A STUDY OF AN INTERSTRATIFIED ILLITE-MONTMORIL LONITE CLAY FROM WORCESTERSHIRE, ENGLAND

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ABSTRACT

This clay has been studied by Fourier transform methods, which show that it is a random interstratification of mica with montmorillonite, subject however to the limiting condition that montmorillonite layers are never contiguous. It is very similar to one of the mixed-layer clays from Kinnekulle, Sweden, described by Mrs. Byström. The "separation rule" is perhaps one of the factors conditioning the appearance of definite stages in the mixed-layer mica-montmorillonite sequence, as noted by Mrs. Byström.

THE WOODBURY CLAY

This clay comes from Woodbury Quarry, Shelsley Beauchamp, Worcestershire. It has not been used commercially to any great extent. It occurs in the Silurian system between the Aymestry limestone and the Lower Ludlow limestone. Above the clay, in the Aymestry group, is a green chloritic quartz-siltstone containing white mica and chlorite.

The clay occurs in seams ranging in thickness from 2 feet to 4 inches. The sample I examined was taken from the thickest seam, which is lighter in color than the others. It readily disaggregates in water giving a voluminous, flocculent suspension. In order to get good aggregates for x-ray photography, it was sodium saturated and centrifugally separated. A very stable suspension was thus obtained, and the aggregates (made by evaporation on a glass plate) showed a high degree of orientation.

It was thus possible to distinguish clearly between the basal and general reflections. Table 1 lists all the basal reflections which were identified on x-ray photographs of glycerol-treated aggregates.

On heating to 500° C, a small flake gives the normal mica series, the intensities of successive orders of the basal series being strong, medium, strong, very weak, and medium-weak, respectively.

A one-dimensional Fourier transform (MacEwan, 1953, 1955, 1956) was calculated from the basal series given by the glycerol-treated clay. The result is shown in Figure 1.

This curve shows 10 A and 18 A peaks, as expected for a mica-montmorillonoid interstratification. A striking feature is the occurrence of the large peaks at 28, 38 and 48 A.

The ratio of the height of the A peak (mica) to the B peak (montmorillonoid) is 0.77:0.23. Taking into account the "combination" peaks, 0.72:0.28 was determined to be the best value for the ratio of the component layers.

We now must find the coefficients p_{rs}; i.e., the coefficients that express the probability of a layer of type s following one of type r. It can be shown (MacEwan, 1956) that for a two-component structure there is only one independent

166

Table 1. — Spacings and Intensities of Basal Reflections of Woodbury Clay, Centrifugally Separated; With Corresponding Data For Kinnekulle II Clay (Bystrom, 1954), For Comparison

	Woodbury		Kinnekulle II	
d (A)	I_{est}		d (A)	I_{est}
32.1	vs			
13.1	w		13.1	s
9.71	s		9.6	vs
5.32	vw		5.46	m
4.79	m		4.74	s
3.42	s		3.44	vs
3.18	w		3.10	s
2.57	vw		2.45	m
			2.12	w
1.994	ms/s		2.04	s
1.650	vw			
1.344	vw			

coefficient of this type, so that fixing it fixes the other three. Thus, if we assume for the above frequencies that $p_{BA} = 1$; i.e., that a montmorillonoid layer is *always* followed by one of the other type (maximum degree of alternation),[1] we obtain the following scheme of coefficients:

$$p_A = 0.72 \qquad\qquad p_B = 0.28$$
$$p_{AA} = 0.61 \qquad\qquad p_{BB} = 0$$
$$p_{AB} = 0.39 \qquad\qquad p_{BA} = 1$$

The height of each peak, calculated from this scheme, is shown above each peak in Figure 1, and also in Table 2. Excellent agreement is obtained.

The structure thus seems to be one in which montmorillonoid layers are interspersed among mica layers at random, subject only to the reservation that two montmorillonoid layers are never contiguous.

In Table 1, the effective spacings and intensities for the Woodbury clay are compared with those reported for a "bentonite" (Kinnekulle II) from Kinnekulle, Sweden (Byström, 1954). The similarity is striking. Figure 2 shows a Fourier transform from Mrs. Byström's data, and of course it also is very like the curve for the Woodbury clay. The probability coefficients deduced from it are as follows:

$$p_A = 0.68 \qquad\qquad p_B = 0.32$$
$$p_{AA} = 0.56 \qquad\qquad p_{BB} = 0$$
$$p_{AB} = 0.44 \qquad\qquad p_{BA} = 1$$

Mrs. Byström deduced the ratio of illite to montmorillonite layers for this clay to be 3:2, but the table suggests a ratio nearer 2:1. She makes this comment (Byström, 1954):

It seems as if some forms of interstratification of illite in montmorillonite are more stable than others, and that in the material investigated [i.e., from Kinnekulle], one thus can recognize two definite types, although one might have expected all transitions from montmorillonite to illite.

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[1] The reason for making this initial assumption is that the high peaks at 28, 38, and 48 A point to the occurrence of many sequences of the types AB, AAB, $AAAB$.
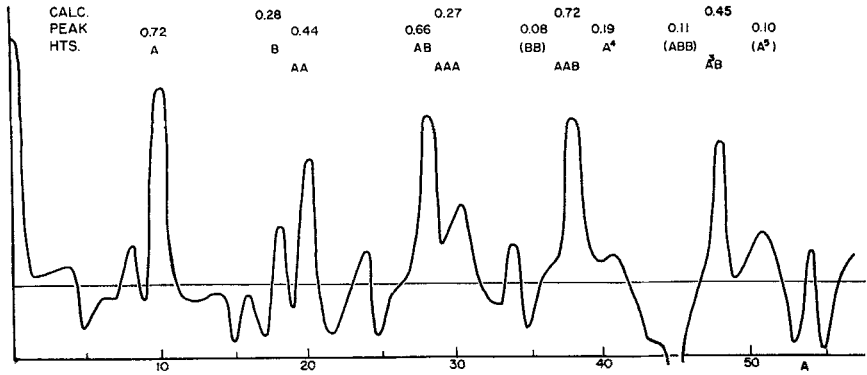
FIGURE 1. — Fourier transform of basal reflections of Woodbury clay (glycerol treated). A = mica, B = montmorillonoid. Figures give calculated heights of peaks.

That the quite distinct Woodbury clay should show essentially the same type of interstratification as the Kinnekulle II material is a most striking confirmation of Mrs. Byström's views. It seems to me that this tendency to form definite stages, in the mica-montmorillonite transition, must be linked up with the special stability of alternating structures. The alternation is not a completely regular one, however, in either clay. This is shown by Table 2, which compares the measured peak heights on the Fourier transform with probability coefficients calculated for the random structure (as already described) and for two types of regular structure. It is obvious that the random structure fits the observations much better. We should probably suppose that there is a tendency towards a structure of the type $AAB \ldots$ or $AAAB \ldots$, but that this is fully realized only in small regions. The tendency however is sufficient to lead to the formation of a fairly well-marked type.

The other clay from Kinnekulle described by Mrs. Byström (no. I), was said by her to have a ratio of mica to montmorillonite layers of 1:4. My Fourier transform, made from her data (Fig. 3), suggests a somewhat higher ratio but otherwise confirms her analysis. It does not suggest that in this clay there is
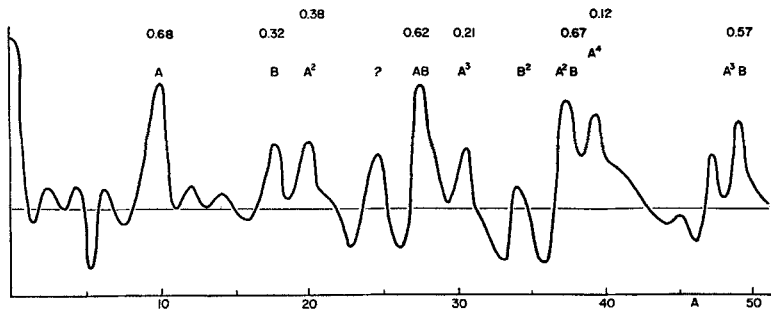

FIGURE 2. — Fourier transform of "Kinnekulle II" clay from Mrs. Byström's data.

TABLE 2. — WOODBURY CLAY. COMPARISON OF PEAK HEIGHTS ON FOURIER TRANSFORM
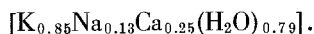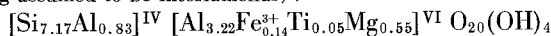WITH CALCULATED HEIGHTS FOR VARIOUS HYPOTHETICAL STRUCTURES

Peak	Observed height	Calculated heights		
		"Random" structure ($BB=0$)	AAB . . . structure	$AAAB$ . . . structure
A	0.76	0.72	0.67	0.75
B	0.24	0.28	0.33	0.25
AA	0.48	0.44	0.33	0.50
AB	0.67	0.56	0.67	0.50
A^3	0.30	0.27	0	0.25
AAB	0.66	0.72	1.00	0.75
A^4	0.12	0.19	0	0
A^3B	0.56	0.53	0	1.00
A^5	0.20	0.10	0	0
ABB	n.o.	0.11	0	0

any departure from complete randomization, but does not rule out the possibil-
ity of some ordering, of the type which occurs in Kinnekulle II and Woodbury
clay. More careful study is required to cast light on this question of the transi-
tion minerals in the illite-montmorillonite series.

NOTE ADDED, JANUARY 1956

Miss Carmen del Pino has kindly supplied me with the following analysis of this clay:
SiO_2 54.15; Al_2O_3 25.96; Fe_2O_3 1.35; TiO_2 0.48; CaO 3.08; MgO 2.79; K_2O 5.00;
Na_2O 0.51; loss + 110° C 7.37; Sum 100.69; CO_2 (included in loss) 1.05.

This analysis leads to the following mean formula (based on 20 O + 4 OH per unit cell,
excess water being assumed to be interlamellar) :

$$[Si_{7.17}Al_{0.83}]^{IV} [Al_{3.22}Fe^{3+}_{0.14}Ti_{0.05}Mg_{0.55}]^{VI} O_{20}(OH)_4$$

$$[K_{0.85}Na_{0.13}Ca_{0.25}(H_2O)_{0.79}].$$

The sum of the octahedral cations is 3.96 (should be 4 for a dioctahedral mineral).
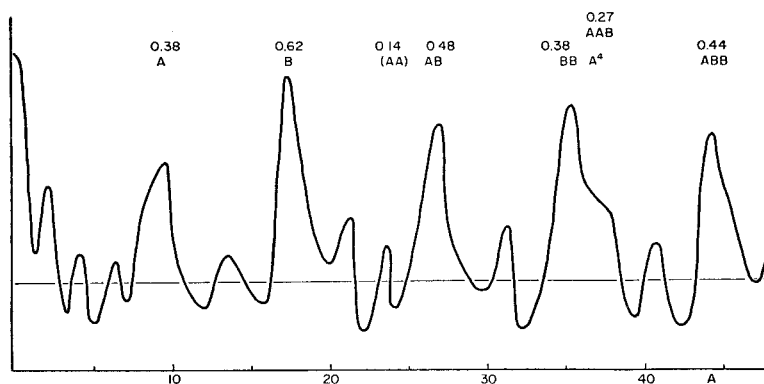

FIGURE 3. — Fourier transform of "Kinnekulle I" clay from Mrs. Byström's data.

APPENDIX ON FOURIER TRANSFORM METHOD OF ANALYZING COMPLEX INTERSTRATIFIED MIXTURES

This method was mentioned during the first U. S. conference on clays and clay technology in Berkeley in 1952 (MacEwan, 1955) and was also described briefly in a note to Nature (MacEwan, 1953). A full description is now in press (MacEwan, 1956). It may nevertheless be useful to summarize it here.

The method makes use of only the measured intensities and positions of lines. These must be lines of the basal series, so that it is necessary to have x-ray photographs showing sufficient orientation for the basal series to be separated clearly from the general reflections. The calculation consists of summing a series of cosine terms that are equal in number to the number of lines observed.

The result is a curve which gives $w(R)$, the probability of finding a given interlayer spacing, or the number of times the spacing occurs, divided by the number of layers. A peak of value 1 occurs at the origin, because the number of zero interlayer spacings is of course equal to the number of layers. Then, in general, the next peaks to occur are the "primary" peaks, i.e., those corresponding to spacings between contiguous layers. These therefore will generally indicate immediately the types of layer present (or, more strictly, types of interlayer spaces), and their proportions. In a mica-montmorillonite (30 percent montmorillonite) mixture, for instance, we will expect to see a peak of value 0.7 at 10 A, and a peak of value 0.3 at, say, 12 or 15 A depending on the state of hydration. If the mineral is glycerol-treated, the second peak will be at 17.7 A. Further out come the "combination peaks," i.e., those corresponding to distances between nonneighboring layers. These give us information about the way in which the layers are superposed, or the "law of succession." In the above case, for instance, if we consider the peaks giving distances between layers having *one* intermediate layer, these distances can be of four types. If we call mica (10 A) A, and montmorillonite (say 12 A) B, then the four possibilities are $A + A$, $A + B$, $B + A$ and $B + B$. These give spacings, respectively, of 20, 22, 22, and 24 A, so that $A + B$ cannot be distinguished from $B + A$.

To see how these peaks give us information about the law of succession, let us take two extreme cases. First, let us suppose we are dealing simply with a mechanical mixture of mica and montmorillonite, so that a complete series of reflections of the two minerals are present. Then no $A + B$ or $B + A$ spacings can occur. All the spacings will be $A + A$ (very nearly equal in number to the number of A layers) and $B + B$ (very nearly equal to the number of B layers). Thus we will get a peak of value 0.7 at 20 A, and a peak of value 0.3 at 24 A. Similarly, it can be seen that there will be peaks at 30, 40 . . . A, and at 36, 48 . . . A. These peaks will be represented, by an obvious shorthand notation, as AAA (or A^3), $AAAA$ (or A^4), and so on (Fig. 4A).

Now suppose we have a regular intergrowth, in which an A layer always succeeds a B layer, and vice versa; i.e., the succession is $ABABABABAB$ . . . . Here no $A + A$ or $B + B$ spacings can occur, only $A + B$ and $B + A$ (which are indistinguishable, and are written AB). Thus we get a peak value 1 at 22 A. Other peaks will be due to interlayer distances, having two, three, . . . intermediate layers. It can readily be verified that we will have a peak of value 0.5 at 32 A (AAB or A^2B), and one of value 0.5 at 34 A (ABB or AB^2), one of value 1 at 44 A (A^2B^2); and so on (Fig. 4B: in this case, of course, the numbers of A and B spacings must be the same).
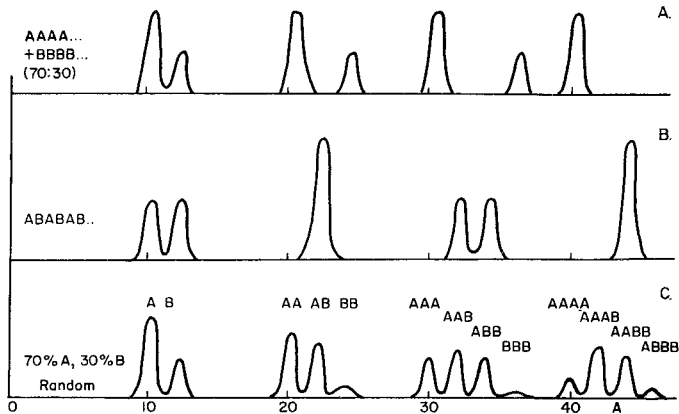
FIGURE 4. — Imaginary Fourier transforms illustrative of different possible successions of layers (A, 10 A; B, 12 A), as indicated on the left-hand side of the diagrams.

Now suppose we have a completely random mixture. In this case, the probability of a layer succeeding a given layer is just equal to the probability of it occurring at all; i.e., if there are 70 percent of A layers, there is a 70 percent chance that A will succeed A or B, and a 30 percent chance that B will succeed A or B. Thus the proportion of AA spacings is 0.7×0.7; of AB, $0.7 \times 0.3 + 0.3 \times 0.7$; and of BB, 0.3×0.3. Thus in this case, we get peaks at 20, 22 and 24 A, in the ratios $0.49:0.42:0.09$ (Fig. 4c).

It is easy to see that intermediate cases are possible, and that each will give a characteristic pattern of peaks. Thus, there may be a *tendency* towards an interleaving sequence, $ABAB$ ..., without its being fully realized. This, we may guess, will give smaller AA and BB peaks, and a larger AB peak, than the random sequence.

In order to calculate the sizes of peaks, we introduce the probability coefficients: p_{AB}, the probability that B succeeds A; p_{AA}, that A succeeds A; p_{BA}, that A succeeds B; p_{BB}, that B succeeds B. It can be shown that, in a two-component system such as we are imagining, only one of these four quantities is independent, so that if any one of them is fixed, the others are also automatically fixed. Thus if $p_{AA} = p_A$, the system is "completely random"; if $p_{AA} < p_A$, there is a tendency towards alternation or interleaving; if $p_{AA} > p_A$, the tendency is towards segregation, with groups of AAA ... and groups of BBB .... In theory, therefore, we have only to measure, say, the A peak, the B peak, and the AA peak, and we know all about the system. In practice, of course, we must try to find a set of coefficients which will explain the relative peak sizes as well as possible. We must also bear in mind that a system of coefficients such as that proposed takes account only of the influence of a layer on its immediate neighbors. Long-term order, of the sort which leads to such a structure as $AAABAAAB$ ..., can not be represented by *any* set of values of p_{AA}, ..., though it will still give a characteristic set of peaks on a Fourier transform. It is easy to see, for instance, that the type of ordering just specified, will give a very high peak, of value 1, at 42 A

(still keeping to our example); i.e., the peak A^3B, whereas with any random arrangement this peak would be lower. This high peak is, of course, due to the fact that in such a regular arrangement, all the reflections are at submultiples of 42 A.

The advantage of the Fourier transform is that it represents in a concise form, *all* the information regarding interlayer spacings which can be obtained from the sequence of basal reflections. It often shows up ambiguities and inadequacies in the data. The process of going *back* from a hypothetical structure to the diffraction peaks to be expected, can only prove that the observed diffraction is compatible with this structure; it cannot prove that other plausible structures do not exist. Moreover, where there is neither complete randomness nor complete regularity (as in the Woodbury clay), the calculations of diffraction peaks are in fact difficult to make.

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