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RECOGNITION OF INTERSTRATIFIED CLAYS

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Abstract—Difficulties in the interpretation of X-ray diffractograms of soil clays are discussed with reference to clay fractions obtained from glacial till and lacustrine soil parent materials. Diffractograms of the coarse clay fractions are readily interpreted by conventional means but it is difficult to determine if the dominant mineral species of the fine clay fraction is an interstratified mineral or a mixture of discrete montmorillonite and mica. A number of methods of interpretation of diffractograms of interstratified minerals are used with varying results. In the case of clays of small particle size, diffraction peaks crucial to the recognition of interstratification are not resolved due to the peak broadening. This phenomenon causes the diffractogram of a mixture of discrete minerals to resemble that of an interstratified mineral.

INTRODUCTION

DURING investigation of the clay mineralogy of soils and soil parent materials of Manitoba, the authors experienced difficulty in interpretation of diffractograms of the fine clay ($< 0{\cdot}2\mu$) fractions. All fine clay patterns exhibited an obvious similarity, and the presence of montmorillonite, mica, kaolinite, and chlorite components was apparent, but the structural arrangement of these components was uncertain. It was felt at one time that the dominant mineral species of the fine clay fraction was an interstratified mica–montmorillonite mineral. This interpretation was always doubtful and the authors now tend to believe that the dominant mineral species are discrete montmorillonite and mica clay minerals.

METHODS

The separation procedure began with the removal of carbonates, organic matter, and free iron following the procedure of Jackson (1956). Dispersion with sodium carbonate, fractionation by centrifugation and decantation, and X-ray slide preparation also followed the procedure of Jackson (1956). Oriented specimens of the clay fractions were X-rayed with a Philips diffractometer using iron filtered CoK_α radiation. One degree scatter and divergence slits were used in conjunction with a 20 mm. specimen width. Due to over-illumination of the specimen, this combination approximately cancelled the rising Lorentz and polarization factors for a single crystal in the region of 2θ from 20° to 4°.

TYPICAL DIFFRACTOGRAMS

Diffractograms of the fine and coarse clay fractions from the C horizons of the Newdale clay loam till and the Red River lacustrine clay are presented in Figs. 1 and 2, respectively. These diffractograms are typical of diffractograms of the clay fractions of glacial till and lacustrine soil parent materials from southern Manitoba.

DISCUSSION

The diffractograms of the coarse clay fraction are reasonably easy to interpret in view of the large number of mineral species present. The dominant minerals are quartz, illite, montmorillonite, and kaolinite; vermiculite, chlorite, and feldspars are minor species. The indication of chlorite in the diffractograms of K-saturated specimens heated to 300° and 550°C is probably partly due to residual interlayer glycerol. Jackson (1956) has discontinued the use of glycerol with K-saturated slides for this reason. With the exception of the possible chlorite, all mineral species appear to be discrete minerals and no evidence for interstratification can be seen.

The diffractograms of the fine clay fraction are less complex than those of the coarse clay due to the absence of quartz, feldspars, chlorite, and vermiculite. Diffraction peaks are noticeably broader. The diffraction peaks at approximately 7·14 Å and 3·55 Å are due to kaolinite which is undoubtedly a discrete species. The remaining peaks as well as part of the 3·55 Å peak are due to the montmorillonite and mica components but it is unclear if these components represent discrete minerals, an interstratified mineral, or a mixture of discrete and interstratified minerals.

INTERPRETATION AS AN INTERSTRATIFIED MINERAL

The first step in the recognition of interstratified mineral species is to determine if the diffraction peaks form an irrational series of orders. In the

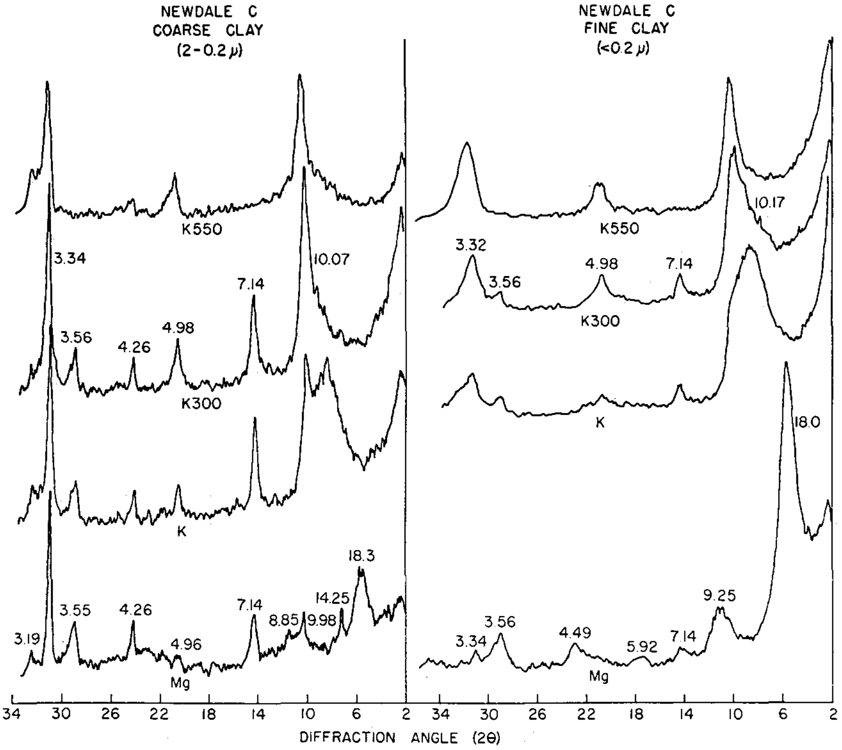

Fig. 1. X-ray diffractograms of glycerol-solvated specimens of the coarse and fine clay fractions of the Newdale clay loam when saturated with magnesium, with potassium, and with potassium and heated to 300° and 550°C.

case of the fine clay fraction of the Newdale and Red River C horizons, this procedure is complicated by the broadness of the peaks, the inherent small errors in *d*-spacing measurement, and the fact that small deviations from an integral series may indicate the presence of significant amounts of interstratification. In addition it is uncertain that the basal spacing of the montmorillonite layers of this clay will be precisely 17·7 Å when glycerol solvated and magnesium saturated. The authors suggest that the method of inspection for irrational series is not sufficient to allow a decision to be made whether or not the fine clay fractions are interstratified. Kodama and Brydon (1966) present diffraction patterns very similar to the fine clay patterns of Figs. 1 and 2 and comment that the higher orders of the 18 Å peak are not a rational series.

Random interstratification

Assuming that the fine clay is interstratified, the simplest interpretation is based upon the variation of peak position with changes in the mixing ratio of the interstratified mineral. MacEwan, Ruiz Amil and Brown (1961) have published peak migration curves for random interstratifications of 10 and 17·5 Å layers. It is apparent from these curves that the 18 Å peak of an interstratified mica–montmorillonite does not migrate significantly with changes in the mixing ratio but principally varies in intensity. This means that the presence of an 18 Å peak in a diffractogram is not diagnostic for montmorillonite since the peak may be entirely due to an interstratified mineral. Higher order peaks must be used to distinguish the two species. Usually the distinction must be based primarily upon the peak which migrates between 8·85 and 10·0 Å as the other peaks are relatively weak or are obscured by peaks of other minerals. Kodama and Brydon (1966), using this technique, determined that the proportion of mica layers in a fine clay fraction of their samples SMC44 and SMH18 was 0·25 and 0·5, respectively. These samples are glacial till and lacustrine materials from Manitoba which should be quite similar to the Newdale and Red River soils, respectively.

In the case of the Newdale C horizon fine clay, the 9·25 Å peak indicates a mica layer proportion

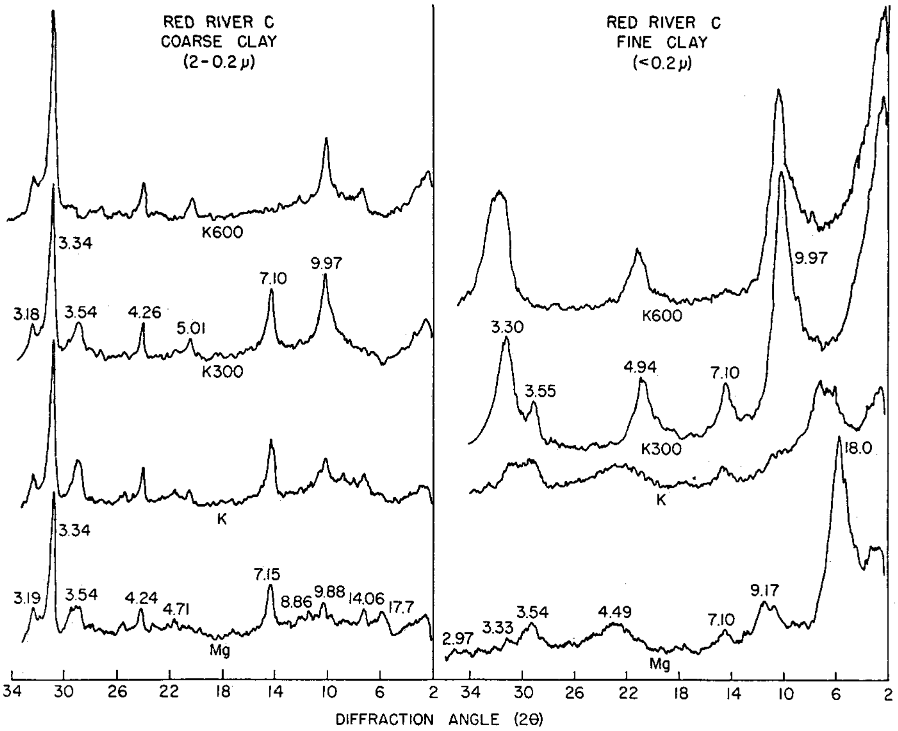

Fig. 2. X-ray diffractograms of glycerol-solvated specimens of the coarse and fine clay fractions of the Red River clay when saturated with magnesium, with potassium, and with potassium and heated to 300° and 600°C.

of 0·5. Similarly the 9·17 Å peak of the Red River C horizon indicates a mica layer proportion of 0·4. Different mixing ratios are, however, obtained from the other peaks of the diffractograms. Confidence in this technique would be improved if the same mixing ratio were obtained for all peaks. The use of this technique implies that the interstratification is random and that only one species of mica–montmorillonite mineral is present. A mixture of two interstratified species or of interstratified and discrete species would cause confusion.

Alternating, random, and segregated interstratification

Ruiz Amil, Garcia and MacEwan (1967) have published mixing function and peak migration curves for a wide range of binary interstratifications. These curves were calculated from the interlayer distance function of the assumed structure and include alternating, random, and segregated structures, as well as intermediate cases. The curves for interstratified 10 and 17·8 Å layers are applicable to mica and glycerol-montmorillonite. Since variations in stacking order as well as mixing ratio are covered by the curves, it is more probable that a curve will be found which fits all the peaks of an actual diffractogram. According to Reynolds (1967), the peak migration curves are less likely to be affected by unforeseen variations in the layer structure factor than are the mixing function curves.

Consequently the diffractograms of the fine clay fractions of the Newdale and Red River C horizons were compared qualitatively to the mixing function curves but the peak positions were fitted to the migration curves to obtain estimates of the mixing ratio and the stacking order. The probability coefficients obtained were $P_A = 0{\cdot}5$, $P_{AA} = 0{\cdot}9$ for the Newdale C horizon and $P_A = 0{\cdot}5$, $P_{AA} = 0{\cdot}8$ for the Red River C horizon. These coefficients indicate that the interstratified minerals contain 50% mica layers with a strong tendency to segregation.

The Fourier transform method

The direct Fourier transform method of MacEwan (1956) appears to be an ideal way to analyze diffractograms of interstratified minerals. MacEwan (1956) notes that somewhat similar Fourier analysis methods have been used with great success in determinations of the structure of crystalline materials. The principle of MacEwan's method is that a Fourier synthesis of the interlayer distance function of the interstratified mineral may be calculated from the X-ray diffraction data. The apparent simplicity of the method is, however, offset by a number of difficulties in its application. Foremost among these is the selection of an appropriate layer structure factor. The use of some published structure factor curves will cause one peak of the diffractogram to dominate the transform and will seriously affect the results obtained. A second major difficulty concerns the selection of diffraction peaks to be used to calculate the transform. For example if a broad peak is taken to be a single peak the results will be different than if the peak is considered to be two overlapping peaks. Again, if peaks due to discrete mica or montmorillonite are included with diffraction data from the interstratified mineral in the calculation, the method will produce an invalid but apparently reasonable Fourier transform.

Fourier transforms of the glycerol-solvated fine clays are presented in Fig. 3. Diffraction peaks due to kaolinite were omitted from the calculation. The layer structure factors used in the calculation were obtained from a curve constructed by the authors using diffraction data for pure montmorillonite and mica in combination with data from Bradley (1945). From the Fourier transforms, the probability coefficients were calculated to be $P_A = 0{\cdot}10$, $P_{AA} = 0{\cdot}60$ for the Newdale soil and $P_A = 0{\cdot}17$, $P_{AA} = 0{\cdot}60$ for the Red River soil. These coefficients and the transforms from which they were obtained are quite different from those presented by Kodama and Brydon (1966). This is probably due to the use of different layer structure factors. In view of the difficulties of application of the method and the inconsistencies noted, the authors feel that very little useful information can be obtained from the Fourier transforms of Fig. 3.

INTERPRETATION AS DISCRETE SPECIES

Regardless of the method used to interpret the diffractograms of the fine clays illustrated in Fig. 1 and Fig. 2, uncertainty always exists that the clays are actually interstratified. Both magnesium-saturated glycerol-solvated diffractograms have a peak at 18 Å, a broad peak between 10 and 9 Å, and a series of approximately integral higher orders of 18 and 10 Å. A minor amount of kaolinite is ubiquitous. These diffractograms are very similar to the two published by Kodama and Brydon (1966). It is apparent that the decision that the clays are or are not interstratified, as well as the determination of the mixing ratio, are highly dependent upon the peak between 9 and 10 Å. This peak should, therefore, be examined in detail. If, for example, the clays are not interstratified but are merely mechanical mixtures of montmorillonite and mica of fine clay size, one might expect to find distinct peaks at 9 and 10 Å.

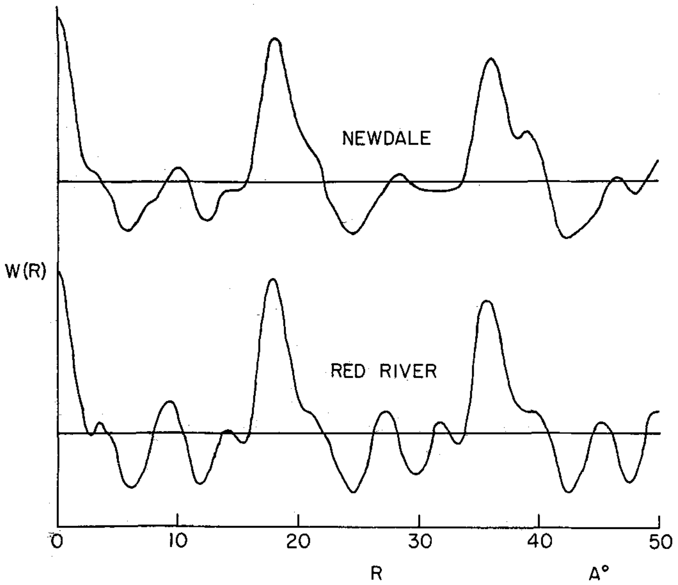

Fig. 3. Fourier transforms of the glycerol-saturated fine clay fractions of the Newdale and Red River C horizons.

However, it is well known that overlapping gaussian peaks will not be resolved if the spacing between the peaks is less than the width at half-maximum of the individual peaks. The authors feel that this is the case for the Manitoba fine clay fractions and that the resultant will be a broad peak whose apparent position varies with the relative amounts of mica and montmorillonite present in the mixture. The broad peak due to the unresolved first order of mica and second order of montmorillonite causes the diffractograms to resemble that of an interstratified mineral and results in a variety of interpretations when methods of analysis of interstratification are applied. This hypothesis fits well with the observed diffractograms of the fine clays and is supported by the fact that the mica and montmorillonite of the coarse clay fractions of the same soils appear to be discrete species.

Another factor which should be considered is the experimental technique. During the isolation of the clay fractions by Jackson's (1956) method, it is quite possible that montmorillonite will be dispersed into single flakes 10 Å thick. When the clays are magnesium or potassium saturated for X-ray diffraction analysis, the montmorillonite flakes flocculate to form thicker crystallites. Because of this monodispersion and flocculation, interstratified species may be created, destroyed, or altered during separation and slide preparation.

CONCLUSIONS

(1) It is the opinion of the authors that the fine clay fraction ($< 0{\cdot}2\mu$) of the Newdale clay loam and Red River clay soil parent materials is composed predominantly of discrete mineral species. The dominant species is montmorillonite; this accompanied by mica and kaolinite.

(2) In the interpretation of X-ray diffractograms of clays and clay fractions, care should be taken to recognize interstratified and discrete mineral species. Recognition will be obvious in some cases but will be extremely difficult in others. Overlapping of broad peaks must be considered for fine clay fractions. In the absence of definite evidence that a clay is interstratified, it is probably best to consider it as a mixture of discrete species.

(3) Comparison with the mixing function and peak migration curves of Ruiz Amil, Garcia, and MacEwan (1967) appears to be the best method of interpretation for X-ray diffractograms of interstratified minerals.

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Résumé—La difficulté que l'on rencontre dans l'interprétation des diffractogrammes X des argiles de sol sont discutées en prenant comme modèle les fractions argileuses obtenues à partir de matériaux d'origine qui sont des argiles de conglomérats glaciaires et des sols lacustres. Ces diffractogrammes des fractions argile grossière sont facilement interprétés par les moyens classiques, mais il est difficile de déterminer si l'espèce minérale dominante dans la fraction argile fine est un interstratifié ou un mélange de montmorillonite et de mica en phases séparées. Un certain nombre de méthodes d'interprétation des diffractogrammes d'interstratifies a été utilisé avec divers résultats. Dans le cas des argiles de petite taille, les pics de diffraction indispensables pour reconnaître l'interstratification ne sont pas résolus à cause de l'élargissement. Ce phénomène fait que le diffractogramme d'un mélange de minéraux en phases séparées ressemble à celui d'un interstratifié.

Kurzreferat—Schwierigkeiten bei der Auslegung von Röntgenbeugungsbildern werden erörtert mit Bezugnahme auf die aus glazialem Moränenschutt und Binnenseeablagerungen erhaltenen Tonfraktionen. Beugungsbilder der groben Tonfrkationen können ohne weiteres auf herkömmliche Weise interpretiert werden jedoch ist es schwierig zu entscheiden ob die vorherrschende Mineralsorte der feinen Tonfraktion ein zwischengeschichtetes Mineral oder eine Mischung getrennter Montmorillonit- und Glimmermateriale ist. Eine Anzahl von Methoden zur Auslegung von Beugungsbildern von zwischengeschichteten Mineralen wurden mit wechselnden Ergebnissen verwendet. Im Falle von

Tonen mit kleiner Teilchengrösse werden Beugungsscheitelwerte, die für das Erkennen von Zwischenschichtung ausschlaggebend sind nicht aufgelöst infolge der Verbreiterung der Scheitel. Diese Erscheinung führt dazu, dass das Beugungsbild einer Mischung separater Minerale dem eines zwischengeschichteten Minerals gleicht.

Резюме — Авторы обсуждают трудности в интерпретации рентгеновских дифрактограмм почвенных глин, ссылаясь на частицы глины, полученной из ледниковых отложений и родственных лакустрину материалов. Дифрактограммы грубых частиц глины легко интерпретировать обычными средствами, но трудно определить, являются ли преобладающие виды минералов мелких частиц глины впластованными минералами или смесью разрозненных частиц монтмориллонита и слюды. Применялся ряд методов для интерпретации дифрактограммы впластованных минералов и результаты получались различные. В случаях глин с малыми размерами частиц, ремающие для распознавания впластования пики дифракции, вследствие их уширения, оказались неразрешимыми. Это явление делает дифрактограмму смеси разорванных минералов подобной дифрактограмме впластованного минерала.