Clays and Clay Minerals, Vol. 31, No. 4, 315–316, 1983.

STRUCTURE DEFECTS IN LAYER SILICATE CLAY MINERALS

Key Words—Defects, Diffraction line profile, Fourier coefficients, Kaolinite, Layer shift, Nontronite.

Mitra and Bhattacherjee (1969a, 1969b, 1970) studied quantitatively two specific layer disorders in kaolinite by single-line techniques based on variances of the pure diffraction profiles. The disorders were characterized by variability of interlayer spacings and shift of the layer. The method assumed the diffraction profile to be the result of convolution of the particle size profile and the profile of the particular defect. Finally, the total variances were calculated by directly adding the variances due to particle size and the specific defect by using the corresponding formulae given by Wilson (1962). In this simple method, some terms were omitted as will be evident from the present work wherein the total variance has been calculated directly from the Fourier coefficients of the diffraction profile applying a convolution technique. The modified technique has been used for further study of kaolinite and nontronite samples and their dehydration products.

EXPERIMENTAL METHODS

A Georgia kaolinite as reported by Mitra and Bhattacherjee (1969a, 1969b, 1970) and a nontronite sample from east of Freeman, Washington (Smithsonian Institution, USNM 106432) dehydrated to different temperatures were investigated. The experimental techniques were the same as described by Mitra and Bhattacherjee (1969a, 1969b, 1970). The differential thermal analysis pattern of the nontronite showed a sharp endothermal peak at 200°C followed by two weak peaks of gradually decreasing intensity around 500°C and 620°C. An extremely weak and broad exothermal peak was present at 880°C.

THEORETICAL CONSIDERATIONS

Single line technique for evaluating the probability of layer shift

As discussed by Mitra and Bhattacherjee (1970), disorder consists of shifting of the layers with respect to the adjacent layers by (1/3)b or (2/3)b and can be studied from reflections of type $hk0$ where $k \neq 3n$. The most suitable line of this type discussed by these authors in kaolinite is 020. In the present study the previous single line technique of Mitra and Bhattacherjee (1970) has been modified.

The total variance W of the line profile corrected for geometrical aberrations is given by Wilson (1962) as:

$$W = -1/4\pi^2[4SA'(O)/A(O) + A''(O)/A(O)], \quad (1)$$

where 2S is the range, A(O) is the Fourier coefficient, and A′(O) and A″(O) are its first and second derivatives, respectively. Using the convolution principle, A(n) can be written as

$$A(n) = N(n)H(n), \quad (2)$$

where N(n) is the nth order Fourier coefficient of the particle size line profile and H(n) is that of the defect profile. H(n) is given by Mitra and Bhattacherjee (1970) as:

$$H(n) = NF^2\exp(-3\alpha n/2), \quad (3)$$

where α is the probability of shift of a normal layer with respect to its adjacent one by (1/3)b or (2/3)b. F is the structure amplitude of a layer for the given reflection. Combining the above three equations and rearranging terms yields

$$W\cos\theta/\lambda\Delta(2\theta) = 1/2\pi^2P - 1/\pi^2(9\alpha^2/16d^2 + 3\alpha/4Td) \cdot \lambda/\Delta(2\theta)\cos\theta, \quad (4)$$

where T = Nd and is the particle size in the direction of reflection, d is the interplanar distance, and $1/P = 1/T + 3\alpha/2d$. From a plot $W\cos\theta/\lambda\Delta(2\theta)$ and $\lambda/\Delta\cos\theta$ where S is the total range and W the variance in 2θ units, α can be estimated.

Single line technique for studying variability

To study the variability defect which consists of variation of the interlayer spacings by a constant fraction g of the interlayer distance, the technique of Mitra and Bhattacherjee (1969a) was modified by a direct approach as mentioned above. According to Mitra and Bhattacherjee (1969a) the Fourier transform H(n) of the intensity profile from a layered structure with variable interlayer spacing in the 001 direction is given by

$$H(n) = NF^2e^{-2\beta n}e^{-ibn}, \quad (5)$$

where $\beta = \gamma/2(1 - \cos 2\pi lg)$, $b = \gamma 2\pi lg$, and γ is the proportion of planes affected by the defect. Using the formula for variance of Wilson (1962) and proceeding as in the previous section yields the expression

$$W\cos\theta/\lambda\Delta(2\theta) = 1/2\pi^2P - (\beta/\pi^2d^2)(\beta + d/T) \cdot\lambda/\Delta(2\theta)\cos\theta, \quad (6)$$

where $1/P = 1/T + 2\beta/d$.

RESULTS AND OBSERVATIONS

Comparison with the expressions of Mitra and Bhattacherjee (1969a, 1969b, 1970) shows more terms in Eqs. (4) and (6). The effects of these additional terms are shown in Table 1. Values of α are, in general, more than the corresponding values of these parameters as reported by Mitra and Bhattacherjee (1969a, 1969b, 1970). The nature of the variation of γ and g in kaolinite is more or less similar by both the methods.

In nontronite, whereas the value of g is quite high, the value of γ is much smaller than in kaolinite. Unlike kaolinite, here values of g are more or less the same whereas the γ value starts rising at 400°C and reaches a maximum at 500°C, corresponding to the second endothermal peak in the thermogram. Thus, it appears that as dehydration proceeds, more and more planes are affected and the process continues, resulting finally in the collapse of the structure to a metaform.

Table 1. Values of α corresponding to 020 reflection of kaolinite and of g and γ of nontronite at different temperatures.

Temperature (°C)	Kaolinite		Nontronite	
	α (present method)	α (literature[1])	g	γ
30	0.016	0.014	0.480	0.008
200	0.026	0.016	0.484	0.009
300	0.031	0.021	0.485	0.007
400	0.035	0.023	0.485	0.011
500			0.484	0.051

[1] Mitra and Bhattacherjee (1969a, 1969b, 1970).

ACKNOWLEDGMENT

The authors are grateful to the Smithsonian Institution for providing the nontronite sample.

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(Received 8 May 1982; accepted 4 February 1983)