Clays and Clay Minerals, Vol. 28, No. 6, 401–411, 1980.

PRECISE IDENTIFICATION OF ILLITE/SMECTITE INTERSTRATIFICATIONS BY X-RAY POWDER DIFFRACTION

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Abstract—The thickness of the two-layer ethylene glycol complex of dioctahedral smectites varies under room conditions between 17.3 and 16.5 Å because of such factors as layer charge density, type of interlayer cation, and relative humidity. Neglecting this variability can give up to 30% error in the X-ray powder diffraction estimation of the smectite:illite ratio of the mixed-layer structures. Three methods have been developed for the interpretation of X-ray powder diffraction patterns of glycolated mixed-layer illite/smectite which take layer-spacing variability into account. The methods include a technique for quantifying the degree of layer ordering. In addition, the proposed techniques minimize the error due to the influence of domain size on positions of reflections. The experimental error can be kept below 5% or below 1% smectite layers, depending on the method applied, provided that the peak positions are measured with the accuracy of $\pm$ 0.02°2θ.

Key Words—Ethylene glycol, Illite, Illite/smectite mixed layer, Interstratification, Smectite, X-ray powder diffraction.

INTRODUCTION

Illite-smectite interstratifications are the most common clay components of sedimentary rocks and are the most sensitive clay indicators of the degree of diagenesis and low-grade metamorphism. Because of their extremely small grain size, illite/smectite interstratifications are easy to concentrate and separate by sedimentation. For these reasons, most clay diagenesis studies concentrate on these minerals (see Dunoyer de Segonzac, 1970; Perry and Hower, 1970; Hower *et al.*, 1976; Środoń, 1979).

X-ray power diffraction (XRD) identification of smectites and mixed-layer clays containing a smectitic component is based on the expansion of these clays with ethylene glycol and glycerol, as proposed by MacEwan and Bradley (see Brindley, 1966). The advantages of using ethylene glycol or glycerol complexes, as compared with water complexes are: (1) increased intensities of second and higher order reflections; and (2) development, under room conditions, of relatively stable, two-layer complexes by all varieties of dioctahedral smectite if ethylene glycol is used (Brindley, 1966; Theng, 1974). Glycerol seems to be less suitable for identifying illite/smectites because some beidellites (Harward and Brindley, 1965; Harward *et al.*, 1969) and some K-, Rb-, Cs-, or NH_4-montmorillonites (Brindley, 1966) form a one-layer, i.e., a vermiculite-type complex.

Pure smectite can be distinguished from mixed-layer clays by the presence of a regular sequence of the 00ℓ XRD reflections. Minor and systematic deviations from regularity, i.e., displacements toward lower angles increasing for low-angle reflections, are caused by small domain[1] size (Reynolds, 1968; Ross, 1968).

Non-systematic deviations from regularity of basal reflections are characteristic of mixed-layer clays. These minerals are usually identified by comparison of positions of mixed reflections with computed theoretical XRD patterns. These positions are influenced by the proportion of the component layers, the type and degree of ordering, the domain thickness (Reynolds and Hower, 1970), and the thickness of the ethylene glycol interlayers, as will be shown below.

The effect of the last factor seems to be underestimated by the authors of identification methods, all of whom have assumed a single fixed value for the thickness of a double layer smectite-ethylene glycol complex: 16.9 Å (Reynolds and Hower, 1970); 17 Å (Tettenhorst and Grim, 1975); and 16.86 Å (Drits and Sakharov, 1976). The difference between 17 Å and 16.86 Å is large enough to account for 15–20% error in estimation of the component ratio of illite/smectite interstratifications if a wrong value of the complex thickness is chosen (e.g., see the data of Reynolds and Hower, 1970, Table 3). The purpose of the present study was to investigate the ethylene glycol complex thickness among expanding clays and to devise XRD methods of

[1] The term "domain" denotes the volume of a structure which scatters X-rays coherently. The term "crystallite size" is a less rigorous term most often used to indicate this property. The domain size is less than or equal to the crystallite size. The relation of this entity to physically separable clay particles is not yet clear.

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identification of mixed-layer clays based upon the variation of their ethylene glycol complex thickness.

ANALYTICAL TECHNIQUES

The <1-μm and <0.2-μm fractions of 37 natural clays as well as 11 synthetic smectites were used in this study. All chemical pretreatments (interlayer cation exchange, acetate buffer reaction) were performed following Jackson's (1974) procedures. Oriented preparations were produced by pipetting a clay slurry, dispersed by ultrasonic treatment, onto a glass slide, or by centrifuging a slurry onto a ceramic tile (Kinter and Diamond, 1956). Clays were solvated with ethylene glycol by pressing the dry preparation upside down against absorbent paper wetted with ethylene glycol and allowing the composite to remain overnight in this position. Excess ethylene glycol was removed just before recording the XRD pattern by pressing the preparation against dry absorbent paper. This technique assured the complete solvation of the clay film, which, in most cases, was achieved in an about one hour and left enough surplus liquid to prevent the evaporation of ethylene glycol from the interlayer space during the recording of the pattern. From the present author's experience, the loss of interlayer ethylene glycol happens fairly readily if a glass slide preparation is solvated by the ethylene glycol vapor method, as suggested by Kunze (1955). On the other hand, excess ethylene glycol, which gives a broad, diffuse band in the XRD pattern, is easily removed, and curling of the clay film is prevented. Curling can take place if a glass slide preparation is solvated by diffusion of drops of ethylene glycol placed at the edges.

XRD patterns were recorded from 50° to 2°2θ using Ni-filtered CuKα radiation. Slits were selected so that the X-ray beam divergence was less than the sample length, as low as 2°2θ. Most of the data were obtained using a strip chart recorder. Goniometer and chart speeds, respectively, were: 1°/min and 720 mm/hr, or 0.4°/min and 12 inch/hr.

The most accurate data were collected automatically by step-scanning at 0.01°2θ intervals and using a 10-sec counting time. The reflections of illite/smectites have broad maxima, 0.15–0.30°2θ in width. The center of a plateaulike maximum was assumed to be the reflection position. The goniometer was aligned precisely to minimize instrumental error. In the 2θ range examined the correction was 0.00°, as checked with powdered quartz.

Experimental patterns were compared with theoretical ones which were produced by a computer program for simulation of the (00ℓ) diffraction profiles of illite/smectites, as developed by Reynolds and Hower (1970), and modified further by R. C. Reynolds (personal communication). The variations in thickness of the ethylene glycol complexes were simulated by changing d(001) of the smectite layers; Z coordinates of ethylene glycol and water molecules, however, were left untouched. This simplification gives slightly incorrect values of the peak intensities, but does not affect the peak spacings. The program was slightly modified to search for local maxima of the diffraction function and to list their positions with an accuracy of 0.01°2θ.

VARIATION OF SMECTITE-GLYCOL COMPLEX THICKNESS

Figure 1 shows three obviously different patterns of natural smectites. The differences are in the relative peak intensities, the peak positions and breadths, and the height ratio of the low-angle "valley" to the 001 peak. The peak positions, Wyoming (17.00 Å), Cheto (16.92 Å), and Garfield (16.65 Å), suggest that the samples are pure smectites with different ethylene glycol complex thicknesses, judging from the high-angle reflections whose positions are not significantly affected by the Lorentz and polarization factors. Different broadening of the reflections and different valley:peak ratios seem to reflect different domain-thickness distribution, but some mixed layering in the Cheto sample may be present because mixed layering also produces the reflection broadening and increased valley:peak ratio (Reynolds and Hower, 1970, Figure 4a). The positions of the 003 and 005 reflections, which are strong and only slightly influenced by domain size (Reynolds and Hower, 1970), were used to clarify this problem. Figure 2 presents a plot of 2θ(003) vs. 2θ(005), expressed in °2θ CuKα, made by hand for an infinite domain size and by computer for two even distributions of the domain size (1–8 and 1–14 layers per domain). These numbers limit the range of the domain size most common among natural smectites (Środoń, in preparation). Also plotted in this figure is an example of a 10% illite, randomly interstratified mixed-layer illite/smectite with domain sizes varying from 1 to 14 layers. The mixed layering moves the projection point above the positions of pure smectites.

The 2θ(003) vs. 2θ(005) spacings of the investigated natural dioctahedral smectites plot essentially within the theoretical lines, proving that the observed variability of peak positions is due mainly to variable thickness of the clay-ethylene glycol complex (17.15–16.65 Å), and not to domain thickness or mixed layering. Also, the studied synthetic materials, montmorillonites and beidellites of variable chemical composition (Figure 3), show a broad range of thicknesses for the clay-ethylene glycol complex (17.3–16.8 Å).

The data show that the variation of the thickness of the two-layer ethylene glycol complex of dioctahedral smectites is at least as large as 16.9 ± 0.3 Å and indicate that such variation must be taken into account by any XRD method of identification of mixed-layer minerals.

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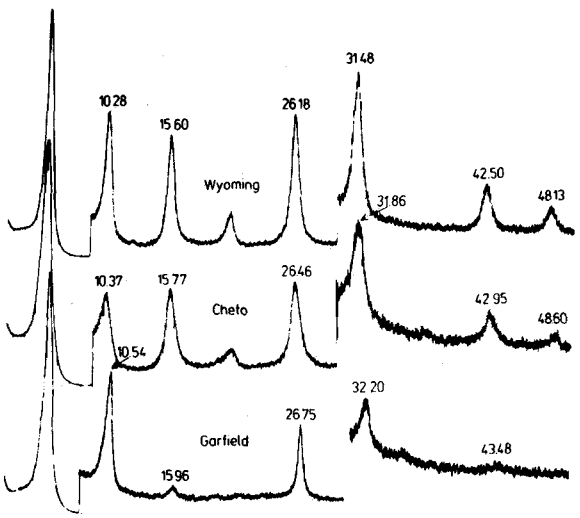


Figure 1. Examples of X-ray powder diffraction patterns of glycolated smectites. 2θ values for CuKα radiation are listed by important peaks. 2θ values of 00ℓ reflections of the Cheto and Garfield samples are regularly shifted with respect to Wyoming, suggesting smaller ethylene glycol-smectite complex thickness.

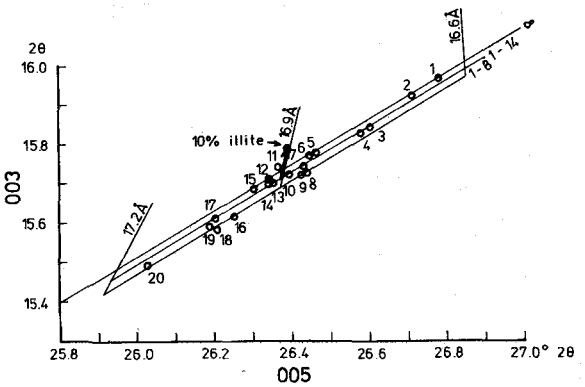


Figure 2. Plot of °2θ(003) vs. °2θ(005) for variable ethylene glycol-smectite thickness. The three lines represent an infinite number, 1–14, and 1–8 layers/domain. The calculated position of a 10/90 is plotted to show the effect of mixed layering. 1 = Garfield, Washington, Ward's Natural Science Establishment; 2 = Uruguay, Ralph Grim collection; 3 = Polkville, Mississippi, Ward's Natural Science Establishment; 4 = No. 30, Ralph Grim collection; 5 = Chmielnik, Poland; 6 = EU-3-75, Wisconsin, Ralph Grim collection; 7 = Black Jack Mine, Idaho, Smithsonian Collection; 8 = Otay, California, Ward's Natural Science Establishment; 9 = hectorite, Hector, California, SHCa-1, CMS Source Clays Repository; 10 = Piaseczno, Poland; 11 = Cheto, Arizona, SAz-1, CMS Source Clays Repository; 12 = Milos, Greece, Ralph Grim collection; 13 = saponite, Riddle, Oregon; 14 = Montmorillon, France, Ralph Grim collection; 15 = Wiślica, Poland; 16 = No. 222, Ralph Grim collection; 17 = Machów, Poland; 18 = Gacki, Poland; 19 = Crook County, Wyoming, SWy-1, CMS Source Clays Repository; 20 = Umiat, Alaska.

IDENTIFICATION PLOTS

The recommended method of Reynolds and Hower (1970) for the determination of illite/smectite ratio in a mixed-layer mineral involves the determination of the position of a single combined reflection (they suggested using the reflection which migrates from 15.7 to 17.7°2θ for CuKα) after having taken into account the type and degree of any ordered interlayering. Using this reflection avoids most, but not all, of the error caused by peak shift due to small domain size. As has been shown in the previous section, it is generally necessary also to include a determination of the layer spacing of the glycolated smectite to obtain accurate illite/smectite ratios. To do this, one must determine an additional peak position because there is an additional variable. Before proceeding with the three recommended methods the factors that caused variations in peak shape, breadth, and position in the XRD patterns of illite/smectite should be noted: Peak positions vary with changes in illite:smectite ratio, domain size, type and perfection of any ordered interlayering, and thickness of the ethylene glycol-smectite complex.

The methods will be described in order of preference. The preferred method avoids any significant error caused by domain size by using peak positions at high diffraction angles. These peaks are relatively weak, however, and may not be measurable for some samples. In addition, the reflections merge at high illite content, and the preferred method cannot be used. In those cases it is recommended that the second or third method be used.

Method I

The difference in 2θ of the two reflections in the region 42°–48°2θ (CuKα) is an accurate measure of the illite/smectite ratio. This difference (defined here as Δd_2) is essentially independent of domain size and is only slightly affected by the ethylene glycol-smectite layer thickness (Figure 4). The relationship between percent smectite layers and $\Delta 2\theta$, as shown in Figure 5A, can be seen to depend significantly on the nature of the interlayering and, for highly expandable, randomly interstratified samples, on the spacing of the ethylene glycol-smectite complex. Illite/smectite exhibiting ordered interlayering is not significantly affected by the thickness of the ethylene glycol-smectite layer. To determine the illite:smectite ratio accurately, one must take into account the type and perfection of any ordered interlayering and, of somewhat lesser importance, the spacing of the glycolated smectite layers. The migration curves for the reflection between 42° and 45°2θ, shown in Figure 5B, can be used to select the correct thickness of the ethylene glycol complex. A complete analysis requires an inspection of the XRD pattern to see if the interstratification is ordered or random. If no reflection occurs between 5.3° and 8.7°2θ (CuKα), the interstratification is random.

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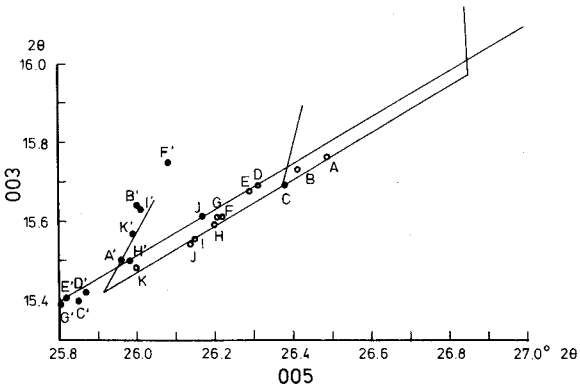


Figure 3. Projection of synthetic, glycolated, dioctahedral montmorillonites and beidellites onto 003 vs. 005 plot. Open circles = Mg-minerals; solid circles = K-minerals.

Random interstratification. Figure 5 can now be used to determine both the illite:smectite ratio and the thickness of the ethylene glycol complex by an iterative approach. A given Δd_2 value will give a range of smectite content, depending on the thickness of the ethylene glycol complex. This range of smectite content, along with the position of the 42°–45°2θ migrating peak, will yield a preliminary value for the thickness of the ethylene glycol complex from the curves in Figure 5B. This value can then be used to refine the determination of smectite content. A few iterations of these determinations will yield a unique value for both variables.

Example: Sample Sr-2M3 (Table 1)

Positions of Reflections

5.22° 10.25° 15.88° 26.46° 43.13° 48.29°

$\Delta d_2 = 5.16°$

The lack of a reflection between 5.3° and 8.7°2θ shows that the interstratification is random. The Δd_2 value of 5.16°2θ yields a range of 73% to 83% smectite from Figure 5A. This range is now translated to Figure 5B and, along with the position of the reflection at 43.13°2θ, the result narrowly defines the thickenss of the ethylene glycol complex as 16.86–16.90 Å. A return to Figure 5A, using this range, allows a final determination of 79% smectite.

Ordered interstratification. If a reflection occurs between 5.3° and 8.7°2θ in the diffraction pattern of an ethylene glycol-solvated illite/smectite, the interstratification is ordered to some degree. A preliminary value for percent smectite is then determined from the "ordered" (IS) curve in Figure 5A. The degree of perfection of ordering can now be estimated from the difference in 2θ between the reflections that occur from 5.2° to 8.2°2θ (CuKα) and from 8.8° to 10.4°2θ (see Figure 4). This difference is defined as Δd_1 and its relationship to the I/S ratio and perfection of ordering is shown in

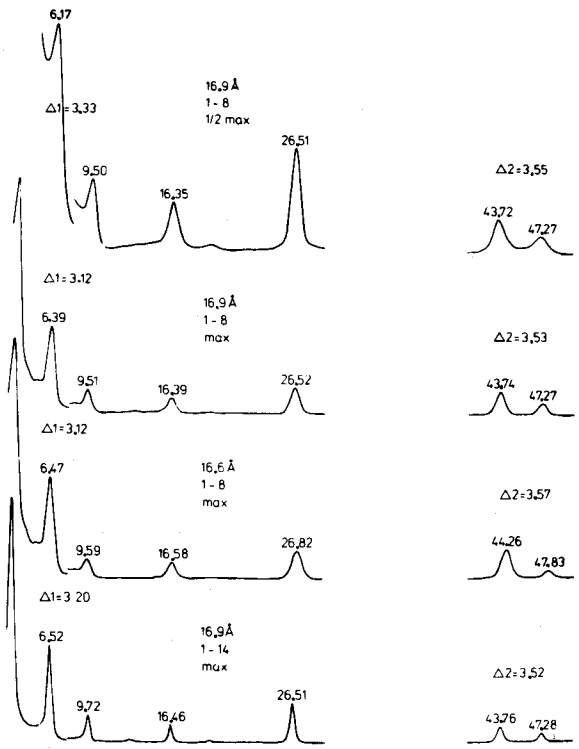


Figure 4. Calculated X-ray powder diffraction profiles illustrating the identification procedures for illite/smectite. 2θ values for CuKα radiation are listed by important peaks. The examples shown are all 49% smectite with variable perfection of IS ordering. The factors varied in calculating the patterns are: (a) domain size (1–8 or 1–14 layers), (b) ethylene glycol-smectite complex layer thickness (16.6 or 16.9 Å), and (c) perfection of IS ordering (maximum or ½ maximum). Δd_1 and Δd_2 are $\Delta 2\theta$ values used for the determination of degree of ordering and composition of the illite/smectite, respectively.

Figure 6.[2] The preliminary value for percent smectite layers is then used in Figure 6 to estimate the degree of perfection of the ordered interlayering. If the interstratification is perfectly ordered, the initial estimate is correct. If it is not perfect, the percent smectite values are picked from both the ordered and the random curves of Figure 5A, and the final value is determined by interpolation.

The above procedure is important in the compositional range 60–30% smectite. For more illitic minerals the error in the percent smectite determination is not significantly affected by degree or type of ordering.

Example: Sample Sr-1M6 (Table 1)

Positions of Reflections

6.44° 9.73° 16.51° 26.57° 44.00° 47.20°

$\Delta d_1 = 9.73° - 6.44° = 3.29°$

$\Delta d_2 = 47.20° - 44.00° = 3.20°$

[2] If the Δd_1 point falls to the left of the "IS maximum ordered" curve, the illite/smectite is ISII ordered.

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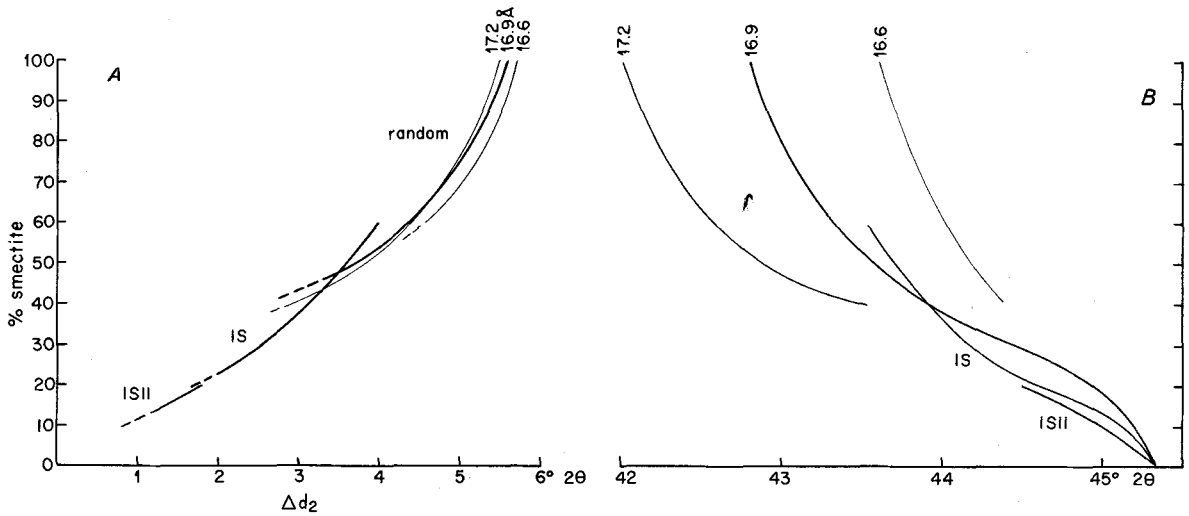


Figure 5. The plot for measuring the smectite:illite ratio, based on the angular distance Δd_2 between reflections in 42°–48°2θ region. The reflection between 42° and 45°2θ is used to select the proper thickness of the ethylene glycol complex for smectite-dominated compositions. Dashed parts of the curves represent the composition range beyond which Δd_2 cannot be measured because of merging of analytical reflections.

First, it can be noted that a reflection occurs between 5.2° and 8.7°2θ (at 6.44°2θ), therefore the sample is ordered to some extent. An initial percent smectite is then determined using the "IS" curve in Figure 5A, yielding a value of 41% smectite. Using this value the degree of ordering can now be determined from Figure 6. Δd_1 = 3.29°, and 41% smectite yields a value close to ½ ordered (see Reynolds and Hower, 1970, for a discussion of degree of ordering). A return to Figure 5A allows a value of 43% smectite to be determined for Δd_2 = 3.20 and random interstratification. Interpolation half way between the IS ordered and IS random results in a final value of 42% smectite layers.

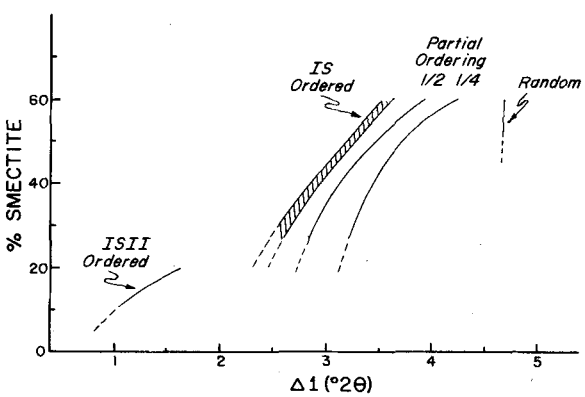


Figure 6. The plot for estimation of the degree of ordering using the initial value of percent smectite obtained using plots in Figures 5, 7, or 8 and the angular distance Δd_1 between the reflections in the range 10–5°2θ. The variations in Δd_1 as affected by the thickness of the ethylene glycol-smectite complex and domain size differences are shown for maximum IS ordering to illustrate their influence. All other curves were calculated assuming 1–14 layer domain size and 16.9-Å ethylene glycol-smectite complex thickness.

The thickness of the ethylene glycol complex layer can now be determined from Figure 5B as approximately 16.8 Å based on the peak spacing at 44.00°2θ and the percent smectite of 42%.

Method II

This method uses, for most of the compositional range, the stronger of the two reflections between 42° and 48°2θ (the 42°–45°2θ migration peak) and the strong reflection that migrates from about 26° to 27°2θ. The determination is slightly affected by domain size and strongly affected by the manner of interstratification and the ethylene glycol-smectite layer thickness. Figure 7 shows the migration curves for these reflections, calculated for 1–8 layers for the randomly and ordered interstratified cases, and for ethylene glycol-smectite layer thicknesses of 16.6, 16.9, and 17.2 Å. The figure also includes points of the migration curve for domains of 1–14 layers and an ethylene glycol-smectite layer thickness of 16.9 Å. It can be seen from these points that the domain size effect is apparent, but minor. Figure 7 includes an additional curve at low smectite contents for the 17.2-Å, ethylene glycol-smectite complex, using the peak that migrates from 45 to 48°2θ. The change to using this peak is caused by the fact that the 42–45°2θ peak is weak in the 17.2-Å, ethylene glycol-smectite complex and cannot be resolved at low smectite contents.

Example: Sample Sr-1M6

The reflections at 26.57° and 44.0°2θ yield the following results:

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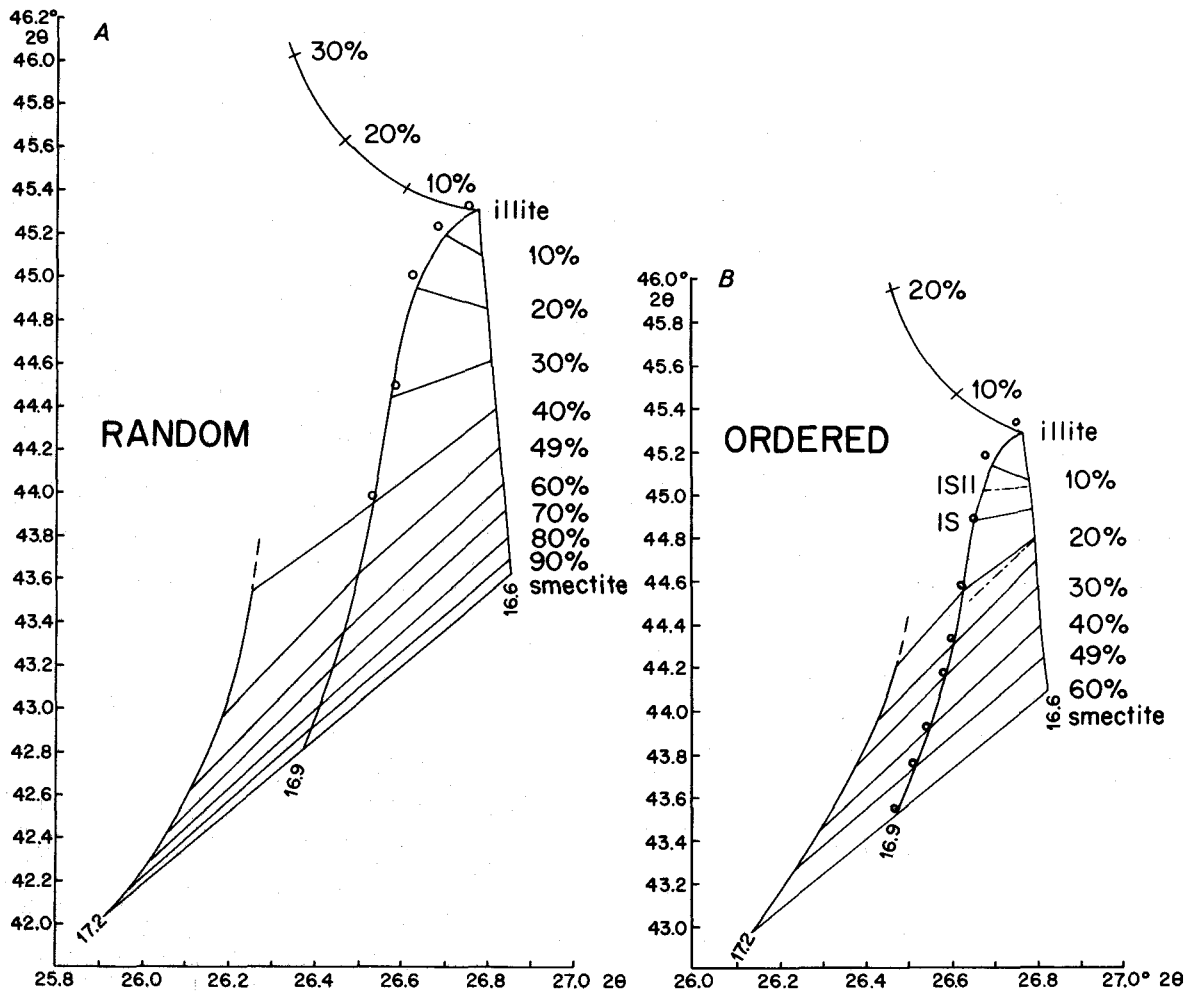


Figure 7. The plot for measuring the smectite:illite ratio, based on two reflections almost unaffected by domain thickness. Random and maximum ordered cases are drawn separately. Definitions of IS and ISII types of ordering are given by Reynolds and Hower (1970). The plot represents 1–8 layers/domain distribution, the open circles are for a 1–14 distribution and a 16.9-Å ethylene glycol complex thickness. Note that for compositions <30% smectite the higher 2θ peak used has been changed (see text for explanation).

	% Smectite	Ethylene glycol-smectite complex layer thickness
Random	40	16.85
Ordered	38	16.90

It has already been determined that Sample Sr-1M6 is ½ ordered, therefore the final result is the average of these values, or 39% smectite, and the ethylene glycol-smectite complex thickness is ~16.9 Å.

Method III

This method uses the peaks which migrate from about 26° to 27°2θ and from 15.4° to 17.7°2θ. The determination is strongly affected by ethylene glycol-smectite layer thickness, manner of interstratification, and domain size. As in Figure 7, points are plotted for domains of 1–14 layers and an ethylene glycol-smectite layer thickness of 16.9 Å. It is obvious from the positions of these points that domain size significantly affects the determination of percent smectite.

Example: Sample Sr-1M6

The peak positions at 26.57° and 16.51°2θ yield the following results:

	% Smectite		Ethylene glycol-smectite complex layer thickness
	1–8 layers	1–14 layers	
Ordered	42	48	16.8 Å
Random	37	40	16.9 Å
Mean	40	44	16.9 Å

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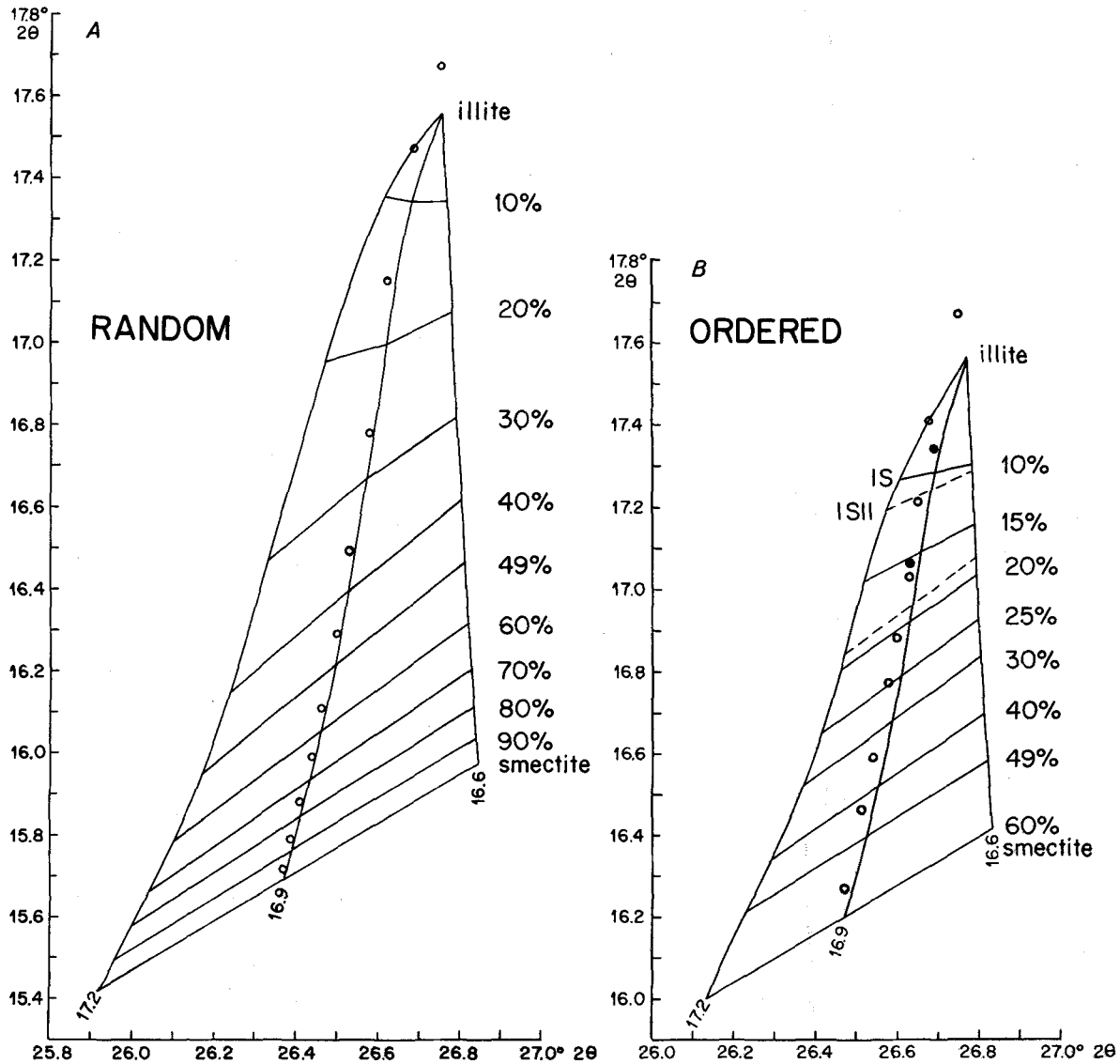


Figure 8. The plot for measuring the smectite:illite ratio, based on two strongest reflections among those only slightly affected by domain size. The solid circles are for ISII type of ordering. The remaining explanations are as in Figure 7.

Comparison of methods

The three methods can be compared theoretically with respect to the analytical error which arises from the domain size effects and the measurement precision. The domain size error is of the order of 5% smectite for Figure 8, and 1% for Figures 7 and 5. The instrumental error is the same for all the reflections, but its influence on the percent smectite determination is an order of magnitude smaller in Δd_2 than in the other two methods. Thus the Δd_2 method is recommended as the most precise one. It should be noted that if only the reflection between 15.5° and 17.5°2θ, and a 16.9-Å value is used for the thickness of the ethylene glycol complex, variation in the complex thickness can give up to a 30% S error for compositions close to the smectite end. This error diminishes towards the illite end.

The data given in Table 1 show that the three proposed methods give consistent results. The differences are not larger than 4% smectite and are not systematic if the 1–14-layers/domain model is assumed for all the mixed-layer clays that have been investigated. These results suggest that the bicomponent model gives good approximations of the real minerals.

CONTROL OVER THE THICKNESS OF THE ETHYLENE GLYCOL COMPLEX

The data given in Figure 2 can be analyzed for the influence of mineral structure on the thickness of clay-

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Table 1. Results of testing the identification methods and for an investigation of the control of exchange cation and mixed-layering over glycol complex thickness (d(001)).[1]

Sample	RH (%)	Peak position (°2θ CuKα)						Δd_1 (°2θ)	Δd_2 (°2θ)	% Smectite from Figure: 5	7	8	Ord	d(001) (Å)	r (Å)	Z/r
Upper Silesian bentonites																
Sr-2M9	52	5.24	10.32	15.83	26.45	43.05	48.46	—	5.41	89	86	89	rand.	16.87	—	—
Sr-2M3	60	5.22	10.25	15.88	26.46	43.13	48.29	—	5.16	83	79	79	rand.	16.87	—	—
Sr-4M2	57	5.22	10.20	15.93	26.48	43.16	48.23	—	5.07	79	79	76	rand.	16.86	—	—
Na-2R50	54	5.25	9.99	16.11	26.51	43.37	47.81	—	4.44	63	65	61	rand.	16.86	—	—
Na-2R49	54	5.99	9.84	16.39	26.56	43.81	47.38	3.85	3.57	49	48	48	<¼	16.86	—	—
Sr-1M6	54	6.44	9.73	16.51	26.57	44.00	47.20	3.29	3.20	40	40	43	<¼	16.87	—	—
Sr-Ch5	54	6.58	9.66	16.67	26.63	44.14	47.07	3.08	2.93	37	37	38	½	16.81	—	—
Na-2R63	56	6.89	9.57	16.82	26.67	44.26	46.93	2.68	2.67	31	32	32	max.	16.78	—	—
Sr-2R62	54	6.71	9.46	16.80	26.65	44.36	46.90	2.75	2.54	31	27	30	<max.	16.81	—	—
Na-T9	58	7.14	9.28	17.07	26.68	44.64	46.24	2.14	1.60	20	20	19	max.	16.80	—	—
K-2R76	50	—	9.77	16.55	26.62	44.05	47.09	—	3.04	40	43	44	rand.	16.80	—	—
Ca-2R76	53	5.21	10.05	16.32	26.66	43.80	47.94	—	4.14	56	56	56	rand.	16.74	—	—
K-Cheto	54	5.11	—	16.39	26.41	—	—	—	—	40	—	—	rand.	17.05	—	—
Ca-Cheto	54	5.34	10.50	15.91	26.65	43.25	49.00	—	5.75	smectite			—	16.74	—	—
K-Garfield	55	5.28	9.86	16.21	26.46	43.48	—	—	—	53	53	—	rand.	16.93	—	—
Ca-Garfield	47	5.21	10.54	15.96	26.75	43.48	—	—	—	smectite			—	16.65	—	—
Wyoming montmorillonite																
NH_4	53	—	—	15.42	25.84	41.96	47.42	—	5.46	smectite			—	17.22	1.43	0.70
K	49	—	—	15.51	26.00	42.18	47.61	—	5.42	—	97	95	—	17.12	1.33	0.75
H	53	—	—	15.54	26.10	42.36	47.92	—	5.56	smectite			—	17.06	—	—
Na	50	—	—	15.60	26.18	42.50	48.13	—	5.63	smectite			—	17.00	0.97	1.03
Li	54	—	—	15.62	26.24	42.63	48.27	—	5.64	smectite			—	16.97	0.68	1.47
Cs	50	—	—	15.72	26.38	42.83	48.52	—	5.69	smectite			—	16.88	1.67	0.60
Be	50	—	—	15.58	26.13	42.44	48.05	—	5.61	smectite			—	17.04	0.35	5.70
Mg	50	—	—	15.65	26.24	42.57	48.16	—	5.59	smectite			—	16.97	0.66	3.03
Ba	53	—	—	15.65	26.27	42.61	48.26	—	5.65	smectite			—	16.95	1.34	1.49
Sr	50	—	—	15.67	26.27	42.67	48.27	—	5.60	smectite			—	16.95	1.12	1.79
Ca	53	—	—	15.69	26.32	42.70	48.34	—	5.64	smectite			—	16.92	0.99	2.02
Arkansas	52	6.64	9.98	16.72	26.88	44.41	48.01	3.34	3.60	47	46	50	½	16.52	—	—
Zempleni	55	7.61	9.26	17.17	26.69	44.66	46.29	1.65	1.63	16	19	19	ISII	16.80	—	—
XIII	55	5.18	10.33	15.81	26.45	—	—	—	—	93	—	—	rand.	16.86	—	—

[1] RH = relative humidity, r = ionic radius (Handbook of Chemistry and Physics, 55th ed., CRC Press), Z/r = ionic potential, Ord = ordering. Δd_1 and Δd_2 are explained in the text. rand. = random. max. = maximum.

ethylene glycol complex. From the minerals whose chemical formulae have been reported in the literature (Table 2), it appears that total charge density, rather than tetrahedral charge, influences the complex thickness: high charge smectites have thinner ethylene glycol complexes, analogous to saponites (Suquet *et al.*, 1977). Only a rough correlation can be established using these data, because neither the interlayer cation nor the humidity were controlled during X-ray analysis. In addition, the chemical data characterize a clay from a given deposit and not the specific sample used in this study.

More precise data were collected to investigate the influence of the exchange cation, the humidity, and the smectite:illite ratio on the thickness of the ethylene glycol complex (Table 1). The detected range of the Wy-

Table 2. Relation between total and tetrahedral layer charge density of several smectites and their ethylene glycol-complex thickness estimated from Figure 2.

Sample locations	Charge density (equivalents/mol $O_{10}(OH)_2$) IV	Total	Source[1]	d(001) (Å)
Garfield, Washington	0.50	0.62	WP	16.66
Polkville, Mississippi	0.06	0.47	WP	16.77
Black Jack Mine, Idaho	0.52	0.50	WP	16.87
Otay, California	0.05	0.59	GG	16.86
Cheto, Arizona	0.07	0.49	GG	16.91
Montmorillon, France	0.20	0.43	GG	16.92
Wyoming, USA	0.14	0.38	GG	17.02
Umiat, Alaska	0.16	0.42	GG	17.13

[1] WP = Weaver and Pollard (1973), GG = Grim and Güven (1978).

https://doi.org/10.1346/CCMN.1980.0280601 Published online by Cambridge University Press

oming montmorillonite complex thickness is 16.88 Å (Cs) to 17.22 Å (NH_4). The relation between the cation and the complex thickness is not a simple one. Among the alkali cations, the complex thickness increases with the ionic radius of the interlayer cation, with the exception of Cs, the largest cation. In the alkaline earth group an inverse relationship holds true; the smallest cations give the thickest complexes. Generally, divalent cations give thinner complexes than monovalent cations: a strong inverse correlation exists between the ionic potential and the thickness of the ethylene glycol complex. This rule is not obeyed by Cs, Be, or Mg, the cations having the most extreme dimensions. The documented sequence is general rather than specific for the Wyoming smectite, as shown by three other samples investigated in K and Ca forms (Table 1).

The influence of humidity was checked in two ways: by equilibration of a Ca-Wyoming preparation overnight with saturated water vapor, and by solvation of Na-Wyoming preparation by a water-ethylene glycol mixture of 6:1 molecular ratio, both at room temperature. Lacking a controlled atmosphere diffractometer chamber, dynamic measurements were made. The positions of two reflections were measured, the first being repeated so that the average value reflected the complex thickness during the time required to record the second reflection. In both samples the thickness of the ethylene glycol complex increased to about 17.15 Å from their 50% RH values of 16.92 Å (Ca) and 17.00 Å (Na).

The set of ten Sr- and Na-illite/smectites (Table 1) represent ion-exchanged samples from a single bed a few meters thick and represent a diagenetic sequence (Środoń, 1976, 1979). The thickness of the ethylene glycol complex is relatively uniform in the whole sequence—only a minor decrease, correlated with growing degree of illitization, was observed. This behavior is consistent with the layer charge control on the thickness of the ethylene glycol complex; the layer charge of the smectite component of these mixed-layer minerals increases slightly with illite:smectite ratio (Środoń, unpublished data). On the other hand, the complex thickness can be quite different for other mixed-layer clays, as shown by the examples given in Figure 3 and Table 1. These samples were selected to represent clays of possibly diverse origin: 3R76 is a diagenetic product; the Arkansas and Zempleni clays are hydrothermal products; XIII was produced hydrothermally by treating Wyoming montmorillonite in 0.5 N KCl at 150°C for 4 months; and the K-Cheto, the K-Garfield, and the mixed-layer clays shown in Figure 3 were obtained by K-exchange of smectites.

The natural smectites studied represent essentially the complete range of layer charge density known among dioctahedral smectites (cf. Weaver and Pollard, 1973). Thus, it is anticipated that the thickness of the ethylene glycol complex of most natural (predominantly Na and Ca) dioctahedral smectites and illite/smectites, analyzed under room conditions, should fall within the 16.6-Å to 17.2-Å analytical range. The trioctahedral analogues (saponites) give a much larger range of thickness of two-layer ethylene glycol complexes (Suquet *et al.*, 1977), but these minerals do not tend to form mixed layers with illite (Eberl *et al.*, 1977).

CONCLUSIONS

The spacing of the two-layer ethylene glycol-clay complex of dioctahedral smectite varies between 16.5 and 17.3 Å depending on the layer charge density, the interlayer cation, the relative humidity, and, perhaps, some other factors. Because of the layer charge influence, no experimental conditions for producing a standard complex thickness can be found, so this variation must be taken into account in any illite/smectite identification procedure based on the ethylene glycol-clay complex. Neglecting the variation in the thickness of the complex can lead to as much as 30% error in estimating the smectite component of a mixed-layer illite/smectite mineral.

The three methods of identifying illite/smectites presented in this paper take into account the variation in thickness of the ethylene glycol complex and avoid the domain size effects. In addition, a method for quantifying the degree or ordering is also described. Experimental data on a number of natural and synthetic samples show that the differences in estimating the smectite component by the three methods are less than 5%.

The identification methods described are adequate for samples essentially free of discrete illite. Significant admixture of illite—common among natural clays—makes the methods useless because of peak interferences in the 26–27° and 42–48°2θ regions. A different approach must be developed for studying such materials.

The variation of the thickness of the ethylene glycol complex may presumably be important also in the identification procedures of other mixed-layer clays involving a smectite component, e.g., kaolinite/smectite minerals.

ACKNOWLEDGMENTS

This study was initiated in 1976, at the Department of Earth Sciences, Case Western Reserve University, Cleveland, Ohio, where the author was able to work due to the Fulbright-Hayes scholarship, and was completed in Poland, within the Academy of Sciences Program MR-I-16. I thank Drs. J. Hower and R. C. Reynolds for introducing me into the computer modeling of XRD patterns of clays, for letting me use their program, and for comments in the course of this work. Dr. B. Velde kindly supplied his synthetic smectites, and Dr. D. Eberl supplied samples of natural clays from the col-

https://doi.org/10.1346/CCMN.1980.0280601 Published online by Cambridge University Press

lection of R. E. Grim at the University of Illinois. J. Gierula modified the computer program. Dr. J. Hower significantly improved both English and construction of this manuscript. I thank Ms. Ellen L. Abell for the final typing of this manuscript.

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(Received 10 October 1979; accepted 19 June 1980)

Резюме—Толщина двух-слойного этиленгликолевого комплекса с диоктаэдрическим смектитом изменяется, при комнатных условиях, в пределах 17,3 и 16,5 Å, вследствие таких факторов как плотность заряда слоя, тип межслойного катиона, и относительная влажность. Неучет этой изменчивости может вызвать ошибку до 30% в оценке отношения смектит:иллит смешанно-слойных структур при использовании порошкового метода рентгено-структурного анализа. Были разработаны три метода для интерпретации картин результатов исследования гликолированного смешанно-слойного иллита/смектита порошковым методом рентгено-структурного анализа, которые учитывают изменчивость расположения слоев. Методы включают прием для количественного определения степени упорядочения. Кроме того, предложенные методы доводят до минимума ошибку, связанную с влиянием размера домена на положение отражений. Экспериментальная ошибка может быть меньше 5% или меньше 1% смектитовых слоев в зависимости от используемого метола при условии, что позиции пиков измерены с точностью ±0,02°2θ. [N.R.]

Resümee—Die Dicke eines Zweischicht-Äthylen-Glykol-Komplexes mit dioktaedrischen Smektiten variiert bei Raumtemperatur Zwichen 17,3 und 16,5 Å aufgrund von Faktoren wie Dichte der Schichtladung, Art des Zwischenschichtkations, und relative Feuchtigkeit. Eine Vernachlässigung dieser so hervorgerufenen Schwankung kann bei der Abschätzung des Verhältnisses von Smektit:Illit in Wechsellagerungsstrukturen mittels Röntgenpulverdiffraktometrie zu einem Fehler bis zu 30% führen. Es wurden drei Methoden für die Interpretation von Röntgendiffraktometeraufnahmen von mit glykol behandelten Illit/Smektit-Wechsellagerungen entwickelt, die die Variation des Schichtabstandes berücksichtigen. Diese Methoden beinhalten eine Methode für die Quantifizierung des Ordnungsgrades. Zusätzlich reduzieren die vorgeschlagenen Methoden den Fehler, der durch den Einfluß der Domänengröße auf die Peaklage herrührt, auf ein Minimum. Der experimentelle Fehler kann kleiner als 5% bzw. als 1% der Smektitlagen gehalten werden, je nach der verwendeten Methode, vorausgesetzt, daß die Peaklagen mit einer Genauigkeit von ±0,02°2θ gemessen werden. [U.W.]

https://doi.org/10.1346/CCMN.1980.0280601 Published online by Cambridge University Press

Résumé—L'épaisseur du complex glycol éthylène à 2 couches avec des smectites dioctaèdrales varie sous des conditions ambiantes entre 17,3 et 16,5 Å , à cause de facteurs tels que la densité de charge de couche, le genre de cation interfolaire, et l'humidité relative. Si l'on néglige cette variabilité, une erreur de 30% peut être introduite dans l'estimation à la diffraction poudrée aux rayons-X de la proportion smectite:illite de structures à couches mélangées. Trois méthodes qui tiennent compte de la variabilité de l'espacement de couches ont été développées pour l'interprétation de clichés de diffraction poudrée aux rayons-X d'illite/smectite glycolatée à couches mélangées. Les méthodes comprennent une technique pour quantifier le degré de rangement. De plus, les techniques proposées minimisent l'erreur due à l'influence de la taille du domaine sur les positions des réflections. L'erreur expérimentale peut être maintenue sous 5% ou sous 1% couches de smectite, dépendant de la méthode utilisée, à condition que les positions des sommets sont mesurées avec une exactitude de $\pm 0{,}02°2\theta$. [D.J.]

https://doi.org/10.1346/CCMN.1980.0280601 Published online by Cambridge University Press