

26. MIXED-LAYER ILLITE/MONTMORILLONITE CLAYS FROM SITES 146 AND 149

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INTRODUCTION

The purpose of this report is to describe the clay mineral composition of twenty-four samples from Sites 146 and 149, Leg 15, DSDP. As the predominant clay mineral in these samples is a mixed-layer illite/montmorillonite, a considerable part of the report is devoted to discussing and applying recently proposed methods for characterizing these types of clay minerals. It is hoped that in future investigations of clay minerals from cores of deep-sea sediments, attempts will be made to describe mixed-layer clays whenever they are present, as it is believed they may yield clues concerning the origin and diagenetic history of the sediment.

PROCEDURE

In order to separate the clay mineral fraction for X-ray diffraction studies, samples were prepared as follows:

- 1) Washed free of salts by centrifugation;
- 2) Treated with an ultra-sonic probe for 10 minutes to disaggregate completely;
- 3) $<2\mu$ fraction separated by centrifugation; and
- 4) Oriented clay aggregates prepared by allowing clay-water suspensions to dry at room temperature on glass slides.

X-ray diffraction data were obtained with a Philips diffractometer. Filtered Cu K_{α} radiation (40 kv, 20 ma) was used; scanning speed was 2 degrees per minute. Each sample was scanned in the air-dry state, after glycol solvation by the vapor technique and after heating to 550°C.

RESULTS

Figures 1 and 2 show diffractometer tracings or glycol-solvated oriented clay aggregates from samples taken from Sites 149 and 146. These representative patterns illustrate the most obvious change in clay mineral composition: kaolinite and illite decrease in abundance with depth. Figure 3 shows a plot of the ratio of the 10Å peak height (001 illite) to the 17Å peak height (001 expandable clay) against core depth in meters. There is a very abrupt decrease in the amount of illite with respect to montmorillonite at a depth of about 90 meters from the sediment surface. The kaolinite/illite ratio stays rather constant in all the samples studied down to a depth of about 400 meters. Thus, kaolinite sharply decreases in abundance relative to montmorillonite at about 90 meters also.

There has been no attempt to make precise quantitative determinations of the amounts of the individual clay minerals for each of the samples because of the numerous problems involved, especially when mixed-layer clays are present, as is the case here. Quantitative estimates of clay mineral abundances based on a scheme similar to that

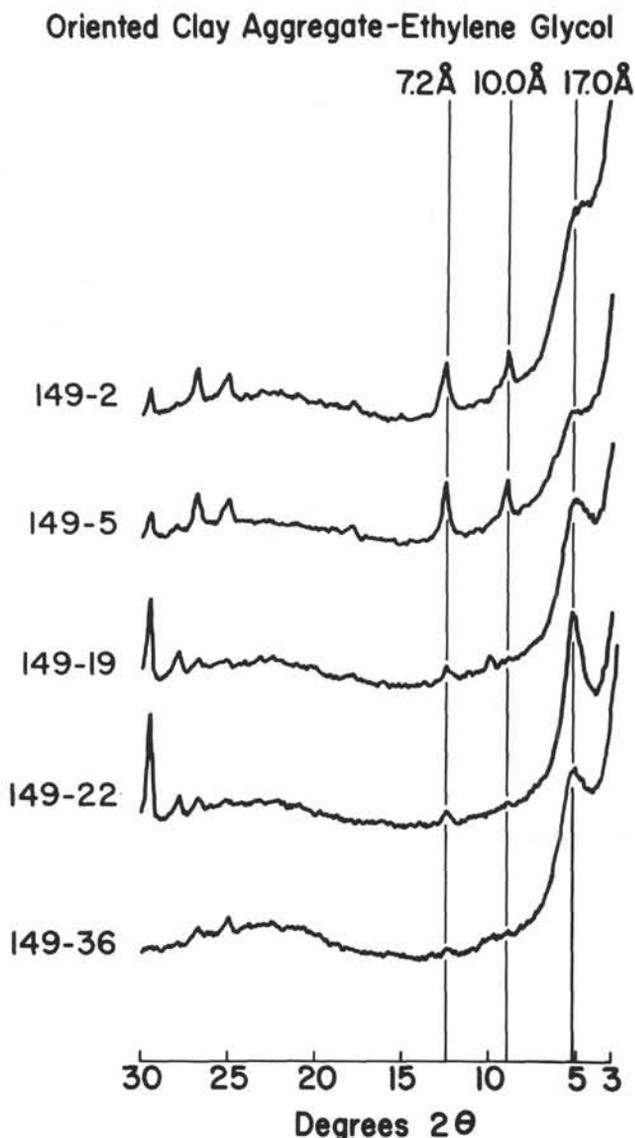


Figure 1. X-ray diffraction patterns of clays from Site 149.

proposed by Johns, Grim and Bradley (1954) were made. Samples from the uppermost 170 meters of Site 149 contain on the average 40 to 60 per cent mixed-layer illite/montmorillonite, 20 to 30 per cent illite, 15 to 25 per cent kaolinite, and 5 to 10 per cent chlorite. Samples below about 170 meters in Sites 149 and 146 contain 80 to 90 per cent mixed-layer illite/montmorillonite, approximately equal amounts of kaolinite and illite, and sometimes, small quantities of chlorite. The presence of chlorite was determined after heating to 550°C. Figures 4 and 5 show that

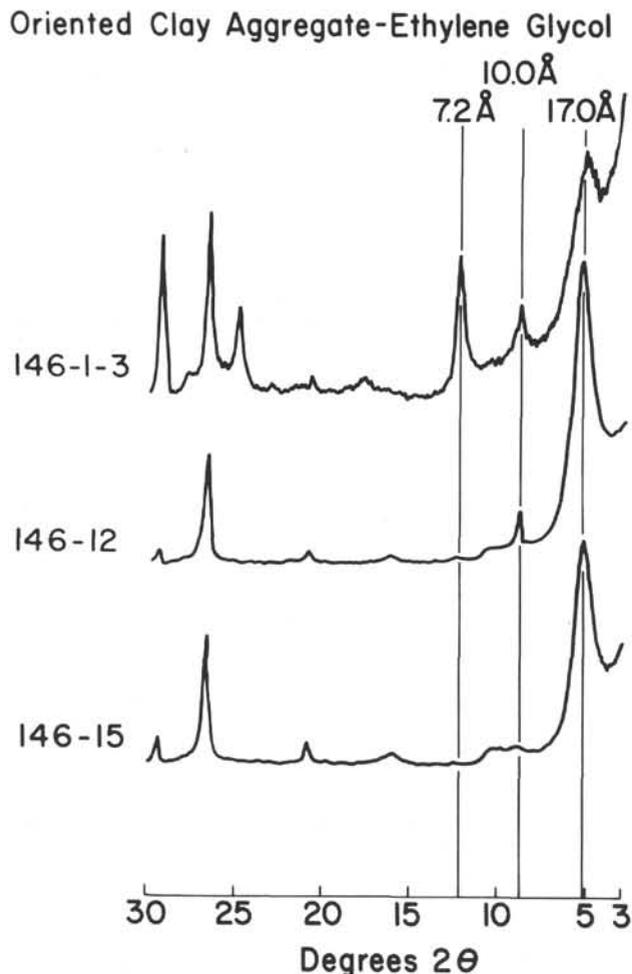


Figure 2. X-ray diffraction patterns of clays from Site 146.

small peaks at 14\AA and 7\AA still persist, indicating the presence of chlorite. The decrease or apparent loss of intensity of the 7\AA peak after heating indicates that kaolinite, which is destroyed at 550°C , is generally much more abundant than chlorite in these samples. The 10\AA peak after heating to 550°C shows that the expandable layers in the mixed-layer illite/montmorillonite are fully collapsed. That none of the 17\AA expandable phase in any of the samples collapsed to spacings below 10\AA on heating indicates the presence of a mixed-layer clay mineral rather than a pure montmorillonite phase which would collapse to a sharp 9.4\AA spacing on heating.

The rather broad and diffuse diffraction maximum at approximately 17\AA for many of the glycolated samples strongly suggested the presence of a mixed-layer phase. Heating to 550°C showed there were few or no interstratified chlorite layers in the mixed-layer clay. Thus, the mixed-layer clay appeared to be a simple random interstratification of illite and montmorillonite layers. Mixed-layer illite/montmorillonite is a common constituent of pelitic sediments and sedimentary rocks (Weaver, 1956; Perry and Hower, 1970), and a method recently proposed by Reynolds and Hower (1970) can be used to characterize

these kinds of minerals. However, in order to apply their methods, it is necessary to obtain several orders of the basal reflections. This presented a problem because the $<2\mu$ fractions from these samples did not give enough basal reflections. Very fine fractions ($<0.05\mu$ equiv. spherical diam.) were collected from some of these samples in order to obtain better preferred orientation of the thinner (more plate-like) clay particles. Size fractionation has been shown to be an effective means of attaining excellent preferred orientation of montmorillonite particles, which then afford a much higher number of basal diffraction maxima than is normally the case for particles settled from $<2\mu$ size fractions (Roberson, Weir, and Woods, 1968). The quality of the X-ray data is also improved because the fine fractions contain considerably smaller quantities of non-clay minerals and coarser clay particles, such as kaolinite and illite, than do the $<2\mu$ fractions.

In most cases, oriented clay aggregates from the very fine fractions gave X-ray diffraction patterns with several basal orders. Figures 6 and 7 show differences between X-ray diffraction patterns of $<2\mu$ fractions and those obtained from the very fine fractions. It can be seen that the relative intensities of all basal reflections are much increased for the clay aggregates from the finer size fractions. The broad diffraction maximum at 16.3 to 16.5 degrees (5.4\AA) which precedes the 5.0\AA maximum (002 for discrete illite) in samples 149-14 and 149-16 shows that the mixed-layer material has about 50 to 60 per cent expandability. That is, 50 to 60 per cent of the layers in the mixed-layer crystallites are fully expanded to 17\AA with ethylene glycol; the other 40 to 50 per cent do not expand with ethylene glycol and have a 10\AA periodicity. Table 1 shows peak positions ($\text{Cu K}\alpha$) and d-values for some reflections of illite-(glycol) montmorillonite. The broad diffraction maximum, referred to above, represents a combination of the 002 reflection for illite and the 003 reflection for the interlayered glycol-montmorillonite. The d-spacings and relative intensities of all the basal reflections from these two samples are in very good agreement with the values calculated by Reynolds and Hower for mixed-layer illite-montmorillonite with 50 to 60 per cent expandability shown in Perry and Hower's study. The d-spacing of the 001 peak in both these samples is slightly lower than the 17\AA d-spacing of Reynolds and Hower's calculated 001 diffraction profiles of mixed-layer illite/montmorillonite. This lower d-spacing may indicate the presence of a small number of interstratified chlorite layers or possibly vermiculite-like layers.

Only a few of the samples were fractionated because this is such a time-consuming operation, and also because many of the samples were still partially flocculated even after thorough washing and addition of deflocculating agents. However, the broad and diffuse shape of the 001 peaks in the diffraction patterns of the samples taken from the uppermost 170 meters in Site 149 is a strong indication that the clays are mixed-layered with an expandability probably in the 50 to 60 per cent range. About 150 to 200 meters below the sediment surface at Site 149, the mixed-layer illite/montmorillonite becomes about 80 per cent expandable. Except for one or two exceptions (e.g. 149-39 shown in Figure 8) the mixed-layer clays appear to

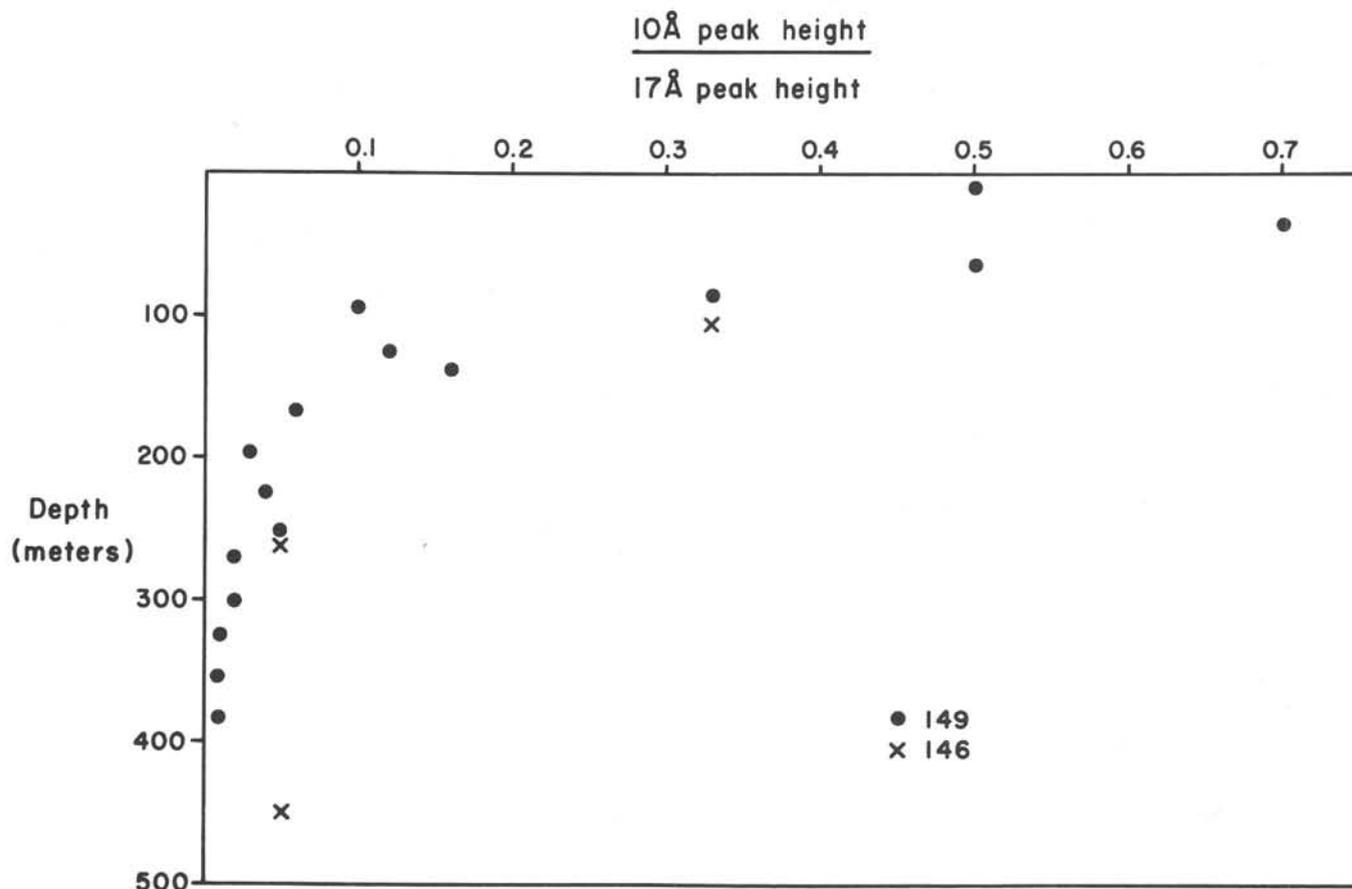


Figure 3. 10\AA (001 Illite)/ 17\AA (001 Expandable Clay) versus depth.

show about the same degree of expandability to the bottom of the hole.

Mixed-layer illite/montmorillonite makes up 90 per cent of the clay fraction from all the samples studied from Site 146 (with the exception of 146-1-3 which is at a depth of 106 meters). The clay fraction of seven samples from Site 146 between 476 meters and 575 meters below the sediment surface is composed of illite/montmorillonite, which has a uniform expandability of about 80 per cent. Figure 9 shows a diffraction pattern of a typical mixed-layer illite/montmorillonite of 80 per cent expandability.

DISCUSSION

Whether the pattern of changes in clay mineral composition with depth for these cores is representative of, or similar to, the clay mineral distribution for other cores in the Caribbean is still not known. Studies of clays from other cores from the Caribbean as well as further studies of clays from DSDP cores in adjoining areas, must be carried out before it is known how much significance can be attached to the observations reported here. Nevertheless, the changes in the clay mineralogy observed in this study can be tentatively evaluated in terms of their possible geological significance.

Kaolinite and discrete illite in these samples (not including biotite) are most likely detrital clay minerals. The sharp increase in the abundance of these minerals in the

uppermost 100 meters of sediment (Early to Mid-Pliocene age and younger) indicates that terrigenous sedimentation was a much more dominant feature than during the earlier part of the Tertiary. There is a rough parallelism in time between this change and the change in the character of the mixed-layer illite/montmorillonite. The mixed-layer illite/montmorillonite in the uppermost 170 meters has only 50 to 60 per cent expandability. The mixed-layer illite/montmorillonite in samples below 170 meters in Sites 149 and 146 has a uniform expandability of about 80 per cent. Perhaps this suggests that some or all of the clays of lower

TABLE 1
Peak Positions (Cu K α) and d-values for some Reflections of Illite- (glycol) Montmorillonite^a

Percent expandable	Randomly interstratified			
	Refl. (001) ₁₀ /(002) ₁₇		(002) ₁₀ /(003) ₁₇	
	2 θ	d(\AA)	2 θ	d(\AA)
0	8.68	10.18	17.65	5.02
10	8.80	10.04	17.50	5.06
20	8.92	9.91	17.19	5.15
30				
40	9.43	9.37	16.58	5.34
60	9.91	8.92	16.15	5.48
80	10.17	8.69	15.87	5.58
100	10.40	8.50	15.78	5.61

^aCalculated by Reynolds and Hower (1970).

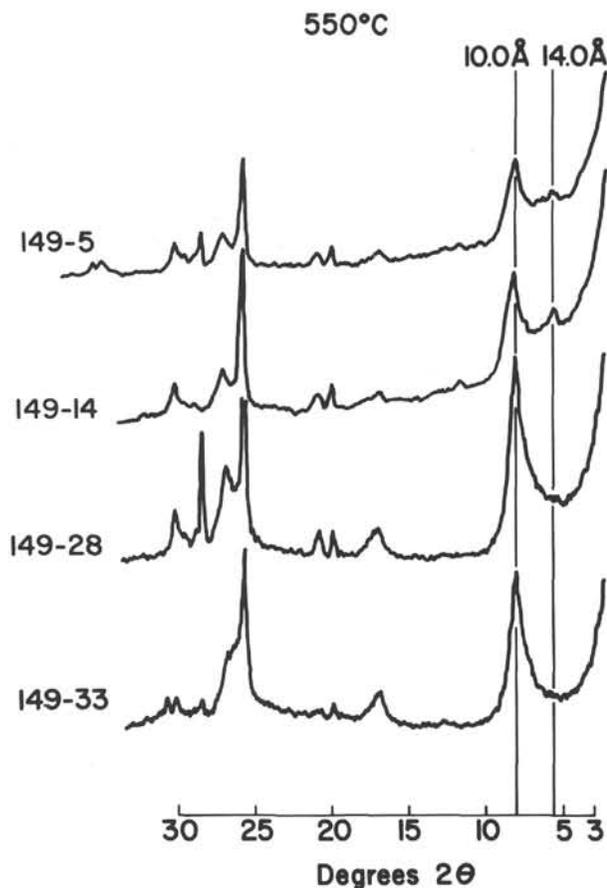


Figure 4. X-ray diffraction patterns of samples heated to 550°C for 1 hour.

expandability in the younger sediments is of terrigenous origin.

The chalks, oozes, and siliceous muds below 100 to 150 meters are interbedded extensively with volcanic ash deposits. It would appear that the illite/montmorillonite of 80 per cent expandability is a product of a devitrification of volcanic ash that was laid down in this deep-water marine environment.

It is interesting to compare these results with the results of Perry and Hower from their study of pelitic sediments (Pleistocene to Eocene) in the Gulf Coast. Mixed-layer clays of 50 to 60 per cent expandability overlie clays of higher expandabilities in Site 149. This would not have been predicted on the basis of observations made by Perry and Hower. They observed a monotonic decrease in expandability from samples 120 meters to 5,200 meters below the surface and interpreted these changes in expandability to be a result of burial diagenesis, mainly as a function of increasing temperature with depth.

The change in these cores from mixed-layer illite/montmorillonite of 50 to 60 per cent expandability to mixed-layer illite/montmorillonite of 70 to 80 per cent expandability with depth is most likely unrelated to differences in temperature, which are probably quite small. If both the illite/montmorillonite of 50 to 60 per cent expandability in the uppermost beds and illite/montmorillonite of 70 to 80 per cent expandability in the underlying beds has formed from the devitrification of ash, it is con-

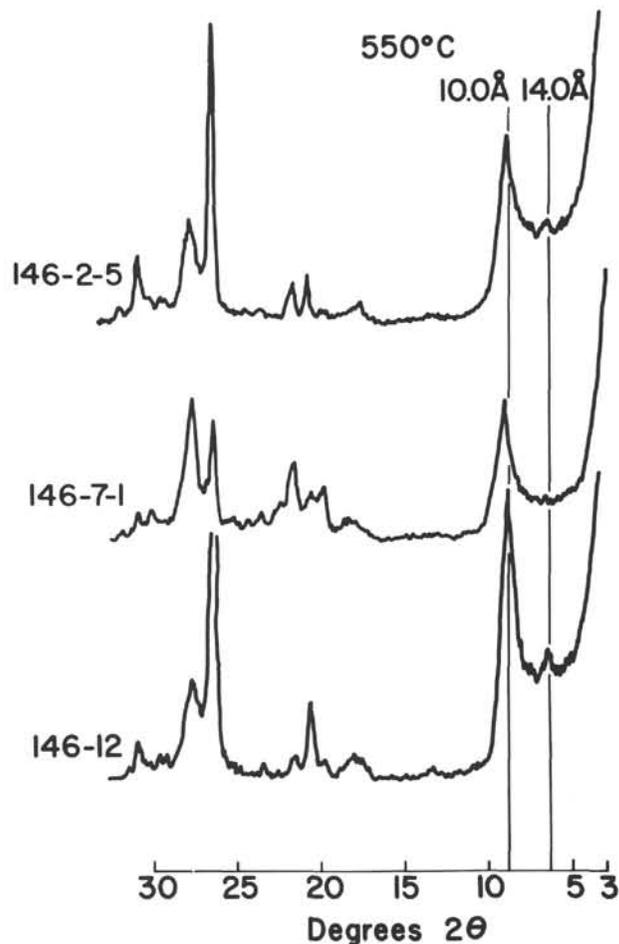


Figure 5. X-ray diffraction patterns of samples heated to 550°C for 1 hour.

ceivable that the differences in the mixed-layer illite/montmorillonite composition are related to differences in composition of the original volcanic ash. One could also envisage, assuming again that all of the mixed-layer illite/montmorillonite regardless of expandability has formed from the devitrification of volcanic ash, that the post-depositional chemical environment of beds of Miocene age and older was somewhat different than that of beds of late Miocene age and younger. Further chemical studies of the clay fraction and pore fluids should help to clarify these relationships.

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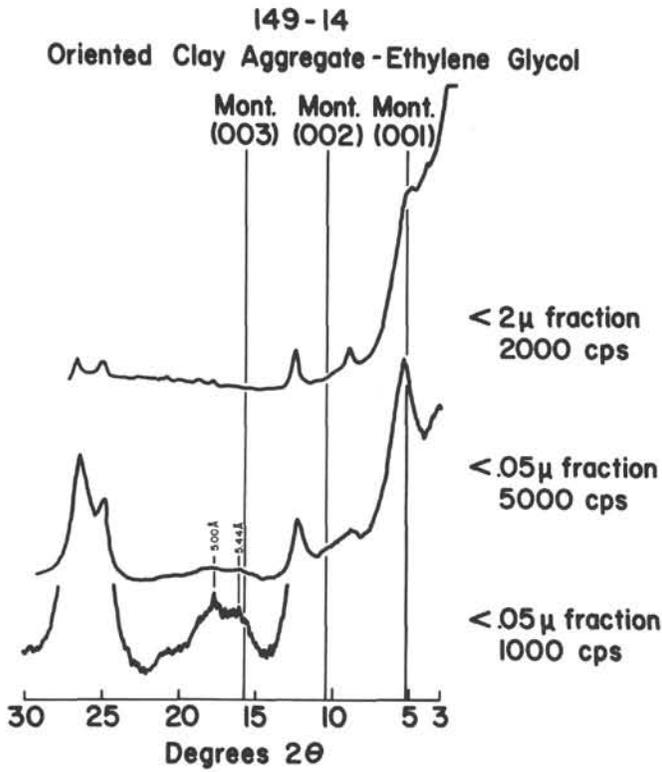


Figure 6. X-ray diffraction patterns of mixed-layer illite/montmorillonite from two different size fractions of same sample.

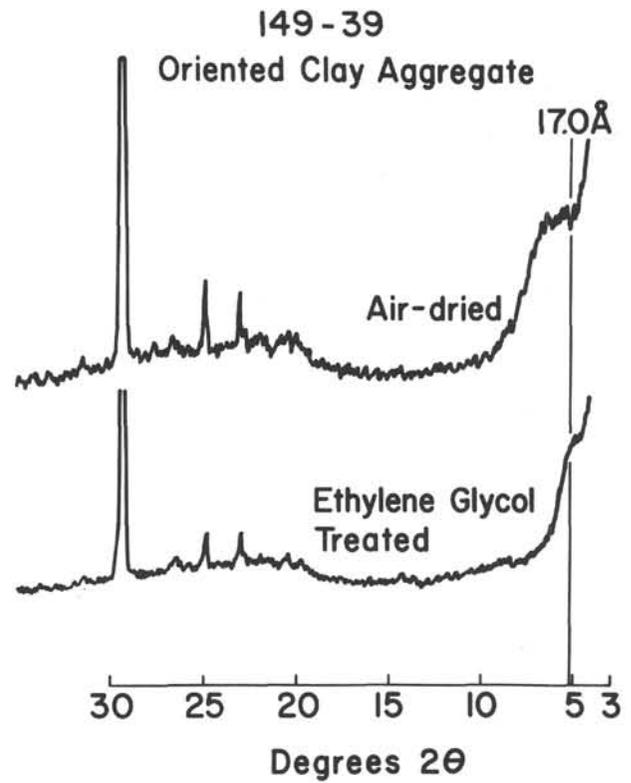


Figure 8. Poorly crystallized mixed-layer illite/montmorillonite which appears to have less than 80 per cent expandability.

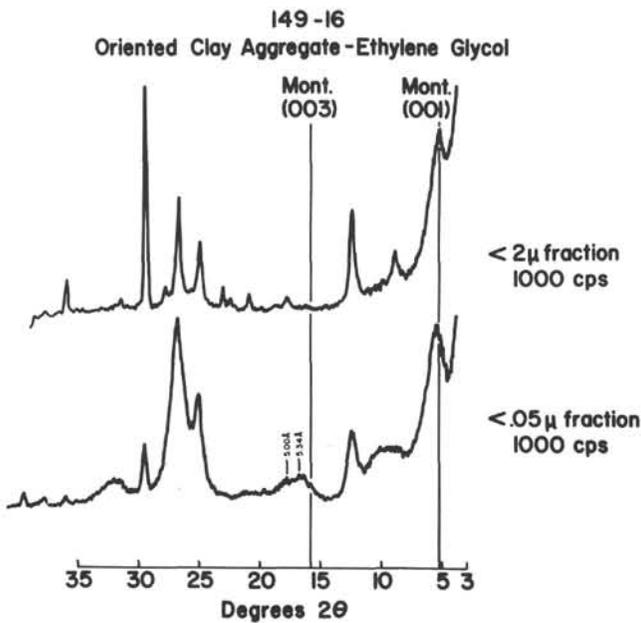


Figure 7. X-ray diffraction patterns of mixed-layer illite/montmorillonite from two different size fractions of same sample.

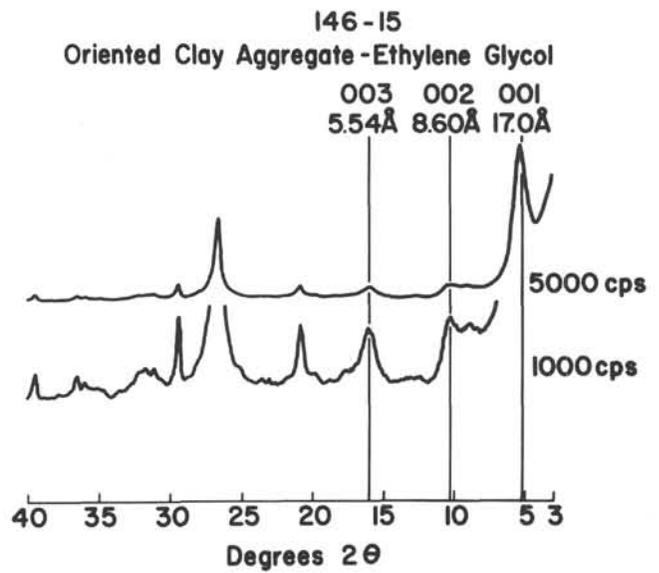


Figure 9. Typical mixed-layer illite/montmorillonite of about 80 per cent expandability.