instrumental complications at low angles suggest that the 001 and 002 "chlorite" reflections should be avoided for quantitative studies, although they are useful for qualitative identification of interstratifications of this kind.

Other kinds of disorder produce line broadening. Diffraction peaks are broadened by particle size, strain, and crystal bending (Güven, 1975), but these cause line

https://doi.org/10.1346/CCMN.1992.0400302 Published online by Cambridge University Press

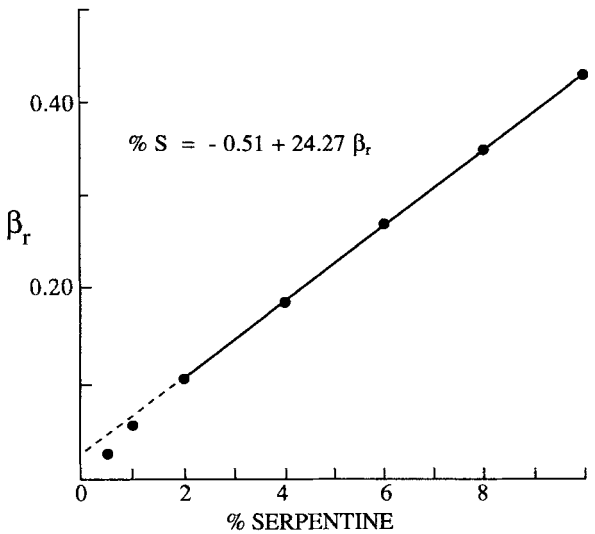


Figure 5. Calculated results for the relationship between residual odd-order line broadening (β_r) and the serpentine content of mixed-layered serpentine/chlorite.

breadth to increase monotonically with respect to θ. None are relevant to the observation that, for example, the 00,10 reflection is sharper than the 003. A non-θ-dependent pattern of 00*l* line broadening can only be explained by mixed-layering, and if the positions of all of the peaks are rational, there is nearly a 2:1 relationship between the *d*(001) values of the two layer types involved.

Chlorite odd-order line broadening is remarkably sensitive to 7-Å interstratification. Only 7 percent serpentine has produced odd-order peaks that are about twice as broad as even orders. In fact, the tedious processes of measuring many peaks and correcting them for instrumental effects are unnecessary for quantifying cases as extreme as this one. The use of such methods, however, might be necessary to detect serpentine interstratification in amounts as low as 2 percent, and it is possible that many so-called normal chlorites will be shown to actually contain such small but detectable concentrations of 7-Å layers.

A simplified method for the analysis of serpentine/chlorite

The methods described here are time-consuming and cannot be applied to most sedimentary rocks because of peak interferences from other minerals. A simplified method of analysis is suggested below.

The chlorite 004 and 005 reflections should be used because they (1) are at high enough diffraction angles to minimize peak shape distortion caused by presently unknown factors in the instrument signature, (2) are at low enough angles to be relatively free from Kα1-Kα2 broadening, (3) have breadths relatively insensitive to departures from an exact 2:1 ratio of *d*(001) values for chlorite and serpentine, (4) are near enough to each other (in 2θ) for almost identical instrumental contributions to line shape, (5) are intense enough for the acquisition of accurate peak profiles with minimum instrument time, and (6) are relatively free of interference from other common minerals in sedimentary rocks.

Instrumental distortion must be minimized by the use of two Soller slits and a fine detector aperture ($\leq 0.05°$), and kaolinite and anatase should produce no significant interference at the chlorite 004 position. If significant kaolinite is present, higher order chlorite reflections must be used which are well separated from kaolinite reflections; however, correction for the instrumental signature is necessary because of significant line broadening caused by CuKα1-CuKα2 separation.

β_r is defined as the residual line broadening caused by interstratification:

$$\beta_r = (\beta_{005}^{1.25} - \beta_{004}^{1.25})^{\frac{1}{1.25}}. \quad (2)$$

β_{005} and β_{004} are, respectively, the widths in degrees 2θ at half peak height for the 005 and 004 "chlorite" reflections obtained from the raw experimental profiles, multiplied by cos θ to eliminate the angle-dependent effects of particle-size broadening [Eq. (1)]. Raw data can be used because instrumental broadening effects are assumed to be identical for the two reflections. The simplicity of Eq. (2) requires some justification.

Odd-order line broadening can be thought of as the convolution of a broadening function on a pure diffraction peak. The breadth of the convolved profile is the sum of some power of the breadths of the two functions involved in the convolution, taken to the power of the reciprocal of that power. Consider two profiles with breadths β_1 and β_2, whose convolution breadth is β_c. If β_1 and β_2 are both gaussian,

$$\beta_2 = (\beta_c^2 - \beta_1^2)^{1/2}.$$

If β_1 and β_2 are both lorentzian (Klug and Alexander, 1974),

$$\beta_2 = (\beta_c - \beta_1).$$

The breadth deconvolution requires subtraction of two breadths, each of which is raised to an exponent that varies between one and ½ depending on the parametric position of the relevant pseudovoigt equation between lorentzian and gaussian limits. Pseudovoigt functions that fit the experimental peaks for the Tuscaloosa chloritic mineral are close to the lorentzian limit, suggesting that the appropriate exponent is near unity. Trial and error calculations with NEWMOD indicated that if the exponent 1.25 is used, the residual line broadening (β_r) is independent of crystallite thickness. The calculation of β_r amounts to using the 004 profile as a shape signature for the undistorted mineral structure (plus instrument effects). Deconvolving it from the 005 (which contains instrument effects) gives the breadth of a pure mixed-layered broadening function.

https://doi.org/10.1346/CCMN.1992.0400302 Published online by Cambridge University Press

The result of this deconvolution (β_r) gives the quantity that is sensitive to the serpentine content of mixed-layered serpentine/chlorite.

Figure 5 shows calculated results for β_r plotted against percent serpentine for a hypothetical mixed-layered serpentine/chlorite series. The empirical equation for the regression line is

$$\% S = -0.51 + 24.27\beta_r, \quad (3)$$

and it is linear from about 1 to 20 percent serpentine. The solution of this equation, using the raw experimental 004 and 005 peak breadths, gives 7.5 percent serpentine, compared to the value of 7 percent obtained from the average of all of the instrument-corrected basal reflections.

Equation (3) is valid for calculating percent serpentine based on the 003 and 004 reflections if the constant is changed from -0.51 to -0.71, and if β_r is calculated from Eq. (2) by substituting β_{003} for β_{005}. A value of 8.2 percent serpentine was obtained by this method. The procedure is somewhat suspect because axial divergence distortion is greater for the 003 reflection than for the 005, and interference from the illite 002 peak is possible; nonetheless, there is an advantage gained by utilizing a more intense odd-order reflection.

CONCLUSIONS

1. Analysis of 00*l* line broadening can provide an estimate of percent serpentine in mixed-layered serpentine/chlorite.
2. Serpentine/chlorite odd-order line broadening is very sensitive to the content of interstratified serpentine. Seven percent serpentine in the Tuscaloosa chloritic mineral roughly doubles the breadths of odd-order reflections. This broadening is about ten times the experimental error of measuring pure diffraction line breadth.
3. A simplified method, using raw experimental breadths of two basal reflections, gives a result for percent serpentine that is about 1 percent different from the value based on the average of 12 basal reflections that were corrected for instrumental effects. If such accuracy is acceptable, there is no need for a more elaborate analysis.

REFERENCES

Ahn, J. H. and Peacor, D. R. (1985) Transmission electron microscopic study of diagenetic chlorite in Gulf Coast argillaceous sediments: *Clays & Clay Minerals* **33,** 228–236.

Bailey, S. W. (1969) Polytypism of trioctahedral 1:1 layer silicates: *Clays & Clay Minerals* **17,** 355–371.

Brindley, G. W. and Gillery, F. H. (1954) Mixed-layer kaolin-chlorite: *Clays & Clay Minerals,* 2nd Nat. Conf., 349–353.

Dean, R. S. (1983) Authigenic trioctahedral clay minerals coating Clearwater Formation sand grains at Cold Lake, Alberta, Canada: in *Programs and Abstracts, 20th Annual Meeting of the Clay Minerals Society,* Buffalo, New York, 1983, p. 79 (Abstract).

Ergun, S. (1968) Direct method for unfolding convolution products—its application to X-ray scattering intensities: *J. Appl. Crystallogr.* **1,** 19–23.

Ergun, S. (1970) X-ray scattering by very defective lattices: *Phys. Rev.* **131,** 3371–3380.

Güven, N. (1975) Evaluation of bending effects on diffraction intensities: *Clay Miner.* **23,** 272–277.

Klug, H. P. and Alexander, L. E. (1974) *X-Ray Diffraction Procedures:* J. Wiley and Sons Inc., New York, 996 pp.

Moore, D. M. and Hughes, R. E. (1990) The clay mineralogy of two Mississippian sandstone reservoirs in the Illinois Basin: in *Programs and Abstracts, 27th Annual Meeting of The Clay Minerals Society,* Columbia, Missouri, 1990, p. 90 (Abstract).

Moore, D. M. and Hughes, R. E. (1991) Characteristics of chlorite interlayered with a 7Å mineral as found in sandstone reservoirs: in *Programs and Abstracts, 28th Annual Meeting of The Clay Minerals Society,* Houston, Texas, 1991, p. 115 (Abstract).

Reynolds, R. C. (1985) *NEWMOD, a Computer Program for the Calculation of Basal X-Ray Diffraction Intensities of Mixed-Layered Clays:* R. C. Reynolds, Hanover, New Hampshire.

Reynolds, R. C. (1986) The Lorentz factor and preferred orientation in oriented clay aggregates: *Clays & Clay Minerals* **34,** 359–367.

Reynolds, R. C. (1989) Diffraction by small and disordered crystals, Chp. 6, in *Modern Powder Diffraction:* D. L. Bish and J. E. Post, eds., *Reviews in Mineralogy* **20,** Mineralogical Society of America, Washington, D.C., 145–181.

Walker, J. R. and Thompson, G. R. (1990) Structural variations in chlorite and illite in a diagenetic sequence from the Imperial Valley, California: *Clays & Clay Minerals* **38,** 315–321.

(Received 17 January 1992; accepted 17 January 1992; Ms. 2090)

https://doi.org/10.1346/CCMN.1992.0400302 Published online by Cambridge University Press