

DETERMINATION OF RANDOM INTERSTRATIFICATION IN MONTMORILLONITE

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ABSTRACT

In the study of clay minerals, x -ray diffraction patterns are often obtained for samples which are not pure minerals but are mixtures in which layers of different types alternate. There are three types of interstratification: (1) random, (2) regular, (3) segregated into zones in the individual crystallites. The usual method of determining the degree and type of random interstratification is by the method of Hendricks and Teller by which theoretical scattering curves are constructed for the various mixtures. The method presented here is a Fourier transform method which can be used to calculate the degree and type of interstratification directly from the measured x -ray data.

Fourier transforms have been calculated for a series of sodium-calcium montmorillonites from 100% sodium and 0% calcium to 0% sodium and 100% calcium. Intensities of the various Fourier peaks give a good representation of the type of random interstratification in the samples. The intensities are also related to the amount of monovalent and divalent ions. Therefore, by using the experimental x -ray diffraction data alone, one can estimate the degree and type of random interstratification in montmorillonite.

INTRODUCTION

Very often in the study of clay minerals x -ray diffraction patterns are obtained for samples which are not pure minerals but are mixed structures in which layers of different types alternate. Naturally occurring clay minerals of this type have often been reported in the literature.¹

These mixed layer type clay minerals are easily formed in nature since most of the clays are layer structures and it is a simple matter for the different layers to alternate. There are three types of interstratification, namely (1) random, (2) regular, and (3) segregated into zones in the individual crystallites. One of the most usual ways in which random interstratification can occur is by the existence of two or more different degrees of hydration. Examples are mixed layers of mica with montmorillonite or vermiculite, glycerol saturated montmorillonites in which a certain proportion of layers of lower glycerol content is present, or two or more successive hydrates of montmorillonite.

It has been shown^{2,3} that ideally at room temperature the sodium montmorillonite would have a "single water layer" resulting in a (001) spacing of 12.4 Å, while calcium montmorillonite would have a "double water layer" and corresponding (001) value of 15.4 Å. Randomly interstratified

¹ Brindley, G. W. (Ed.): *X-ray identification and crystal structure of clay minerals: The Mineralogical Society, London (1951).*

² Roth, R. S., Ph.D. Thesis, University of Illinois, Urbana, Illinois (1951).

³ Williams, F. J., Neznayko, M., Weintritt, D. J.: *J. Phys., Chem.*, **57**, 6 (1953).

mixtures of these two types of hydration would lead to intermediate (001) values and non-integral higher orders.

Hendricks and Teller⁴ have calculated the scattering which would be given by random and partly random mixtures. By use of these formulae, it is possible to construct curves showing the type of scattering to be expected from various mixtures.⁵ However, since this method can require the calculation of a very large number of curves it has been found desirable to have a direct method of getting the required information from the measured x -ray data.

Mering⁶ has pointed out that the Fourier transform of the diffraction diagram can be utilized to obtain the needed information on interstratification. MacEwan⁷ has applied a Fourier transform technique to theoretical random mixtures of 10 and 12 Å spacings with mica-type layers. These results indicated the usefulness of this method.

The purpose of this investigation was to apply the method of Fourier transforms to analyze random interstratification mixtures of sodium and calcium montmorillonites. By using the experimental diffraction data alone it is possible to estimate the degree and type of interstratification in this system.

MATERIALS AND EXPERIMENTAL METHODS

The purified bentonite samples employed were prepared by the method described by Williams, Neznayko, and Weintritt.³ The preparation of samples for x -ray examination involved a procedure which would yield diffraction data of only the basal spacings. A dilute, fully hydrated suspension of the clay was allowed to slowly air dry on a glass microscope slide. The air dried sample was then placed in a desiccator maintained at a relative humidity of 52%, and allowed to come to equilibrium. These oriented samples were then run on a North American Philips High Angle Spectrometer using Ni filtered Cu $K\alpha$ x -radiation. The relative humidity of the room in which the x -ray diffraction was carried out was maintained at approximately 50%, so that there was no change in the spacings during the x -ray examination.

EXPERIMENTAL RESULTS AND DISCUSSION

The Fourier transformation which was employed in these calculations was that published by MacEwan.⁷ The cosine transform

$$T(R) = \int_0^{\infty} \frac{I(\mu)}{\Theta |F_l|^2} \cos 2\pi\mu R d\mu$$

⁴ Hendricks, S. B., and Teller, E.: *J. Chem. Phys.*, **10**, 47 (1942).

⁵ Brown, G., and MacEwan, D. M. C.: *J. Soil Sci.*, **1**, 239 (1949).

⁶ Mering, J., *Acta Cryst.*, **2**, 371 (1949).

⁷ MacEwan, D. M. C.: *Nature*, **171**, 616 (1953).

TABLE 1. X-RAY DIFFRACTION BASAL SPACINGS AND RELATIVE INTENSITIES OF SODIUM-CALCIUM MONTMORILLONITES

Sample	1st Order		2nd Order		3rd Order		4th Order		5th Order	
	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0
100% Na- 0% Ca	12.6	100	6.23	8.9	4.25	0.2	3.12	32.0		
80% Na- 20% Ca	12.6	100	6.23	8.8	4.20	0.2	3.10	38.6		
60% Na- 40% Ca	14.0	100	6.22	0.6	5.18	0.5	4.01	0.3	3.09	35.0
40% Na- 60% Ca	14.7	100			5.13	0.6	4.03	0.3	3.07	23.8
20% Na- 80% Ca	14.9	100			5.04	9.4	3.78	0.1	3.02	17.4
0% Na-100% Ca	15.1	100			5.03	12.1	3.75	0.2	3.01	13.4

is essentially the Patterson line projection on the c -axis of the crystallites. Its values are proportional to the mean number of layers at a distance R from any arbitrary layer chosen as the origin. This form of function gives a peak at the origin and the terms are as follows: $I(\mu)$ is the observed intensity for each value of the reciprocal spacing, F_l is the structure factor of a single layer and Θ is the Lorentz-polarization factor.

The above transform may be approximated by the following summation:

$$T(R) \approx \sum_R \frac{I_R}{\Theta |F_l|^2} \cos 2\pi\mu R$$

This sum makes use of the observable data and has the number of terms equal to the number of lines. The technique employed in obtaining the x -ray diffraction data leads only to basal reflections, consequently all the diffraction peaks observable were employed in the calculations. Table 1 gives the x -ray diffraction and relative intensity data of the series of purified montmorillonites.

Since there were only a few basal lines observed the high order terms were artificially diminished by application of an artificial temperature factor, $\exp(-A \sin^2 \theta)$ where A has a value of 25. This value of A was chosen so as to reduce the value of the exponential to about 0.10 at a value of $\sin \theta/\lambda = 0.25$, which corresponds to the smallest observed spacing in this series of clays.

The calculated transforms are shown in Fig. 1. It will be noted that good separation of the 12.4 and 15.4 \AA spacings is obtained. The relative intensities of the various peaks are shown in Table 2, the most intense peak having a value of 100 arbitrary units. Peaks of the single water layer or sodium type have been designated as A , while the double water layer or calcium type is labeled B . The combination peaks such as $AA B$ arise from two units of the 12.4 \AA type and one of the 15.4 \AA type in any order. The relative intensities of the combination peaks approximate the randomness of the mixture.

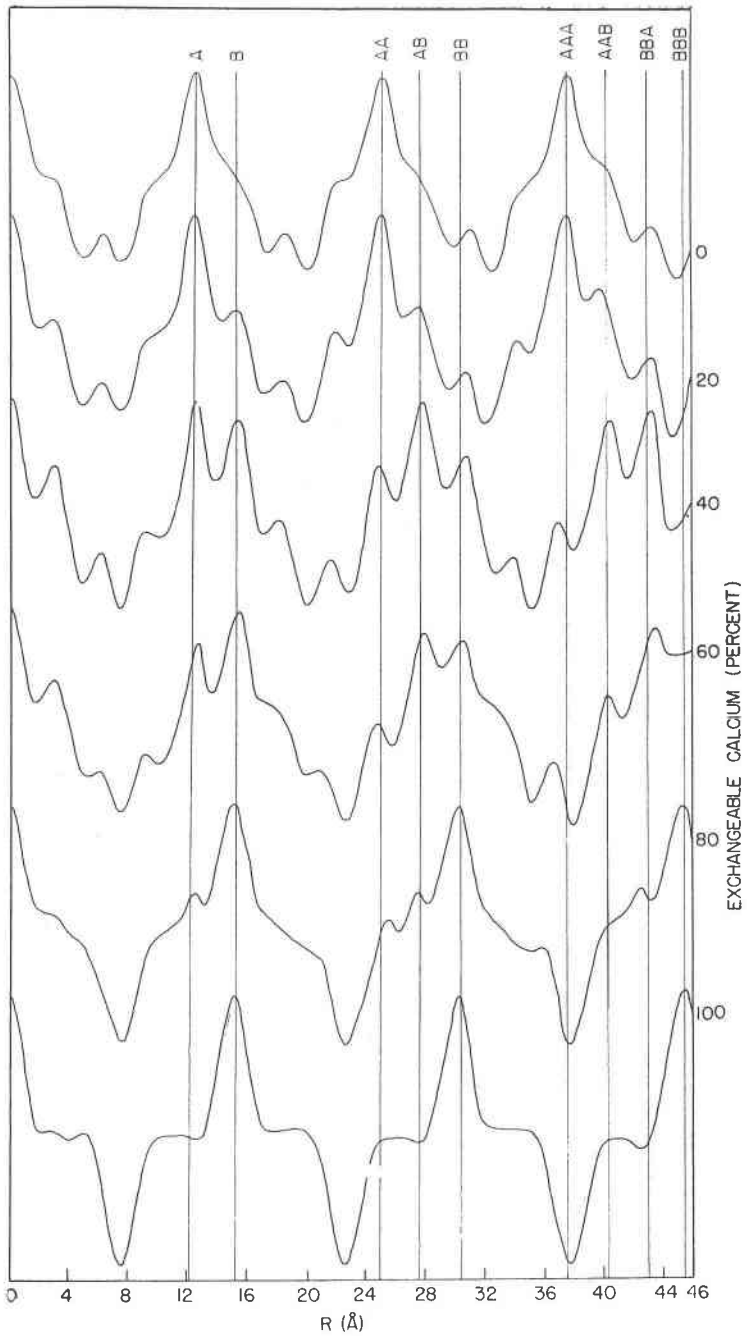


FIG. 1. Fourier transforms of sodium-calcium montmorillonites.

TABLE 2. RELATIVE INTENSITIES OF THE CALCULATED FOURIER PEAKS OF SODIUM-CALCIUM MONTMORILLONITES

Sample	Relative Intensities of Fourier Peaks								
	A 12.5 Å	B 15.2 Å	AA 25.0 Å	AB 27.7 Å	BB 30.4 Å	AAA 37.5 Å	AAB 40.2 Å	BBA 42.6 Å	BBB 45.6 Å
100% Na- 0% Ca	100		100			100			
80% Na- 20% Ca	100	20	100	25		100	30		
60% Na- 40% Ca	100	75	35	100	50		70	80	
40% Na- 60% Ca	70	100		80	70		20	80	55
20% Na- 80% Ca	20	100		25	100			30	100
0% Na-100% Ca		100			100				100

The transforms of the 100% sodium and 100% calcium montmorillonites show only the peaks related to the 12.4 Å and 15.4 Å lines, respectively. The transform of the 80% sodium, 20% calcium sample shows that there is a relatively large amount of material of the *AB* type and *AAB* type.

The relative intensities of the peaks of the 60% sodium, 40% calcium sample show a very large amount of the *AB* type, in fact much more than either the *AA* or *BB* types. There is also a considerable amount of *AAB* and *BBA* material as represented by the peaks at 40.2 and 42.6 Å. These results would indicate that for the most part this sample is made up of alternating layers of *A* and *B*, with lesser amounts of other combinations. It will be noted that for the 40% sodium, 60% calcium samples there are about equal amounts of *AB* and *BB* type material. This is a somewhat different distribution than observed for the preceding sample. In the 20% sodium, 80% calcium sample it is shown that a large amount of the *A* type material is combined with *B* as *AB* or *BBA*.

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