

The Determination of the Type of Stacking in Mixed-Layer Clay Minerals

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X-ray scattering distribution from monodimensionally disordered structures as a function of degree of randomness has been investigated in connection with practical application to the study of two-component interstratified clay minerals, by means of the interference function formula recently developed by G. Allegra.

The positions in reciprocal space of the maxima of functions calculated for several statistical configurations and for pairs of spacings occurring in mica-montmorillonite type interstratified minerals, are tabulated. A direct application of these data to the interpretation of some classical and original diffraction patterns is also given.

Introduction

The structures of mixed-layer clay minerals may be considered, along the directions normal to basal planes, to be typical monodimensionally disordered structures.

To resolve these structures by X-ray diffraction techniques, the application of a direct Fourier transform method has been proposed by MacEwan (1956*a*). Nevertheless, a convenient and correct application of such a method is possible only in the few cases where the X-ray diffraction patterns present several basal reflexions and the nature of layers is very similar and known.

The reverse method, based on the calculation of intensity distribution by means of theoretical interference functions, appears, in practice, much more efficient.

An important set of interference functions has been calculated by Brown & Greene-Kelly (1954) and more extensively by MacEwan & Ruiz Amil (1959), by the well-known Hendricks & Teller formula (1942), Méring formula (1949, 1950) and MacEwan method (1958), covering a wide range of two-component mixed-layer clay minerals. The statistical configuration, however, taken into account in those papers, was a completely random one, except in a case of interstratifications built up by equal parts of two layer types (MacEwan & Ruiz Amil, 1959). According to our experience, the mixed-layers, especially of mica-montmorillonite type, which are the most widespread in sedimentary rocks, generally present a poor X-ray diffraction pattern, which cannot be interpreted on the basis of random stacking.

For these reasons, fairly extensive investigation of the possible X-ray scattering distributions, as a function of degree of randomness for different proportions of the components, was considered to be of some theoretical interest, as well as of practical utility.

The interference function formula developed recently by Allegra (1961*a, b*), has been used in this work.

Definition of the type of stacking

With the limitations considered in the previously cited papers, the structure formed by the stacking of two types of layer can be sufficiently defined (by associating the nature of layers with the difference in interlayer distances) by means of the following parameters: the values of c_1 and c_2 spacings, their frequencies p and $(1-p)$, the probabilities q_1 (and q_2) that c_1 (c_2) spacing succeeds another c_1 (c_2) (moving in an arbitrary but defined direction). Only two of the three latter parameters are essential for fixing the statistical configuration of stacking, in accordance with the relation:

$$p(1-q_1) = (1-p)(1-q_2). \quad (1)$$

Nevertheless, in the present investigation it has been found very useful to make use of some other coefficients to express, for different values of p , the same degree of randomness and of segregation.

By choosing in every case $p \leq 0.5$, we can define the degree of randomness (or disorder) by:

$$D = q_1/p \quad (\text{for } 0 \leq q_1 \leq p), \quad (2)$$

and the degree of segregation by:

$$S = 1 - \frac{(1-q_1)}{(1-p)} \quad (\text{for } p \leq q_1 \leq 1). \quad (3)$$

Of course, complete disorder is defined equally by $D=1$ and $S=0$, while a simple mixture of two types of crystal is indicated by the formal value $S=1$.

Calculations of interference functions and results

As the purpose of the present research was to investigate the general effect of the type of stacking on the interference function rather than to resolve a pattern of an actual sample of clay mineral, the Allegra function, valid for a packing of $N \rightarrow \infty$ layers, was considered the most suitable, because of its high sharpness.

It has been of some interest, however, to compare functions, calculated by the Allegra formula, with some others obtained by the MacEwan method for

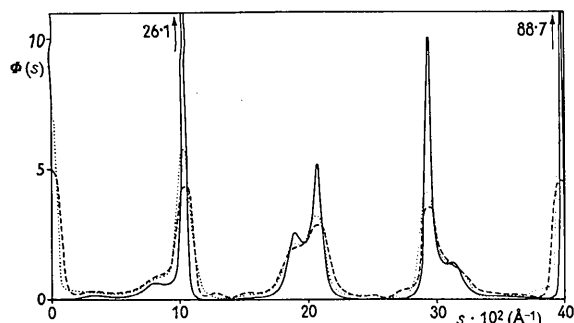


Fig. 1. Interference functions ($c_1=17.8$, $c_2=10.0$ Å; $p=0.2$, $D=0.0$) calculated by means of the Allegra formula (full line) and following the MacEwan method (dashed line: 5 layers; dotted line: 7 layers).

Table 1. Fourier transform coefficients, σ_n

$c_1=17.8$, $c_2=10.0$ Å; $p=0.20$, $D=0.00$

n	R_n	$\sigma_n \times 10$	
		$N=5$	$N=7$
0	0.0 Å	50.0	70.0
1	10.0	32.0	48.0
2	17.8	8.0	12.0
3	20.0	18.0	30.0
4	27.8	12.0	20.0
5	30.0	9.0	18.0
6	37.8	10.0	20.0
7	40.0	3.4	10.1
8	45.6	1.0	2.0
9	47.8	5.2	15.8
10	50.0		5.1
11	55.6	1.4	4.1
12	57.8		10.1
13	60.0		1.9
14	65.6		4.6
15	67.8		4.6
16	73.4		0.3
17	75.6		3.0
18	83.4		0.4

the same statistical configuration. In Fig. 1, an Allegra interference function, valid for a configuration defined by $p=0.20$, $D=0$ and $c_1=17.8$, $c_2=10.0$ (Å), is plotted together with two MacEwan functions, evaluated for packing of five and seven layers. The calculated coefficients σ_n of the Fourier transform,

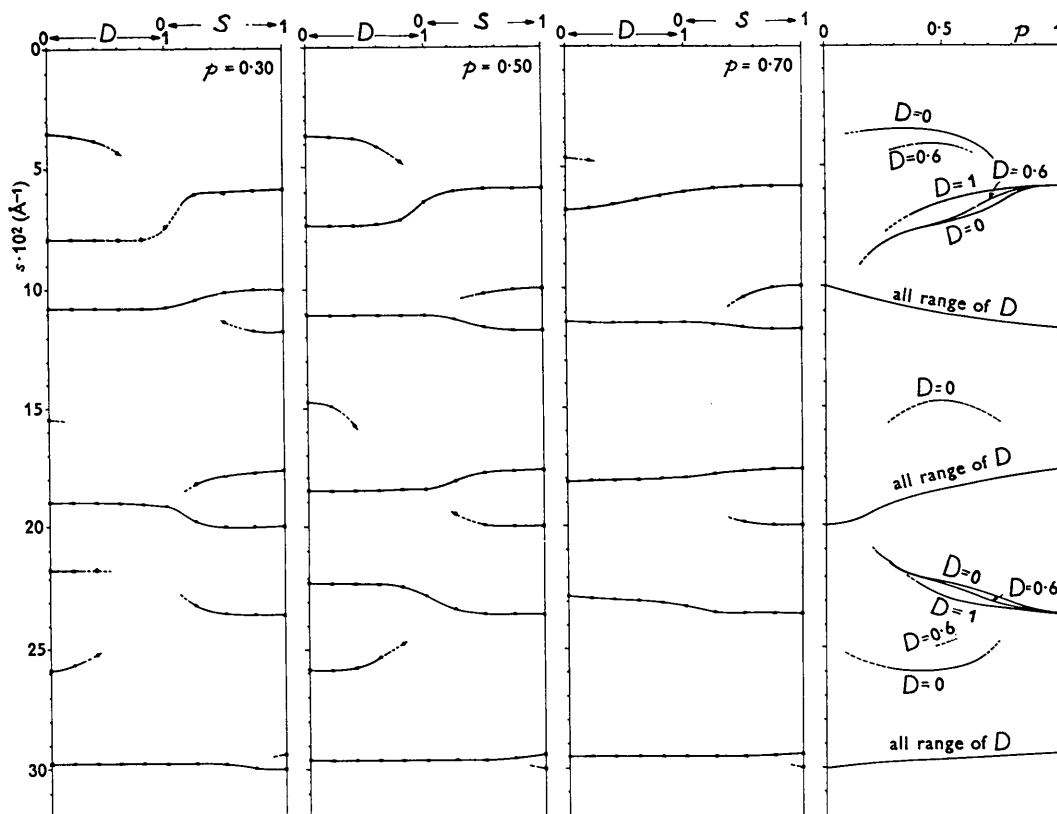


Fig. 2. Diagrams showing the migration of Φ maxima as a function of p and $D(S)$. For further details see text.

$$\Phi(s)N = \sigma_0 + 2\sum_n \sigma_n \cos 2\pi R_n s$$

are given in Table 1; we remember that in the notation of MacEwan, σ_n represents the relative frequency of the interlayer vector \mathbf{R}_n in the packing; \mathbf{s} is the reciprocal vector.

The substantial agreement of the three curves is remarkable in spite of the evident difference in sharpness. An increase of resolution and an attenuation of spurious peaks are observed by passing from the MacEwan function for $N=5$ to one for $N=7$, but a noticeable improvement, in this respect, would probably be obtained for much higher N values, involving extremely heavy computing work which has

been thought unnecessary in the present research.

A large set of interference functions has been calculated, for some pairs of spacings and for several values of p , as a function of degree of disorder (and segregation) by means of the Allegra formula:

$$\Phi(s) = \frac{(q_1 + q_2)(1 - q_1)(1 - q_2)[1 - \cos(\varphi_1 - \varphi_2)s]}{[2 - (q_1 + q_2)]\{[1 - (q_1 + q_2) + (q_1^2 + q_2^2 + q_1 q_2)] + [q_2 - q_1 - q_2(q_1 + q_2)] \cos \varphi_1 s + [q_1 - q_2 - q_1(q_1 + q_2)] \times \cos \varphi_2 s - [1 - (q_1 + q_2)] \cos(\varphi_1 + \varphi_2)s + q_1 q_2 \times \cos(\varphi_1 - \varphi_2)s\}}$$

where: $\varphi_1 = 2\pi c_1$, $\varphi_2 = 2\pi c_2$, $s = 2 \sin \theta / \lambda$.

Table 2. *Interference function maxima for various pairs of spacings as functions of p and $D(S)$*

$$c_1 = 12.5, \quad c_2 = 10.0 \text{ \AA}$$

p	ℓ_{12}	$D = 0.00$		$D = 0.20$		$D = 0.40$		$D = 0.60$		$D = 0.80$		$S = 0.00$ $D = 1.00$		$S = 0.25$		$S = 0.50$		$S = 0.75$		$S = 1.00$		ℓ_1	ℓ_2		
		Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ				
0.1	1																					1	1		
	2	9.80	23	9.80	22	9.80	22	9.80	21	9.85	21	9.85	20	9.90	21	8.5*	8.10	1	10.00	63	8.00	$\rightarrow\infty$			
	3																						2		
	4	20.00	7	20.00	7	20.00	8	20.00	8	20.00	9	20.00	9	20.00	15	16.65	<1	16.10	<1	16.05	1	16.00	$\rightarrow\infty$		2
0.2	1	4.9*																					1	1	
	2	9.55	16	9.55	15	9.55	13	9.55	12	9.60	12	9.65	11	9.75	10	8.5*	8.05	2	10.00	28	8.00	$\rightarrow\infty$			
	3	12.4*																						2	
	4	19.20	3	19.45	3	20.00	3	20.00	3	20.00	4	20.00	4	20.00	7	16.55	1	16.10	1	16.05	2	16.00	$\rightarrow\infty$		2
0.3	1	4.55	<1	4.85	<1	5.3*																	1	1	
	2	9.30	20	9.30	16	9.30	14	9.30	11	9.35	10	9.40	8	9.60	6	8.4*	8.05	3	9.95	16	8.00	$\rightarrow\infty$			
	3	12.80	1	12.70	1	12.6*																		2	
	4	18.45	3	18.45	3	18.55	2	18.75	2	19.40	2	20.00	2	20.00	4	16.40	1	16.10	1	16.05	3	16.00	$\rightarrow\infty$		2
0.4	1	4.45	<1	4.55	<1	4.70	<1	5.5*															1	1	
	2	9.05	33	9.05	23	9.05	17	9.05	13	9.10	10	9.15	8	9.30	5	8.35	3	8.05	5	9.95	11	8.00	$\rightarrow\infty$		
	3	13.10	2	13.10	1	13.10	1	13.15	1	13.35	<1													2	
	4	18.05	7	18.05	5	18.05	3	18.15	2	18.35	2	20.00	2	20.00	3	16.30	1	16.05	2	16.05	5	16.00	$\rightarrow\infty$		2
0.5	1	4.45	$\rightarrow\infty$	4.45	<1	4.55	<1	5.05	<1	6.0*													1	1	
	2	8.90	$\rightarrow\infty$	8.90	62	8.90	30	8.85	18	8.85	11	8.85	7	8.80	5	8.25	4	8.05	7	9.95	7	8.00	$\rightarrow\infty$		
	3	13.35	$\rightarrow\infty$	13.35	3	13.35	1	13.45	1	13.85	1	17.35	1	16.25	2	9.75	4	9.95	7	10.00	$\rightarrow\infty$			2	
	4	17.80	$\rightarrow\infty$	17.80	12	17.75	6	17.75	3	17.70	2	17.35	1	20.00	2	16.05	3	16.00	7	16.00	7	16.00	$\rightarrow\infty$		2
0.6	1	4.65	<1	4.75	<1	5.00	<1	5.5*															1	1	
	2	8.75	40	8.70	27	8.70	19	8.70	14	8.65	11	8.65	8	8.50	6	8.15	6	8.05	11	9.95	5	8.00	$\rightarrow\infty$		
	3	13.65	2	13.65	1	13.80	1	14.20	1	14.9*														2	
	4	17.45	8	17.45	5	17.45	4	17.35	3	17.15	2	16.70	2	16.15	3	16.05	5	16.00	11	16.00	11	16.00	$\rightarrow\infty$		2
0.7	1	5.2*		5.5*		6.0*																	1	1	
	2	8.55	23	8.55	20	8.50	17	8.50	14	8.45	12	8.45	10	8.35	8	8.15	9	8.05	16	9.95	3	8.00	$\rightarrow\infty$		
	3	14.15	1	14.45	1	14.8*																		2	
	4	17.10	4	17.05	4	16.95	3	16.85	3	16.60	3	16.40	3	16.15	4	16.05	7	16.00	16	16.00	16	16.00	$\rightarrow\infty$		2
0.8	1																						1	1	
	2	8.35	21	8.35	20	8.30	18	8.30	17	8.30	16	8.25	15	8.15	12	8.05	14	8.00	28	9.95	2	8.00	$\rightarrow\infty$		
	3																							2	
	4	16.55	4	16.45	4	16.40	4	16.35	4	16.25	4	16.20	5	16.05	7	16.00	12	16.00	28	20.00	2	16.00	$\rightarrow\infty$		2
0.9	1																						1	1	
	2	8.15	24	8.15	25	8.15	25	8.15	26	8.15	26	8.15	26	8.05	26	8.05	27	8.00	63	9.90	1	8.00	$\rightarrow\infty$		
	3																							2	
	4	16.15	9	16.15	9	16.15	9	16.10	10	16.10	10	16.05	10	16.05	15	16.00	27	16.00	63	20.00	1	16.00	$\rightarrow\infty$		2

Table 2 (cont.)

$$c_1 = 17.0, c_2 = 10.0 \text{ \AA}$$

P	ξ_{12}	D = 0.00		D = 0.20		D = 0.40		D = 0.60		D = 0.80		S = 0.00 D = 1.00		S = 0.25		S = 0.50		S = 0.75		S = 1.00		ξ_1	ξ_2			
		s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ					
0.2	1	3.55	<1	3.75	<1	4.0*																	1			
	2	8.55	1	8.4*		8.2*																		1		
	3	10.55	13	10.55	12	10.50	11	10.50	10	10.45	9	10.45	9	6.15	<1	8	5.90	1	5.90	2	5.90	$\rightarrow\infty$		2		
	4																17.90	1	17.70	2	17.65	$\rightarrow\infty$	3			
	5	19.30	7	19.30	6	19.35	6	19.45	5	19.50	5	19.55	5	19.90	7		19.95	12	20.00	28	20.00	$\rightarrow\infty$		2		
	6	21.20	2	21.2*		21.2*								23.05	1		23.45	1	23.50	2	23.55	$\rightarrow\infty$		4		
	7	25.7		25.0*																				5		
	8	29.80	55	29.80	54	29.80	53	29.80	52	29.80	51	29.80	49	29.80	36		29.85	30	29.95	28	30.00	$\rightarrow\infty$		3		
	9	32.75	<1	32.80	<1	32.80	<1	32.95	<1																	
	10	37.95	1	38.10	1	38.5*								35.40	<1		35.30	1	35.30	2	35.30	$\rightarrow\infty$		6		
	11	40.35	24	40.35	23	40.35	22	40.35	21	40.35	20	40.35	19	40.25	14		40.10	15	40.00	28	40.00	$\rightarrow\infty$		4		
	12																								7	
	13	49.15	4	49.20	3	49.35	3	49.80	3	50.00	4	50.00	4	50.00	7	48.0*	50.00	12	50.00	28	50.00	$\rightarrow\infty$		8		
0.3	1	3.55	<1	3.65	<1	3.85	<1	4.3*																1		
	2	7.90	2	7.90	1	7.90	1	7.9*																	1	
	3	10.75	16	10.75	14	10.75	11	10.75	10	10.75	8	10.70	7	10.40	5		10.10	8	10.05	16	10.00	$\rightarrow\infty$		2		
	4	15.5*																						2		
	5	18.95	8	18.95	7	19.00	6	19.00	5	19.05	4	19.15	4	18.2*			17.85	2	17.70	3	17.65	$\rightarrow\infty$		3		
	6	21.70	3	21.70	2	21.65	2	21.55	2	21.2*				19.80	4		20.00	7	20.00	16	20.00	$\rightarrow\infty$		2		
	7	25.90	<1	25.65	<1	25.2*								23.15	1		23.45	1	23.50	3	23.55	$\rightarrow\infty$		4		
	8	29.75	16	29.75	19	29.75	22	29.75	25	29.75	27	29.75	29	29.75	31		29.80	24	29.95	19	30.00	$\rightarrow\infty$		5		
	9	33.00	1	33.05	1	33.10	<1	33.35	<1	33.9*															3	
	10	37.50	1	37.50	1	37.45	1	37.45	1	37.20	1	36.00	1	35.35	1		35.30	1	35.30	3	35.30	$\rightarrow\infty$		6		
	11	40.50	42	40.50	34	40.50	28	40.50	24	40.50	20	40.50	17	40.45	11		40.20	9	40.05	16	40.00	$\rightarrow\infty$		4		
	12	45.0*																							7	
	13	48.65	5	48.70	4	48.70	3	48.75	3	48.90	2	49.60	2	47.8*			50.00	4	50.00	7	50.00	$\rightarrow\infty$		8		
0.4	1	3.60	1	3.65	1	3.75	<1	4.15	<1	4.7*														1		
	2	7.65	4	7.65	3	7.65	2	7.60	1	7.45	1	6.90	1	6.05	1		5.90	2	5.90	5	5.90	$\rightarrow\infty$		1		
	3	10.95	22	10.95	18	10.95	14	10.95	11	10.95	9	10.95	7	10.85	4		10.15	5	10.00	11	10.00	$\rightarrow\infty$		2		
	4	15.0*																						2		
	5	18.75	18	18.75	12	18.75	9	18.75	6	18.75	5	18.75	4	18.5*			17.80	2	17.70	5	17.65	$\rightarrow\infty$		3		
	6	22.00	6	22.00	4	22.00	3	22.00	2	22.00	2	22.15	1	19.7*			19.95	5	20.00	11	20.00	$\rightarrow\infty$		2		
	7	26.00	<1	25.90	<1	25.60	<1	25.5*						23.25	1		23.45	2	23.50	5	23.55	$\rightarrow\infty$		4		
	8	29.70	80	29.70	94	29.70	94	29.70	86	29.70	74	29.70	61	29.70	40		29.70	23	29.90	13	30.00	$\rightarrow\infty$		5		
	9	33.15	2	33.20	1	33.25	1	33.45	1	34.0*															3	
	10	37.25	2	37.20	2	37.20	1	37.10	1	36.80	1	35.65	1	35.35	1		35.30	2	25.30	5	35.30	$\rightarrow\infty$		6		
	11	40.60	40	40.60	38	40.60	32	40.60	26	40.60	21	40.60	16	40.60	10		40.30	6	40.05	11	40.00	$\rightarrow\infty$		4		
	12	44.50	<1	44.70	<1	45.2*																			7	
	13	48.40	10	48.35	7	48.35	5	48.35	4	48.35	3	48.30	2	47.55	1		47.15	2	47.10	5	47.05	$\rightarrow\infty$		8		

The pairs of spacings considered more useful in the study of mica-montmorillonite interstratified clay minerals, are essentially two:

- (1) 12.5–10.0 Å
- (2) 17.5–10.0 Å,

the first for sodium-saturated material, the second for material expanded with glycol or glycerol, although for other pairs as:

- (3) 17.0–10.0 Å
- (4) 17.8–10.0 Å

some calculations have been performed particularly to test the influence on $\Phi(s)$ of small variations in spacings.

In order to detect correctly even small details, the functions were calculated at intervals of 0.001 Å⁻¹ in s . Table 2 reports the position in reciprocal space of the maxima and the values of the Φ function at these points. The second decimal place has been rounded off to the nearest 0.05 or 0.10.

The shape of the maxima, although important, has not been specified but it is possible to observe that peaks of low intensity are generally broad, especially when they arise from the splitting of high ones.

For the diffuse and overlapped maxima, generally weak also, only an approximate position, marked with an asterisk, has been tabulated. Almost all the functions have first been plotted on semilogarithmic

Table 2 (cont.)

$c_1 = 17.5, c_2 = 10.0 \text{ \AA}$

p	$l_1 l_2$	D = 0.00		D = 0.20		D = 0.40		D = 0.60		D = 0.80		S = 0.00 D = 1.00		S = 0.25		S = 0.50		S = 0.75		S = 1.00		l_1	l_2	
		s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ			
0.1	1	3.5*																				1		
	2																						1	
	3	10.20	25	10.20	24	10.20	24	10.20	23	10.15	22	10.15	22	10.10	22	10.05	<1	5.75	<1	10.00	63	10.00	$\rightarrow\infty$	2
	4																						2	
0.2	1	3.45	<1	3.60	<1	3.95	<1	4.4*															1	
	2	8.25	1	8.2*																			1	
	3	10.45	19	10.45	18	10.45	16	10.40	15	10.40	14	10.40	13	10.25	10	10.10	13	5.75	1	10.00	28	10.00	$\rightarrow\infty$	2
	4	16.0*																					2	
0.3	1	3.45	<1	3.55	<1	3.75	<1	4.1*															1	
	2	7.75	1	7.75	1	7.75	1	7.7*		7.5*		7.1*		5.85	1	5.75	1	5.75	2	5.70	$\rightarrow\infty$		1	
	3	10.65	25	10.65	21	10.65	18	10.60	15	10.60	13	10.60	11	10.45	7	10.15	8	10.05	16	10.00	$\rightarrow\infty$		2	
	4	15.2*		15.5*																			3	
0.4	1	3.50	1	3.55	1	3.65	1	3.95	<1	4.5*													1	
	2	7.45	3	7.45	2	7.45	1	7.40	1	7.25	1	6.45	1	5.85	1	5.75	2	5.75	5	5.70	$\rightarrow\infty$		1	
	3	10.80	41	10.80	31	10.75	23	10.75	18	10.75	12	10.75	11	10.75	6	11.05	4	11.35	5	11.45	$\rightarrow\infty$		2	
	4	14.65	1	14.75	1	15.2*																	3	
0.5	1	3.65	$\rightarrow\infty$	3.65	2	3.75	1	3.95	1	4.4*													1	
	2	7.30	$\rightarrow\infty$	7.25	7	7.25	3	7.15	2	6.95	1	6.15	1	5.85	2	5.75	3	5.75	7	5.70	$\rightarrow\infty$		1	
	3	10.90	$\rightarrow\infty$	10.90	87	10.90	44	10.90	27	10.95	17	10.95	12	10.95	7	11.20	5	11.35	7	11.45	$\rightarrow\infty$		2	
	4	14.55	$\rightarrow\infty$	14.60	<1	14.85	<1	15.5*															3	
0.6	1	3.90	1	4.00	1	4.25	1	4.5*															1	
	2	7.00	4	6.95	3	6.90	2	6.75	2	6.40	1	6.00	2	5.80	3	5.75	5	5.70	10	5.70	$\rightarrow\infty$		1	
	3	11.00	35	11.00	31	11.05	25	11.05	20	11.05	16	11.05	13	11.15	9	11.25	7	11.40	11	11.45	$\rightarrow\infty$		2	
	4	14.85	<1	15.0*		15.3*																	3	
0.7	1	4.55	1	5.0*																			1	
	2	6.65	3	6.55	2	6.35	2	6.15	2	6.00	2	5.90	3	5.75	4	5.75	7	5.70	16	5.70	$\rightarrow\infty$		1	
	3	11.15	23	11.15	21	11.15	19	11.15	18	11.15	18	11.15	17	11.20	12	11.30	11	11.40	18	11.45	$\rightarrow\infty$		2	
	4	15.5*																					3	
0.8	1	6.05	3	6.00	3	5.95	3	5.80	4	5.80	4	5.80	4	5.75	7	5.70	12	5.70	26	5.70	$\rightarrow\infty$		1	
	2																						1	
	3	11.25	20	11.25	21	11.25	21	11.25	22	11.25	22	11.25	22	11.30	19	11.35	16	11.40	28	11.45	$\rightarrow\infty$		2	
	4	17.45	9	17.45	8	17.45	8	17.40	8	17.40	7	17.35	7	17.25	8	17.15	12	17.15	15	17.15	$\rightarrow\infty$		3	
0.9	1	5.80	8	5.75	8	5.75	8	5.75	9	5.75	9	5.75	9	5.75	14	5.70	25	5.70	47	5.70	$\rightarrow\infty$		1	
	2																						1	
	3	11.35	18	11.35	18	11.35	18	11.35	17	11.35	18	11.35	19	11.40	29	11.40	41	11.40	42	11.45	$\rightarrow\infty$		2	
	4	17.25	14	17.25	14	17.25	14	17.25	13	17.25	13	17.25	14	17.20	18	17.15	19	17.15	20	17.15	$\rightarrow\infty$		3	

paper in order to minimize these errors; one of these plots has been reported by Allegra in one of his recent works (Allegra, 1964).

It is easily verified that each peak observed for random configuration ($D=1$), by increasing the segregation ($S \rightarrow 1$), splits into two others tending to the basal reflexions of regular stackings of c_1 and c_2 ; and conversely, that, by increase of order ($D \rightarrow 0$),

the peak splits generally into two others tending to those expected for a regular structure having a c spacing equal to $c_1 + c_2$. Actually these last values are attained exactly only when $p=0.5$, in which case alone a complete regular configuration can be defined by means of statistical coefficients q_1 and q_2 . In the other cases, relative small shifts remain, the amount of the shifts as well as the disappearance of some

Table 2 (cont.)

$$c_1 = 17.8, c_2 = 10.0 \text{ \AA}$$

p	l_{12}	D = 0.00		D = 0.20		D = 0.40		D = 0.60		D = 0.80		S = 0.00 D = 1.00		S = 0.25		S = 0.50		S = 0.75		S = 1.00		l_1	l_2		
		s	ϕ	s	ϕ	s	ϕ	s	ϕ	s	ϕ	s	ϕ	s	ϕ	s	ϕ	s	ϕ	s	ϕ				
0.3	1	3.40	<1	3.50	<1	3.60	<1	4.1*				7.10	1	5.70	1	5.65	1	5.60	3	5.60	$\rightarrow\infty$	1			
	2	7.65	1	7.65	1	7.60	1	7.60	1	7.60	1	7.10	1	5.70	1	5.65	1	5.60	3	5.60	$\rightarrow\infty$		1		
	3	10.55	24	10.55	23	10.55	21	10.55	19	10.55	17	10.55	14	10.40	9	10.20	9	10.00	16	10.00	$\rightarrow\infty$				
	4	14.85	<1	15.0*											17.40	1	17.00	1	16.90	3	16.85	$\rightarrow\infty$		3	
	5	18.50	4	18.50	3	18.55	3	18.60	2	18.75	2	19.0*						28.40	2	28.20	3	28.10	$\rightarrow\infty$		5
	6	21.15	7	21.10	6	21.10	5	21.10	4	21.00	4	20.85	3	20.10	4	20.00	7	20.00	16	20.00	$\rightarrow\infty$			2	
	7	24.6*																22.30	1	22.40	3	22.45	$\rightarrow\infty$		4
	8	29.15	13	29.15	10	29.15	9	29.15	8	29.20	7	29.25	6	29.70	5	29.90	7	30.00	16	30.00	$\rightarrow\infty$			3	
	9	31.85	2	31.85	2	31.85	2	31.75	1	31.5*								33.40	1	33.60	1	33.70	$\rightarrow\infty$		6
	10	35.95	<1	35.70	<1	35.4*																			7
	11	39.70	83	39.70	76	39.70	69	39.70	48	39.70	40	39.70	36	39.70	29	39.75	18	39.95	16	40.00	$\rightarrow\infty$			4	
	12	42.80	1	42.80	1	42.90	1	43.00	<1	43.50	<1	44.80	<1	44.90	1	44.90	1	44.90	3	44.90	$\rightarrow\infty$			8	
	13	47.10	1	47.10	1	47.00	<1	46.90	<1	46.1*								50.00	4	50.00	7	50.00	$\rightarrow\infty$		5
0.5	1	3.60	$\rightarrow\infty$	3.60	2	3.70	1	3.80	1	4.2*															
	2	7.20	$\rightarrow\infty$	7.20	6	7.20	3	7.10	2	6.80	1	6.00	1	5.70	2	5.70	3	5.60	7	5.60	$\rightarrow\infty$			1	
	3	10.80	$\rightarrow\infty$	10.80	107	10.80	59	10.80	36	10.80	23	10.80	16	10.80	9	11.00	6	10.05	7	10.00	$\rightarrow\infty$			1	
	4	14.40	$\rightarrow\infty$	14.50	<1	14.60	<1	15.1*										11.20	8	11.25	$\rightarrow\infty$			2	
	5	18.00	$\rightarrow\infty$	18.00	16	18.00	7	17.90	4	17.80	3	17.70	2	17.10	2	16.90	3	20.00	2	20.00	7	20.00	$\rightarrow\infty$		2
	6	21.60	$\rightarrow\infty$	21.60	28	21.60	13	21.60	8	21.60	5	21.70	3	22.10	3	22.30	3	22.40	6	22.45	$\rightarrow\infty$			4	
	7	25.20	$\rightarrow\infty$	25.00	<1	24.3*																			
	8	28.80	$\rightarrow\infty$	28.80	39	28.80	22	28.80	14	28.80	9	28.70	6	28.60	4	28.30	5	28.10	6	28.10	$\rightarrow\infty$			5	
	9	32.35	$\rightarrow\infty$	32.40	10	32.40	5	32.50	3	32.60	2	33.00	1	33.50	2	33.60	3	33.70	7	33.70	$\rightarrow\infty$			6	
	10	36.00	$\rightarrow\infty$	36.00	1	35.80	<1	35.40	<1	34.7*															
	11	39.60	$\rightarrow\infty$	39.60	11	39.60	22	39.60	31	39.60	36	39.60	34	39.60	26	39.60	16	39.40	11	39.35	$\rightarrow\infty$			7	
	12	43.15	$\rightarrow\infty$	43.20	4	43.20	2	43.30	1	43.80	1	44.90	1	45.00	3	45.00	3	40.00	7	40.00	$\rightarrow\infty$			4	
	13	46.75	$\rightarrow\infty$	46.75	3	46.70	2	46.60	1	46.00	1							45.00	6	44.95	$\rightarrow\infty$			8	
																	50.00	7	50.00	$\rightarrow\infty$			5		

peaks being dependent upon p as well as upon the relative difference of the spacings.

In the range $0 \leq D < 1$, the peaks were indexed by irrational indices, l_{12} : this formal indexing allows us to recognize the peaks easily in their evolution in a set of functions.

The modulating effect of the degree of disorder on the interference functions is clearly shown in Fig. 2, where the position of the possible peaks has been plotted as a function of D for different proportions of p , and as a function of p for some D values; the pair of spacings involved being 17.0–10.0 Å. It may be observed that some peaks, generally intense, are almost independent of D and markedly influenced by p , while others, whose importance is more or less limited to the central range of p values, are essentially functions of D .

Application

The data reported in Table 2, besides some others calculated expressly, have been used directly to reinterpret the X-ray diffraction patterns of the well-known samples of the clay minerals from Kinnekulle and Woodbury previously investigated by Byström (1954) and MacEwan (1956b) and of a sample from Pachino, Sicily, studied by us (Cesari, Morelli &

Favretto, 1961) by means of a more limited number of calculated interference functions.

In this application, the positions in reciprocal space of the observed reflexions (s_0) have been compared with those of the peaks of the calculated interference functions (s): effects of displacement of broad maxima due to the Lorentz-polarization factor and to the continuous structure factor have been neglected, while the reflexions very near to the origin, where the slope of these functions is very great, were given slight consideration.

As a first criterion to establish the extent of agreement between observed and calculated values, the following coefficient was computed:

$$\Delta = \left[\frac{\sum_n (s_{0n} - s_n)^2}{n} \right]^{\frac{1}{2}}$$

where n is the number of reflexions considered. No complete calculation of the intensities has been carried out; nevertheless a very rough estimate of them has been obtained by taking into account the height of Φ maxima and the product $F^2(s)Lp$.

The $F(s)$ utilized was that given by Bradley (1953) for montmorillonoid structures.

In Table 3 the experimental data for each sample are reported with values of the function chosen from

calculated ones, which present the minimum Δ coefficient; the reflexions in brackets are not included in this computation.

For the untreated sample from Pachino, the choice has been made from the Φ functions of the 12.5–10.0 set and for the other samples, which were glycol or glycerol treated, from the functions of the 17.0–10.0, 17.5–10.0 and 17.8–10.0 sets.

The determination of a shorter range of p and D has been supported by observing the calculated maxima which do not correspond to any experimental reflexion and were not taken into account in the Δ coefficients. Obviously the Φ functions whose corresponding maxima were lower have been considered to give better agreement.

In the case of the clay from Pachino, the absence of 3, 6, 9 and of 10 l_{12}° reflexions in the untreated sample and the 4, 7, 11 and 12 l_{12}° reflexions in the glycol treated sample induces the consideration that the most probable configuration of stacking is of the partially disordered type, *i.e.* $D=0.4-0.5$.

This result is in complete agreement with the interpretation given previously ($p=0.3$, $q_1=0.15$); the increase of the Δ coefficient is also noticeable on passing from a 17.0–10.0 Φ function to a 17.5–10.0 one, according to the value of 17.0–17.2 Å normally accepted as the interlayer spacing of glycol-expanded montmorillonoid minerals.

MacEwan's interpretation, by means of his Fourier transform method, of X-ray diffraction patterns of glycerol treated samples from Kinnekulle and Woodbury is strictly similar for the two samples: his results are, in fact, respectively $p=0.32$, $D=0.0$ and $p=0.28$, $D=0.0$ and the common pair of spacings 17.8–10.0 Å.

Our interpretation is not far from the former, as can be demonstrated by means of the data reported in Table 3. In comparison with the Pachino sample, we notice that, in this case, the fairly high values of the Δ coefficient, computed for a large range of p and D , are caused by the exceptionally strong disagreement of a few reflexions, *i.e.* the 11 and 14 l_{12}° for Kinnekulle and the 11 l_{12}° for the Woodbury

Table 3. Interpretation of diffraction patterns of natural samples

Sample from Pachino

l_{12}°	Kinnekulle II		Woodbury		$p = 0.2$ $D = 0.0$		$p = 0.3$ $D = 0.0$		$p = 0.4$ $D = 0.0$		$p = 0.2$ $D = 0.2$		$p = 0.3$ $D = 0.2$		$p = 0.4$ $D = 0.2$		$p = 0.3$ $D = 0.4$		$ F(s) ^2 Lp$
	s_o	I_o	s_o	I_o	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	s	Φ	
1			(3.1) vs		3.40	<1	3.40	<1	3.50	1	3.50	<1	3.50	<1	3.50	1	3.60	<1	800
2	7.63	s	7.63	w	8.10	1	7.65	1	7.40	3	8.30	<1	7.65	1	7.40	2	7.60	1	120
3	10.42	vs	10.30	s	10.35	26	10.55	24	10.70	38	10.35	24	10.55	23	10.70	37	10.55	21	30
4	14.29	vwbr			14.8*		14.85	<1	14.50	<1	15.3*		15.0*		14.50	<1			2
5	18.32	m	18.80	vw	18.95	3	18.50	4	18.20	8	19.20	2	18.50	3	18.20	6	18.55	3	15
6	21.10	s	20.87	m	20.75	5	21.15	7	21.40	15	20.70	5	21.10	6	21.40	10	21.10	5	12
7	24.75	vwbr			24.3*		24.6*		24.6*				24.3*						1
8	29.06	vs	29.23	s	29.40	10	29.15	13	29.00	18	29.40	9	29.15	10	29.00	15	29.15	9	18
9	32.26	s	31.44	w	31.30	1	31.85	2	32.20	5	31.2*		31.85	2	32.10	10	31.85	2	20
10	36.10	vwbr			35.30	<1	35.95	<1	36.00	<1	35.2*		35.70	<1	35.90	<1	35.4*		6
11	40.80	m	38.91	vw	39.80	89	39.70	83	39.60	28	39.80	82	39.70	76	39.60	25	39.70	69	1
12					42.50	<1	42.60	1	43.00	2	42.50	<1	42.80	1	43.00	1	42.90	1	1
13	47.15	w			47.35	<1	47.10	1	46.90	2	47.40	<1	47.10	1	46.90	1	47.00	<1	4
14	49.02	s	50.15	ms	50.20	47	50.25	45	50.30	45	50.20	42	50.25	42	50.30	40	50.25	40	3
	Kinnekulle		Δ		0.67		0.53		0.54		0.79		0.57		0.55		0.59		
	Woodbury				0.37		0.36		0.50		0.44		0.36		0.48		0.35		

Samples from Kinnekulle and Woodbury

l_{12}°	Untreated sample	$a_1 = 12.5$ $a_2 = 10.0$								$ F(s) ^2 Lp$	Ethylene glycol treated sample	$a_1 = 17.0$ $a_2 = 10.0$								$ F(s) ^2 Lp$
		$p = 0.3$ $D = 0.0$		$p = 0.3$ $D = 0.4$		$p = 0.3$ $D = 0.6$		$p = 0.3$ $D = 0.8$				$p = 0.3$ $D = 0.0$		$p = 0.3$ $D = 0.4$		$p = 0.3$ $D = 0.6$		$p = 0.3$ $D = 0.4$		
		s_o	I_o	s	Φ	s	Φ	s	Φ			s	Φ	s_o	I_o	s	Φ	s	Φ	
1	(4.0) vwv	4.55	<1	5.3*						500	(4.0) vwv	3.55	<1	3.85	<1	4.3*		3.75	<1	500
2	9.29 vs	9.30	20	9.30	14	9.30	11	9.35	10	50	7.92 ms	7.90	2	7.90	1	7.9*		7.75	1	100
3		12.80	1	12.6*						5	10.63 m	10.75	16	10.75	11	10.75	10	10.65	18	25
4	18.97 m	18.45	3	18.55	2	18.75	2	19.40	2	15		15.5*								5
5	21.05 w	21.55	3	21.45	2	21.25	2	20.60	2	9	19.16 m	18.95	8	19.00	6	19.00	5	18.70	4	15
6		27.20	1	27.4*						11	21.70 mv	21.70	3	21.65	2	21.55	2	21.30	4	10
7	30.77 s	30.70	20	30.70	14	30.70	11	30.65	10	20		25.90	1	25.2*						2
8	(34.7) vwv	35.45	<1	34.7*						10	29.94 vs	29.75	16	29.75	22	29.75	25	29.35	18	20
9		40.00	$\rightarrow \infty$	40.00	$\rightarrow \infty$	40.00	$\rightarrow \infty$	40.00	$\rightarrow \infty$	1	(33.0) wbr	33.00	1	33.10	<1	33.35	<1	32.25	1	15
10		44.55	<1	45.3*						2	(37.8) vwbr	37.50	1	37.50	1	37.45	1	36.25	1	3
11	49.55 w	49.30	20	49.30	14	49.30	11	49.35	10	3		40.50	42	40.50	28	40.50	24	40.00	$\rightarrow \infty$	1
12												45.0*						43.75	<1	2
13											(49.3) wbr	48.65	5	48.70	3	48.75	3	47.75	1	3
14											(51.3) vwbr	51.35	5	51.30	3	51.25	3	50.65	18	2
	Δ		0.35		0.28		0.17		0.30		Δ		0.14		0.12		0.14		0.39	

sample. This disagreement does not improve if the 17.8–10.0 set of Φ functions used is exchanged for the other calculated set, while the agreement deteriorates sensibly for all other reflexions.

In spite of this, the general observations made in the preceding section on the behaviour of Φ maxima as functions of D and p allow us to define markedly the difference between the two samples. In the pattern of the Kinnekulle clay are present, in fact, some reflexions such as the 4, 7, 10 and 13 (the 1 l_{12} was very probably overlapped by central diffusion) which are conversely absent in that of Woodbury: their corresponding Φ maxima disappear principally by increase of D , secondly by decrease of p . By inspection of Table 3, in accordance with the Δ values a stacking configuration defined by p ranging between 0.3–0.4 and $D=0$ can reasonably be assigned to the Kinnekulle sample, while a more disordered structure with D between 0.2 and 0.4 and p very near to 0.3 seems to be the most probable for the Woodbury mineral.

Conclusion

The results of this research show how far the statistical configuration of the stacking influences the Φ distribution of the diffracted energy from lamellar structures such as that of mixed-layer clay minerals.

The practical application given in this paper shows also the possibility of distinguishing fairly well small differences in the statistical configuration of mixed-layers. This is done by considering essentially the positions of observed and calculated maxima without too much regard for definite assumptions about the structure factors, *i.e.* about the nature of the layers.

Refinements, however, in the interpretation of X-ray diffraction patterns of the type considered, are generally very difficult to carry out: they depend on many factors, already extensively discussed by MacEwan, Ruiz Amil & Brown (1961).

Among such factors, which are due to simplifications in the theoretical approach, the most important in our opinion is the assumption that only two spacings

are involved in the stacking. The lack of good agreement between observed and calculated data for some reflexions corresponding to relatively small spacings (the 11 and 14 l_{12} for the clay from Kinnekulle and the 11 l_{12} for that from Woodbury), may probably be justified by admitting the presence, even in small proportions, of spacings additional to the main two.

The calculation of the functions was carried out on the ELEA 9002 Olivetti electronic computer, with the kind cooperation of Mr M. Italiani, to whom we are grateful.

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