Clays and Clay Minerals, 1973, Vol. 21, pp. 15–17. Pergamon Press. Printed in Great Britain

MIXED-LAYER KAOLINITE–MONTMORILLONITE: A COMPARISON OF OBSERVED AND CALCULATED DIFFRACTION PATTERNS

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(*Received* 17 *July* 1972)

Abstract—X-ray diffraction patterns for mixed-layer kaolinite–glycerine–saturated montmorillonite were calculated, taking into account the differences of scattering power of kaolinite and montmorillonite layers. The data were compared with the experimental results for two kaolinite–montmorillonite mixed-layer minerals. The probability parameters and the total number of layers in crystals were established.

In the case of a mixed-layer structure consisting of layers with essentially different scattering powers, the diffraction curves must be calculated taking into account the structure factors of each type of layer. This study was concerned with an analysis of mixed-layer kaolinite–montmorillonite structures. For such structures diffraction patterns were calculated using the Kakinoki and Komura method (1952). The complete scattering intensity of X-rays in the reciprocal space along the axis C by the mixed-layer crystals consisting of N layers and 2 types of layers, can be expressed as follows:

$$I(r^*) = N\overline{V(r^*)}^2 + \left[\sum_{n=1}^{N-1} (N-n)\,\mathrm{Spur}\,V(r^*) \times FQ^n(r^*) + \mathrm{conj.}\right] \qquad (1)$$

where

$F = \begin{vmatrix} W_k & 0 \\ 0 & Wm \end{vmatrix}$ the matrix of the probabilities of finding kaolinite and montmorillonite layers,

$$V(r^*) = \begin{vmatrix} F_k(r^*)F_k^*(r^*) & F_m(r^*)F_k^*(r^*) \\ F_k(r^*)F_m^*(r^*) & F_m(r^*)F_m^*(r^*) \end{vmatrix}$$

the matrix of the structure factors,

$$Q(r^*) = \Phi(r^*)P$$

$$\Phi(r^*) = \begin{vmatrix} \exp -2\pi i r^* d_k & 0 \\ 0 & \exp -2\pi i r^* d_m \end{vmatrix}$$

the matrix of the phase factors,

$$P = \begin{vmatrix} P_{kk} & P_{km} \\ P_{mk} & P_{mm} \end{vmatrix}$$

the matrix of the transition probabilities of finding kaolinite and montmorillonite layers.

Spur ≡ Trace, the sum of the diagonal elements of a square matrix,

d_k, d_m—the thicknesses of the kaolinite and montmorillonite layers,
N—the total number of layers in the crystal,
r^*—the coordinate of the arbitrary point in the reciprocal space along the axis C^*.

If the layers in a crystal of a mixed-layer mineral alternate so that the "Reichweite" $S = 1$ (Kakinoki, Komura, 1952), i.e. the appearance of one of the types of layer in the position n (n being the serial number of the layer within the crystal) depends on the type of $(n-1)$-th, then for a two-component structure the following relationships of the probability parameters hold:

$$W_k + W_M = 1$$

$$P_{KK} + P_{KM} = 1$$

$$P_{MK} + P_{MM} = 1$$

$$W_K P_{KM} = W_M P_{MK}.$$

For characterizing such a mixed-layer structure, it is sufficient to determine two independent probability parameters, e.g. W_M and P_{MM}.

The following statements were assumed to hold for the kaolinite–montmorillonite mixed-layer structure under investigation. The glycerine molecules can be located either between two 2:1 layers or between 2:1 and 1:1 layers, always between the oxygen basal planes of tetrahedra. Hence, glycerine molecules are in contact only with one side of a kaolinite layer. This is confirmed by the fact that the diffraction patterns of these mixed-layer structures, saturated with Mg cations, contain reflections with $d = 7{\cdot}25$ and $3{\cdot}6$ Å. In these conditions all 1:1 layers within every particle must be equivalent in respect of the sequence of tetrahedral and octahedral sheets. That is, in a given direction along the normal to the layers, the kaolinite layers begin with an identical sheet type. An essential feature of the model of mixed-layer structure under consideration is the fact that the hydrogen bonds are formed not only between two neighboring kaolinite layers but also between the OH-groups of the kaolinite layer and the oxygen atoms of the adjacent 2 : 1 layer.

In calculating the structurel factors, the origin of coordinates of 2 : 1 and 1 : 1 layers was chosen at the surface of the basal oxygens of the tetrahedral network, since these atom planes are most similar as regards the composition and the scattering power. On the other hand, this choice of the origin of coordinates is explained by the fact that one of the outer crystal surfaces is always formed by the oxygen surface of the tetrahedral sheet, independent of the types of the first and the last layers of the crystal. Regrettably, we do not know whether the glycerine layers adhere to the outer surface of the crystal beginning and (or) ending with 2 : 1 layers. We have chosen the "asymmetrical" version of the location of the glycerine molecules on one outer crystal surface only, when the crystal begins and (or) ends with 2 : 1 layers. The errors due to the inadequate account of the scattering from the material located on the outer crystal surfaces are insignificant at large enough N, especially in view of the relatively weak scattering power of glycerine molecules. Moreover, in the case of a high content of kaolinite layers in a crystal of a mixed-layer mineral, the probability of occurrence of two 2 : 1 layers at both crystal surfaces is insignificant.

Using a computer, according to expression (1), the curves of X-ray scattering intensity in the reciprocal space along the axis C^* for mixed-layer glycerine-saturated kaolinite–montmorillonite were calculated. The input data were the probable parameters W_M and P_{MM} and the total number of layers in crystal N. W_M was varied from 0·1 to 0·9 in steps of 0·05, P_{MM} from 0 to 1 in steps of 0·05. The structure factors of the unit cells of kaolinite and montmorillonite, for an arbitrary point in the reciprocal space r^* along the axis C^*, were calculated using the expression:

$$F(r^*) = \sum_j K_j f_j \exp 2\pi i r^* Z_j, \qquad (2)$$

where:

Z_j – the coordinate in a direction perpendicular to layers of j-atom in the unit cell in Å
K_j – the number of j-atoms,
f_j – the atomic scattering factor of j-atom.

Coordinates of the atoms of the unit cells of kaolinite and glycerine-saturated montmorillonite respectively, are borrowed from: Drits, Kashaev (1960) and Hamilton (1967) (Table 1). The real condition of photographing the diffraction pattern leads to a distortion of the "ideal" profile of diffraction lines which depends solely on the structure of the object being investigated, due to the "instrumental" effect. The measured profile of the lines $H(\theta)$ is a convolution of the "ideal" diffraction profile $I(\theta)$ and the function $G(\theta)$ describing the influence of the instrumental factors:

$$H(\theta) = \int I(\theta')G(\theta-\theta')\, d\theta'. \qquad (3)$$

The "instrumental" function $G(\theta)$ was assumed as the profile of the lines of the standard sample of triclinic kaolinite. The computer-calculated "ideal" diffraction profiles of the lines of intensity $I(\theta)$ according to expression (1), were then adjusted taking into account the "instrumental" function $G(\theta)$ and the geometrical and polarization factors for the random powder aggregate.

The objects of study were sample 99–70 of hydrothermally altered clay from Southwestern Kamchatka, and sample 244–8 from the weathering crust of the Eocenic volcanogenic series of the Black Sea coast of Adjaria diagnosed as mixed-layer kaolinite–montmorillonite formations.

Figure 1 gives the diffraction patterns from the oriented preparations of glycerine saturated samples and the theoretical diffraction curves for mixed-layer crystals consisting of layers of kaolinite and montmorillonite in the interlayers of which molecules of glycerine are situated.

The calculated diffraction curves are in good agreement with the experimental observations. For sample 99–70 the following parameters were obtained: $W_k = P_{kk} = P_{mk} = 0{\cdot}75$; $W_m = P_{km} = P_{mm} = 0{\cdot}25$; $N = 20$, and for sample 244–8, $W_k = P_{kk} =$

Table 1. The composition and the coordinates of atoms of the unit cells of the kaolinite and glycerine-saturated montmorillonite

Kaolinite (7·15 Å)		Montmorillonite (17·78 Å)	
Composition	Z(Å)	Composition	Z(Å)
6 O	0	6 O	0
4 Si	0·58	4 Si	0·58
4 O; 2 OH	2·20	6 O	2·24
4 Al	3·31	4 Al	3·29
6 OH	4·31	6 O	4·34
		4 Si	6·00
		6 O	6·58
		2·25 OH; 2·25 C	9·74
		2·25 OH; 2·25 C	10·54
		0·5 Na	12·18
		2·25 OH; 2·25 C	13·82
		2·25 OH; 2·25 C	14·62

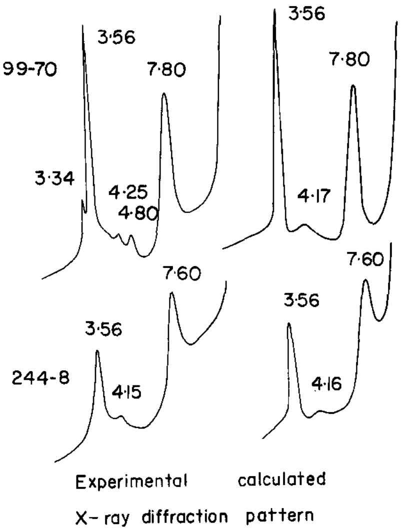

Fig. 1. Diffraction patterns from the oriented preparations of glycerine saturated samples and the theoretical diffraction curves for mixed-layer crystals.

$P_{mk} = 0{\cdot}8$ and $W_m = P_{km} = P_{mm} = 0{\cdot}2$; $N = 10$.

The findings of the investigation thus attest to the existence in nature of mixed-layer kaolinite–montmorillonite minerals. At present we have at our disposal an atlas of theoretically calculated diffraction curves for mixed-layer glycerine-saturated kaolinite–montmorillonite structures with differing ratios and sequences of layers and for crystals of different thicknesses.

Schultz *et al.* (1970) described with mixed-layer minerals a kaolinite–montmorillonite from the deposits of Ticul, Tepacan, and Becal. A comparison of the spacings of the basal reflections from these samples with the spacings determined from the calculated diffraction patterns of mixed-layer structures with a random alternation of 2 : 1 and 1 : 1 layers has shown that the best agreement of the results is obtained with the following ratio of kaolinite and montmorillonite layers in the samples being compared. Ticul: $0{\cdot}70 \times 0{\cdot}30$, Tepacan: $0{\cdot}65 \times 0{\cdot}35$, Becal: $0{\cdot}60 \times 0{\cdot}40$. Our data on ratios of 2 : 1 and 1 : 1 layers considerably differ from the results obtained by Schultz *et al.* from chemical analyses of the samples. It should be noted that we did not compare the experimental and calculated intensities of basal reflections.

Wiewiora (*1971*, *1972*) also investigated a mixed-layer kaolinite–montmorillonite. Using the method of Fourier transformations, he found the structure to consist of: 86 per cent of kaolinite layers and 14 per cent of montmorillonite layers randomly interstratified. The spacings of basal reflections for this sample agree well with the results of our calculations for mixed-layer structure having the same ratio of randomly interstratified components.

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Résumé—Les diagrammes de diffraction X d'interstratifiés kaolinite–montmorillonite saturée de glycérol ont été calculés en tenant compte des différences des pouvoirs diffusants des couches de kaolinite et de montmorillonite. Ces données ont été comparées avec les résultats expérimentaux fournis par deux interstratifiés kaolinite–montmorillonite. On a pu ainsi déterminer la probabilité d'apparition et le nombre total de feuillets dans les cristaux.

Kurzreferat—Es wurden die Röntgenbeugungsbilder für gemischte Schichten von Kaolinit, Glyzerin und gesättigtem Montmorrillonit berechnet, wobei die unterschiedlichen Streuleistungen der Kaolinit- und Montmorillonitschichten berücksichtigt wurden. Die errechneten Werte wurden mit den Versuchsergebnissen für zwei gemischte Kaolinit- und Montmorillonitgesteine verglichen. Es wurden die Wahrscheinlichkeitsparameter und die Gesamtzahl der Schichten in den Kristallen bestimmt.

Резюме— Оценивались диффракционные картины рентгенограмм каолинита смешанного наслоения и насыщенного глицерином монтмориллонита, принимая во внимание различные рассеивающие способности слоев каолинита и монтмориллонита. Полученные данные сравнивались с результатами экспериментов с двумя минералами смешанного наслоения: каолинита и монтмориллонита.