X-RAY IDENTIFICATION OF RANDOMLY INTERSTRATIFIED ILLITE-SMECTITE IN MIXTURES WITH DISCRETE ILLITE

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ABSTRACT: Proportions of the component layers in randomly interstratified illite-smectites can be determined precisely in the presence of discrete illite if two reflections (at 15–16 and 31–32°2θ Cu Kα) are strong enough to be measured accurately. The method takes into account the variable thickness of the smectite-ethylene glycol complex and involves a correction for the interference from illite reflections.

Mixed-layer illite-smectite is a common mineral, occurring in diagenetically altered bentonites, hydrothermal alteration zones, fine-grained sediments, and soils. Bentonites and hydrothermal alteration products are usually either monomineralic or they contain minerals that can either be easily separated (e.g. quartz, biotite, feldspar), or do not interfere with the determination of illite-smectites (e.g. chlorite or kaolinite). Illite-smectites from such rocks can be identified precisely by the method worked out by Reynolds & Hower (1970) and corrected for variable thickness of the smectite-ethylene glycol complex (Środoń, 1980).

In soils and sediments, mixed-layer illite-smectite occurs almost always with discrete illite, and it is not possible to separate these two minerals mechanically. Most X-ray reflections from these two minerals interfere, making the methods of identifying pure illite-smectites useless, unless the illite admixture is small enough to be neglected (e.g. Perry & Hower, 1970).

Typically, the low-angle region of the XRD pattern of an ethylene glycol-treated and chlorite-free sample shows either a strong 10 Å peak with an ancillary low-angle 'tail', shoulder or minor peak, or separate 10 and 17 Å peaks. The former pattern results from a mixture of illite and ordered illite-smectite and the latter represents a mixture of illite and smectite or randomly interstratified illite-smectite. This interpretation is based on Reynolds & Hower (1970). In older publications, the 17 Å peak was identified as smectite, and the scattering between 10 and 17 Å ascribed to a mixed-layered clay.

It has been widely recognized that the randomly interstratified mixed-layer minerals are smectite-dominated and the ordered ones are illitic (Shutov *et al.*, 1969; Perry & Hower, 1970; Parachoniak & Środoń, 1973; Hower *et al.*, 1976; Środoń, 1976; Schultz, 1978; Hoffman & Hower, 1979). Based on the present author's experiences with illite-smectites in mixtures with illite, there is no universal identification approach applicable to the whole range of mixed-layering. The random and the ordered cases have to be considered separately. The aim of this paper is to present a technique suitable for a precise identification of randomly interstratified illite-smectites in mixtures with discrete illite.

Previous methods of Schultz (1978), Eslinger & Savin (1976) and Hoffman (1979) will also be discussed.

EXPERIMENTAL

When attempting to identify a mineral in a multicomponent mixture, the first step is to concentrate it as much as possible. Illite-smectite is the finest grained component of a rock, so the size-fraction used should be as fine as possible. Working with the finer size fractions has an additional advantage—improved orientation of clay particles, resulting in intense basal reflections on the XRD patterns. This phenomenon has been attributed by Roberson *et al.* (1968) to the abundance of aggregates in coarse fractions, and although these authors worked with smectites, in the present author's experience illite-smectites behave similarly. The peak intensity of an oriented mount of a <0.2 μm fraction is 4–6 times higher than that of a 0·5–2 μm fraction from the same monomineralic samples. A finer size separation, for instance at 0·1 μm, does not improve orientation significantly. For this reason, the <0.2 μm fraction, rather than the widely used <1 or <2 μm fractions, was adopted for routine work and it is recommended for identification of mixed-layer clay minerals in sedimentary rocks. Only in the rare instance of the rock being exceptionally rich in mixed-layer minerals is the use of coarser grain fractions satisfactory.

The natural materials described here were processed in the following way: 10–20 g of powdered shale or of dried and crushed clay were soaked overnight in 100 ml of sodium acetate buffer (Jackson, 1974), treated for 3–5 min with an ultrasonic probe and subjected to acetate buffer, H_2O_2, and citrate-dithionite treatments (*op. cit.*) as necessary. After these treatments, the material was washed with 1 N NaCl, excess salt being removed by centrifuging in distilled water and then by dialysis. The <0.2 μm fraction was separated in a centrifuge, and the suspension air-dried. 80 mg of clay was resuspended using ultrasonics in 4 ml of distilled water and the slurry was pipetted on to a glass slide.

Similarly, artificial mixtures were made of <0.2 μm pure fractions by dispersing 80 mg portions of weighed and mixed clays in 4 ml of distilled water using an ultrasonic probe for a few seconds. The use of such concentrated suspensions effectively prevents Na-smectite from swelling and thus excludes the possibility of the mechanical formation of mixed-layer minerals. Such a phenomenon was reported by Frey & Lagaly (1979) from very dilute suspensions of two differently charged smectites (see also Lagaly, 1981).

The identification methods are based on XRD patterns of ethylene glycol-solvated preparations. The arguments in favour of ethylene glycol instead of glycerol are given elsewhere (Šrodoń & Eberl, 1980). The ethylene glycol solvation technique, XRD operating conditions and the details of using the computer program of Reynolds & Hower (1970) are the same as reported in the previous paper (Šrodoń, 1980).

THE IDENTIFICATION TECHNIQUE

It has been shown recently that the thickness of the smectite-ethylene glycol complex varies in natural samples within the range of 16·6–17·2 Å (Šrodoń, 1980). This complicates the XRD identification procedure as, instead of three, there are four variables controlling the peak positions of illite smectites, i.e. (i) illite:smectite layer ratio; (ii) smectite-ethylene glycol complex thickness; (iii) domain (crystallite) size distribution; (iv) type and degree of ordering.

If there is no ordering—the random case considered herein—and the influence of the domain size distribution can be evaluated independently, two variables remain. Consequently, two peak positions have to be measured in order to determine precisely the proportions of the component layers. This approach is followed in this paper.

Fig. 1 presents examples of natural clays consisting of illite-smectite, discrete illite, and kaolinite. Both the proportions of illite and mixed-layer mineral, and the component ratio of the illite-smectite vary from sample to sample.

In all the cases shown, the methods utilizing the reflection between 26° and 27°2θ (Šrodoń, 1980) have to be ruled out, because of the complete coincidence of this reflection with the illite 003 peak. If the reflections at about 42–44° and 46–48°2θ are far apart (highly smectitic mixed-layer mineral), and the reflection at 45·3°2θ is small (low content of the discrete illite), the former reflections can be measured accurately (Fig. 1A), and their angular distance Δd_2 can be used for the precise determination of the illite:smectite ratio (*op cit.*). These measurements are possible only if the preparations are thick enough
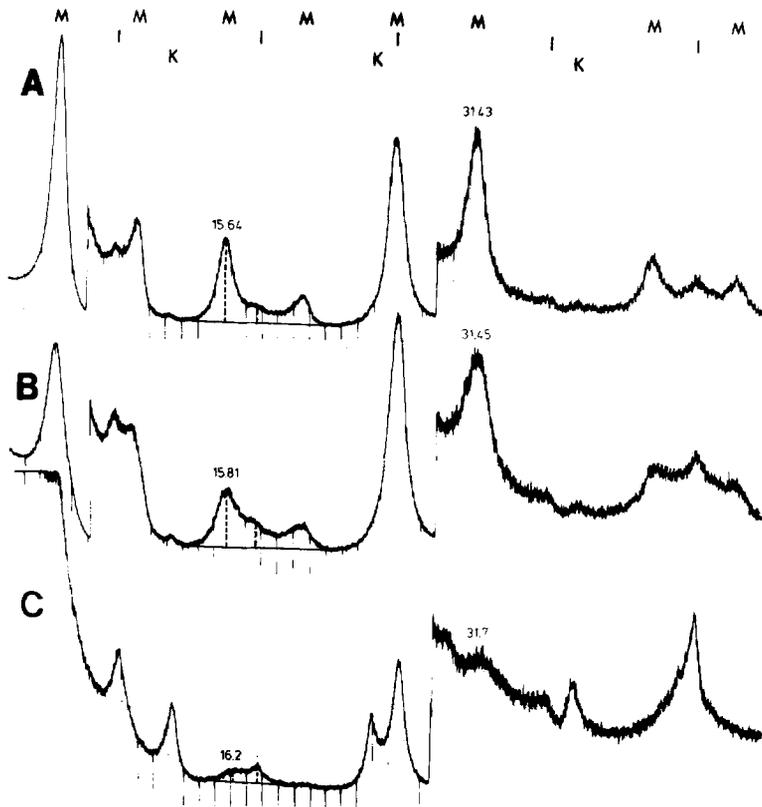

FIG. 1. XRD patterns of oriented preparations of <0·2 μm fractions of clays with different proportions of illite-smectite (M) and discrete illite (I). K = kaolinite. Illite-smectite in sample A can be identified by the Δd_2 method (Šrodoń, 1980). Samples B and C are suitable for identification by the method described in this paper. The non-coincident illite-smectite reflections, used in Fig. 2, are marked with their 2θ positions. The method of measuring peak heights, used in Fig. 3 (I_I/I_{I-S}), is also shown. A, B: from Miocene of SE Poland; C: from Jurassic of central Poland.

and well oriented, because the reflections in question are rather weak (those in Fig. 1 were recorded at 1000 cps).

In less favourable cases (Fig. 1B, C), it is impossible to measure Δd_2, but there are still two measureable reflections of illite-smectite: at about 15–16 and 31–32° 2θ. A plot of the theoretical positions of these two reflections, obtained from the computer-simulated XRD patterns of randomly interstratified illite-smectites is given in Fig. 2. The calculations, assuming domain thickness distributions of 1–8 layers and 1–14 layers, were made for ethylene glycol-smectite complex thicknesses of 16·6, 16·9, and 17·2 Å. A 16·6–17·2 Å range covers the values exhibited by natural smectites (Środoń, 1980), and so does the chosen range of the domain thickness distribution (Środoń, in preparation). Therefore, the distance between the lines representing 1–8 and 1–14 layer domain distributions in Fig. 2 depicts the maximum error due to the unknown domain thickness distribution. This error is <5% smectite component. To make the determination, the measured peak positions are plotted in Fig. 2; the percentage of smectite layers is estimated by interpolation between the solid lines and the dashed lines, the middle value being accepted.

For pure monomineralic mixed-layer clays, results obtained using this procedure are identical with those obtained from the two-peak techniques described previously (Środoń, 1980). The results for illite-smectites mixed with illite are systematically lowered due to the displacement of the analytical reflections by the interference from neighbouring 002 and 003 illite peaks. It can be anticipated that this error should increase with an increasing proportion of discrete illite (stronger illite peaks) and for more illitic mixed-layer minerals (broader reflections and the 15–16° 2θ reflection closer to the illite 002—see Reynolds & Hower, 1970).

The interference error was evaluated experimentally using artificial mixtures of an illite with pure illite-smectites of a known layer ratio. The data on the mixtures and on the pure mixed-layer components are given in Table 1. Fig. 3 shows the plot for evaluating the interference error constructed from these data. Having an approximate percent smectite (% S) obtained from Fig. 2 and an intensity ratio I_I/I_{I-S}. (illite 002 and the mixed-layer
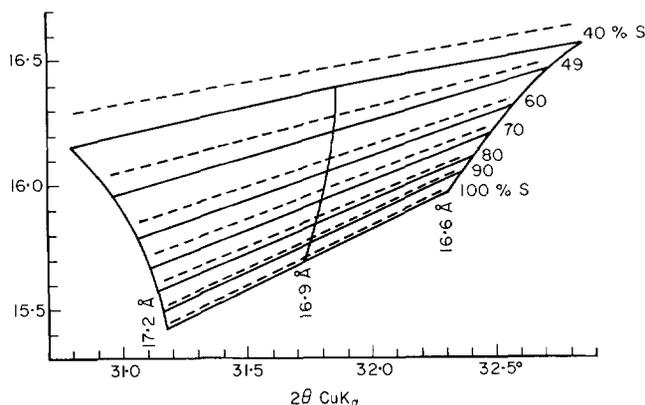

Fig. 2. Plot of computer-calculated peak positions (2θ CuK$_\alpha$) for measuring percent smectite (% S) in illite-smectites occurring with discrete illite. Solid lines: 1–8 layers domain size, dashed lines: 1–14 layers domain size. Steep curved lines represent selected thicknesses of smectite-ethylene glycol complex.

TABLE 1. XRD data for <0·2 μm fractions of smectite and randomly interstratified illite-smectites—as pure samples and also in artificial mixtures with the <0·2 μm fraction of an illite

Expanding mineral	Weight % in mixture	% S of pure sample	Analytical reflections °2θ CuKα		% S from Fig. 2	I_I/I_{I-S}*	Valley/ 17Å peak
Wyo[1]	100	100					0·06
	50		15·70	31·69	97	0·30	0·18
	30		15·67	31·61	95	0·64	0·24
	10		15·65	31·48	90	2·14	0·37
2M9[2]	100	88					0·15
	50		15·79	31·59	80	0·58	0·39
	30		15·83	31·58	75	1·26	0·52
3R83[2]	100	75					0·30
	50		15·98	31·72	66	0·67	0·50
3R80[2]	100	67					0·29
	70		16·04	31·62	59	0·42	0·73
	50		16·10	31·67	56	0·74	0·75
	30		16·13	31·52	53	1·50	0·86
37H[3]	100	46					1·00
	50		16·53 diffuse		?	1·32	1·00

* Peak height ratio of illite 002 and illite-smectite reflection at 15–16° 2θ (see Fig. 1).

[1] From Wyoming bentonite CMS-SWy-1 (Source: Clay Mineral Repository); [2] from Upper Silesian Carboniferous bentonites (author's materials); [3] from Ordovician Kinnekulle bentonite supplied by Dr A. M. Byström-Brusewitz).
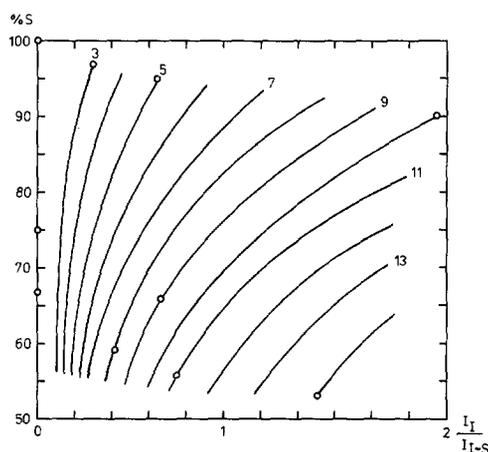

FIG. 3. Empirical plot for correcting % S obtained from Fig. 2 for interference from illite reflections. The intensity ratio I_I/I_{I-S} (Fig. 1) and uncorrected value of % S is plotted on the figure and ΔS is read from the curves. ΔS is then added to % S. The open circles are data points from Table 1 used to construct the graph.

reflection at 15–16° 2θ) it is then possible to read from the curves the ΔS value to be added to % S in order to correct for the interference error.

Fig. 1(C) will be used to illustrate the identification procedure. Analytical reflections are at 16·20° and 31·70° 2θ. These, when plotted in Fig. 2, give about 50% S. The intensity ratio of the 17·7° and 16·2° reflections measured as peak heights from Fig. 1(C) is 1·75. From Fig. 3 the correction ΔS = 15% is obtained, leading to a final estimate of 65% S.

Fig. 1(C) is an extreme example: if the mixed-layer mineral content is even smaller, analytical reflections cannot be measured. If it is bigger, as in Fig. 1 (B), the positions of the reflections can be measured more accurately ($\pm 0·01°$ 2θ), allowing a more precise determination of % S.

It is tempting to try to use I_I/I_{I-S} also for quantitative estimation of the amount of an expanding mineral vs. discrete illite in a sample, because having identified the mixed-layer mineral it should then be possible to correct for the variation of intensity as a function of the illite:smectite layer ratio. Preliminary results are discouraging, however. Fig. 4 shows XRD patterns of two pure smectites mixed 1:1 with the same illite. Cheto smectite reflections are about three times weaker than Wyoming smectite reflections when compared with the illite reflections. This difference, which probably results from differences in orientation (R. C. Reynolds, personal communication), is so big that X-ray quantification of clay minerals cannot be considered reliable unless the degree of orientation of each mineral is determined separately.

COMPARISON WITH PREVIOUS METHODS

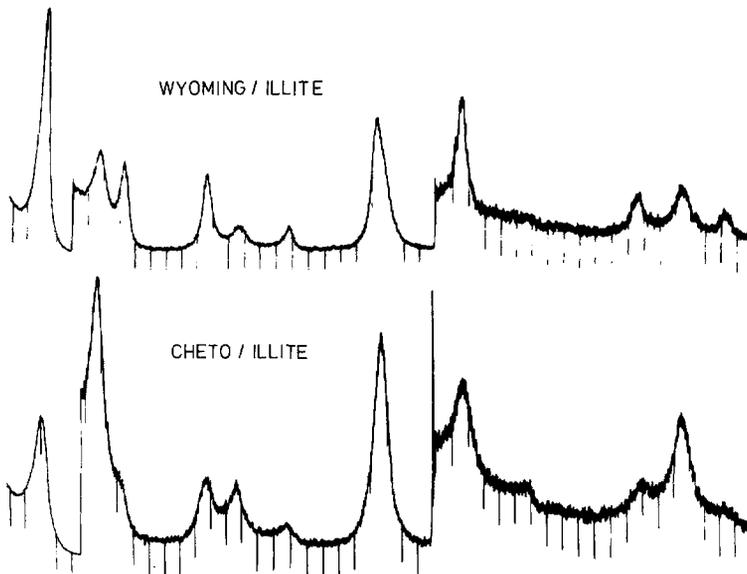A technique for identifying mixed-layer minerals in mixtures was proposed by Schultz

WYOMING / ILLITE

CHETO / ILLITE

Fig. 4. XRD patterns of oriented preparations of 1:1 mixtures of <0·2 μm fractions of two smectites and the same illite. Note differences in relative intensities due mainly to different degree of orientation of the smectites.

(1978). It consists of measuring the intensities of basal reflections from glycolated and heated preparations and in reading % *S* from an empirical graph calibrated by the Reynolds & Hower (1970) method. The error shown in the graph is $\pm 10\%$, and the error due to the unknown smectite-ethylene glycol complex thickness (Šrodoń, 1980) must be added to it.

Another method, also based on Reynolds & Hower (1970) was proposed by Eslinger & Savin (1976) and Hoffman (1979). The intensity ratio of the 17 Å peak and the 'valley' on the low-angle side of this peak has to be measured, and % *S* is read from a working curve, prepared from the data from computer-simulated XRD patterns.

The valley:peak ratio depends strongly on the domain size distribution, the difference between 1–8 and 1–14 layers domain distributions accounting for a 10% error (Šrodoń, in preparation). The valley:peak ratio is also different for a pure mineral and for a mixture containing it. Using the data in Table 1 it was found that the resulting error can be as high as 30% *S* if the contribution of the expanding mineral is small. For these reasons, the valley:peak ratio allows only a rough identification of a mixed-layer mineral in mixtures.

The accuracy of measuring % *S* by the method described in this paper is better than 5% if the peak positions are measured with an accuracy of $0 \cdot 01° 2\theta$. The error results from the unknown domain size distribution, and effects the values obtained both from Figs 2 and 3. Fortunately, these errors tend to cancel out. For example, an unknown but extremely fine domain size will result in overestimation of % *S* in Fig. 2 but underestimation of ΔS in Fig. 3.

The method is applicable as long as the analytical reflections are distinct enough to be measured. It may not be possible if the reflections are very diffuse (soil minerals), or if the amount of an expanding mineral in the mixture is small. Pure smectite can be identified in amounts as low as 10%. At the other end of the randomly mixed-layered series it may be difficult to identify precisely 40–45% *S* mineral in quantities as high as 50% of a sample (Table 1) because at this illite:smectite layer ratio the 31–32° 2θ peak becomes weak and diffuse.

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RÉSUMÉ: Les proportions des feuillets composant une illite/smectite interstratifiée au hasard, peuvent être déterminées avec précision en présence d'illite pure si deux réflexions sont suffisamment fortes pour qu'elles puissent être mesurées avec précision (à 15–16 et 31–32°2θ CuK$_\alpha$). La méthode tient compte de l'épaisseur variable du complexe smectite-éthylène glycol et utilise une correction de l'interférence due aux réflexions de l'illite.

KURZREFERAT: Die Anteile der Schichtkomponenten von unregelmäßig wechselgelagerten Illit-Smectiten lassen sich in Gegenwart von Illit genau bestimmen, wenn zwei Reflexe (bei 15–16 und 31–32°2θ, CuK$_\alpha$) deutlich genug sind, um genau gemessen werden zu können. Die Methode berücksichtigt die variable Dicke des Smectit-Ethylenglycol-Komplexes und beinhaltet eine Korrektur für die Interferenzen von Illitreflexen.

RESUMEN: La proporción de los diferentes componentes de un mineral interestratificado al azar ilita-esmectita puede ser determinada exactamente en presencia de cantidades discretas de ilita si dos reflexiones (a 15–16 y 31–32°2θ CuK$_\alpha$) son lo suficientemente fuertes para ser medidas exactamente. El método se basa en el espesor variable del complejo esmectia-etilenglicol e incluye una correción por la interferencia de las reflexiones de la ilita.