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SOME NATURALLY OCCURRING ILLITE–SMECTITE INTERSTRATIFICATIONS

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Abstract—Two different types of interstratified illite–smectite are found in a section of Paleozoic sediments in the Negev, Israel. One of these is detectable only by a decrease in peak width and a concomitant increase in symmetry of the 10 Å peak on glycolation. This material is regarded as illite, randomly interstratified with about 20 per cent expanding layers.

INTRODUCTION

THE CRYSTALLINITY of illite or degraded mica has been used as a measure of the extent of diagenesis in argillaceous sediments and of the degree of metamorphism in regions of low grade metamorphism (e.g. Dunoyer de Segonzac *et al.*, 1968). The criteria applied for characterizing the crystallinity of illite differ: Weaver (1960) used the ratio of the X-ray intensity above background at 10 and 10·5 Å, while Dunoyer de Segonzac *et al.* measured the peak width at half height under controlled experimental conditions.

In a recent study of Paleozoic sediments from the Negev, Israel (Heller and Nathan, 1971) it was found that the diffraction maximum at about 10 Å was frequently asymmetrical, falling off more gradually on the low angle side. On glycol treatment the symmetry of the 10 Å peaks is considerably increased. An additional diffraction maximum at lower values of θ may or may not appear. An increase in sharpness and symmetry of 10 Å peaks on glycol treatment was recently also observed by Triplehorn (1970), who noted that this effect is not accompanied by a distinct increase in intensity at any particular higher spacing.

In view of the current confusion about the nature of illite and the criteria for measuring its crystallinity it seemed pertinent to investigate these observations in greater detail.

EXPERIMENTAL

Oriented samples of the clay fractions in air-dried, glycolated and heat-treated states were scanned automatically on an X-ray diffractometer using CuK_α radiation and a scanning speed of 1° per min. In addition, some of the peaks were investigated in greater detail by manual point-by-point scanning.

RESULTS

Figures 1 and 2 show two sets of diffraction patterns; sample TW834* (Fig. 1a) gives rise to a broad asymmetrical peak at approximately 10 Å before glycolation, and to a more symmetrical peak at 10 Å together with an additional peak at about 12·6 Å after glycolation (Fig. 1b). With sample TW1675* a similar asymmetrical 10 Å peak is observed before glycolation (Fig. 2a), but on glycolation this becomes more symmetrical, without the appearance of an additional peak (Fig. 2b). On heating at 110° and 200°C respectively for 48 hr a single peak at about 10 Å is observed with both samples.

Figures 3a–d show intensity curves obtained by point-by-point counting of air-dried, glycolated and heated specimens of sample TW1675. To facilitate direct comparison, the background was subtracted at each point and the peaks were normalized to give the same maximum intensity.

Figures 4a–d show corresponding normalized curves corrected for the Lorentz-polarization and structure factors, i.e. $I(2\theta)_{cor.} = I(2\theta)_{obs.}/F^2(2\theta)\,LP(2\theta)$. The choice of the appropriate Lorentz-polarization factor (LP) for an oriented aggregate is debateable. Two sets of curves were therefore

*The samples were kindly provided by T. Weissbrod of the Israel Geological Survey.

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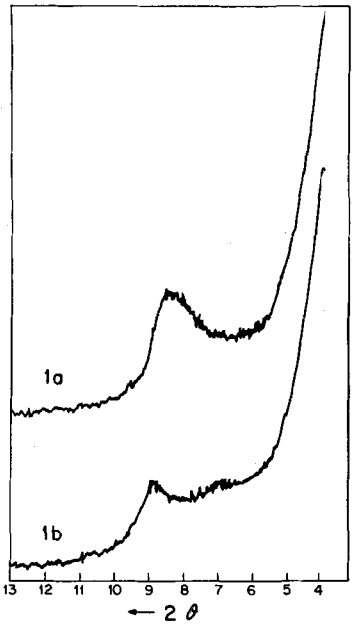


Fig. 1. Diffractometer trace of sample TW834, (a) air-dried, (b) glycolated.

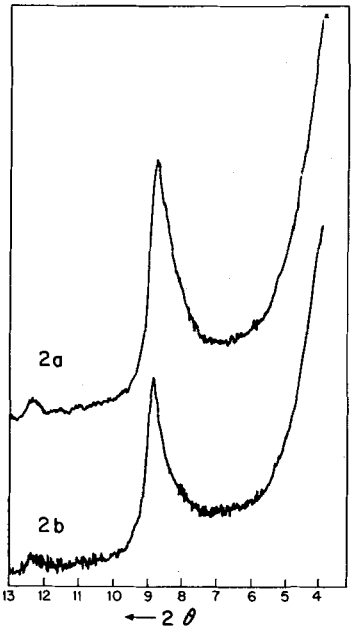


Fig. 2. Diffractometer trace of sample TW1675, (a) air-dried, (b) glycolated.

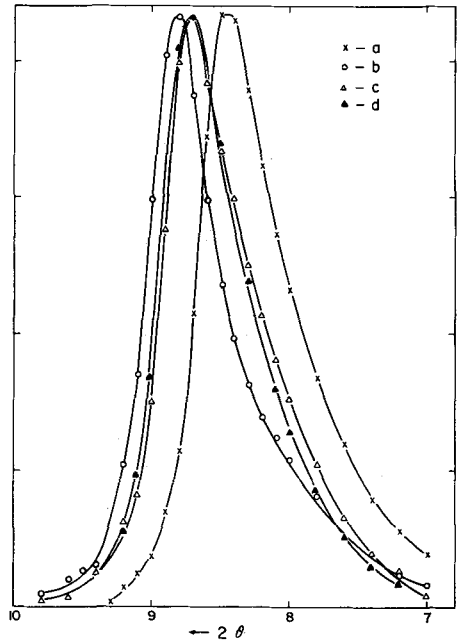
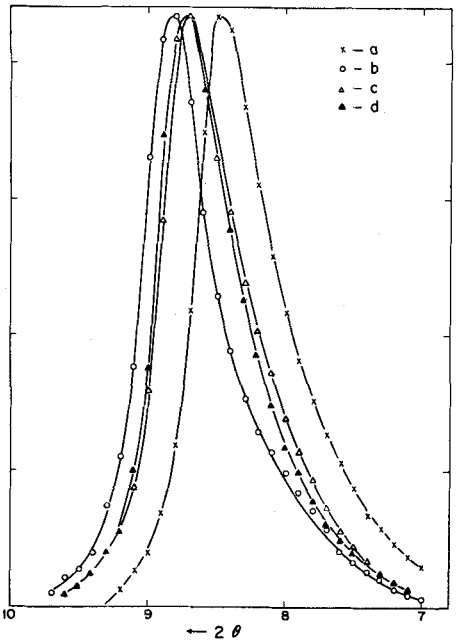


Fig. 3. Intensities obtained by point-by-point counting, subtraction of background and normalizing of sample TW1675, (a) in an air-dried state, (b) glycolated, (c) heated at 110°C, and (d) heated at 200°C.



Figs. 4a–d. Derived from curves 3a–d by dividing by the appropriate values of F^2LP (single crystal).

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calculated, applying the correction factors for powder and single crystals respectively. Since the peak positions and line profiles of corresponding traces do not differ appreciably, only one set of curves is presented, namely that based on single crystal corrections. The structure factor (F) was calculated at each point, assuming $d(001) = 10$ Å and the following structural units:

Type of atom	No. of atoms	Atomic coordinates (Å)
O	6	3·28
Si	4	2·68
O	6	1·07
Al	2	0
K	0·7	5·0

i.e. tetrahedral and octahedral substitution and the presence of interlayer water and glycol molecules were neglected. An average potassium occupancy of 0·7 atoms per unit cell was assumed.

DISCUSSION

The two samples described are typical of specimens from the entire Paleozoic section studied. The first (TW834) is clearly composed of a mixture of illite or fine-grained mica and randomly interstratified illite–smectite. The illitic component gives rise to a maximum at 9·9 Å, while the 12·6 Å peak obtained on glycolation corresponds to an interstratification of illite and expanding clay. Completely randomly interstratified 17 and 10 Å material does not cause any diffraction maxima between 17 and 10 Å (Reynolds and Hower, 1970). It appears, therefore, that the interstratified material is composed of partially ordered 10 and 17 Å layers, although the presence of some layers of different spacing cannot be excluded. Since no higher orders of reflexion were detected, the identity of the randomly interstratified material could not be unequivocally determined.

On routine examination sample No. TW1675 (Fig. 2) would probably be characterized as illite or degraded mica. However, it is apparent from the figures that on glycol treatment the ~ 10 Å peak characteristic of the air-dried material becomes considerably narrower and more symmetrical and is shifted to higher values of θ. Heating the air-dried samples at 110° and 200°C respectively also causes a shift in peak position and a progressive decrease in the width and asymmetry of the peak, but the changes are less pronounced than those produced on glycolation.

The asymmetry may be expressed by the ratio $R = (2\theta_2 - 2\theta)/(2\theta - 2\theta_1)$, where θ is the Bragg angle corresponding to the diffraction maximum and $2\theta_1$, $2\theta_2$ are the angles at which the intensity of the line profile falls to $1/e$ of the peak value on the low and high angle side respectively. The values of R, together with some other features of the line profiles, are summarized in Table 1. The 10 Å peak of a sample of mica, observed under the same experimental conditions, is much narrower than the peaks of the clay material under discussion, but is also asymmetrical, confirming that some asymmetry of the line profile is intrinsic in the experimental conditions (for detailed discussion see Wilson, 1963). Conclusions can therefore be based only on comparison of asymmetries and not on their absolute values.

The phenomena observed can be interpreted if the 10 Å peak is assumed to be composite, comprising maxima due to illite and randomly interstratified illite–smectite. The illite peak is not affected by the various treatments, while the peak due to the illite–smectite mixtures is sensitive to the experimental conditions. In the air-dried state the maximum lies on the low angle side of the 10 Å peak, corresponding to interstratification of 10 Å with 12·6 and/or 15 Å layers. On heating at 110° or 200°C most of the layers collapse to 10 Å, but the width and asymmetry of the diffraction maxima indicate that some interlayer water remains. Glycolation causes a shift of the maxima to higher angles. If interstratification is completely random

Table 1. Some characteristic features of the line profiles

	Intensities corrected for background and normalized (curves Fig. 3)			Corrected and normalized intensities divided by the appropriate F^2LP factors (Curves Fig. 4)		
Sample treatment	Peak position (°2θ)	Peak width at 1/e maximum(°)	R*	Peak position (°2θ)	Peak width at 1/e maximum(°)	R*
Air dried	8·46 ± 0·02	0·96 ± 0·01	0·41 ± 0·04	8·46 ± 0·02	0·92 ± 0·01	0·43 ± 0·04
Glycolated	8·82 ± 0·02	0·82 ± 0·01	0·58 ± 0·05	8·83 ± 0·02	0·80 ± 0·01	0·57 ± 0·05
Heated 110°C	8·72 ± 0·02	0·96 ± 0·01	0·41 ± 0·04	8·72 ± 0·02	0·92 ± 0·01	0·42 ± 0·04
Heated 200°C	8·73 ± 0·02	0·92 ± 0·01	0·51 ± 0·04	8·73 ± 0·02	0·87 ± 0·01	0·47 ± 0·04

*For a definition of R see text.

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and the expanding component constitutes no more than about 30 per cent of the mixture, $001_{10Å}$/$002_{17Å}$ interaction will cause the peak at approximately 10 Å to shift to higher angles and no additional lower angle diffraction maxima will appear (Reynolds and Hower, 1970). The peak actually observed may thus be attributed to superposition of a 10 Å peak assigned to illite or degraded mica and a peak at a somewhat higher angle due to $001_{10Å}/002_{17Å}$ interaction of interstratified illite–smectite.

It is difficult to simulate the changes in profile of the composite 10 Å peak theoretically, since the exact chemical composition of the individual components is unknown. Comparison of the observed diffraction effects with those calculated by Reynolds and Hower suggests that the expanding component does not exceed 20 per cent. According to Reynolds and Hower, naturally occurring illite–smectites of less than 35–40 per cent expandability have partially ordered interstratification. The present observations indicate that this does not apply to the Paleozoic sediments typified by sample TW 1675. It is possible that interstratification of this kind may, in fact, occur more commonly, but escapes detection on routine examination.

CONCLUSIONS

Detailed analysis of the 10 Å region of X-ray patterns derived from Paleozoic clays from the Negev showed that the peaks are composite, even when routine examination indicated the presence of a single 10 Å mineral. Two different types of clay mixtures could be distinguished: both contained illite or degraded mica as a principal constituent, associated with some interstratified illite–smectite. However, while in one series of samples the interstratification is completely random, in the other some short-range order seems to prevail.

The difference in type of interstratification may reflect either different provenance of the parent material or response to different post-depositional effects. It must be taken into consideration in any attempt to correlate clay mineralogy with environmental conditions.

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Résumé—Deux types différents d'interstratifiés illite–smectite ont été trouvés dans une coupe des sédiments paléozoiques dans le Néguev (Israël). L'un d'eux est seulement détectable par une diminution de la largeur de raie et une augmentation concomitante de la symétrie de la raie à 10 A après traitement au glycol. Ce matériau est considéré comme une illite interstratifiée au hasard avec environ 20% de réseau gonflant.

Kurzreferat—In einem Abschnitt von paleozoischen Ablagerungen im Negev (Israel) wurden zwei verschiedene Illit–Smektit Wechsellagerungen gefunden. Ein derselben ist nur durch eine Abnahme der Linienbreite und eine begleitende Zunahme in der Symmetrie des 10 Å Linienprofils bei Glykolierung erkennbar. Dieses Material wird als Illit, unregelmässig zwischengelagert mit etwa 20% quellungsfäehigen Schichten angesehen.

Резюме — В Негеве, Израэль, в одном участке Палеозойских отложенй, найдены два различных типа впластования иллита-смектита. Один из них обнаруживается только благодаря уменьшению пиковой ширины и сопуствующим увеличением симметрии пика 10 Å при обработке гликолем. Считают, что это иллит, беспорядочно напластованный растянутыми примерно на 20% слоями.

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