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INTERSTRATIFICATION OF 10- AND 7-Å LAYERS IN HALLOYSITE: ALLEGRA'S MIXING FUNCTION FOR RANDOM AND PARTIALLY ORDERED STACKING

Key Words—Allegra's mixing function, Halloysite, Interstratification, Ordering.

When examining occurrences of halloysite in New South Wales (Slansky, 1983), the author was confronted with the problem of interpreting X-ray powder diffractograms of partly dehydrated and partly glycolated specimens of halloysite. In both types of patterns the 001 reflections appeared in two relatively narrow regions within a band of increased intensity. For partly hydrated halloysite this phenomenon was first noted by Brindley and Goodyear (1948) and subsequently studied by others (Harrison and Greenberg, 1962; Hughes, 1966; Hughes and Foster, 1970).

Churchman *et al.* (1972) concluded that dehydration of halloysite takes place via an interstratification in which partial segregation of two basic layers at 7.2 and 10.1 Å exists. They also estimated approximate basal peak profiles from the interstratification of these hydrated and dehydrated layers using the method of MacEwan (1958) and calculated MacEwan's mixing function for a set of statistical parameters p_A and $p_{A.A}$ ranging from 0.1 to 0.9, and 0.1 to 1.0, respectively. The parameter p_A is generally accepted as the frequency of occurrence of layer A, such as a 10.1-Å layer, and $p_{A.A}$ is the probability that a layer succeeds another layer A in a given direction (see Reynolds, 1980). The best fit with experimental results, obtained from halloysite occurring near Te Puka, New Zealand, was achieved by Churchman *et al.* (1972) for curves calculated with $p_A < p_{A.A} < 1.0$, when these parameters were related to each other according to the "degree of segregation" of Cesari *et al.* (1965).

In the determination of the type of stacking in mixed-layer clay minerals by means of an interference function developed by Allegra (1961), Cesari *et al.* (1965) defined this degree of segregation as

$$S = 1 - [(1 - p_{A.A})/(1 - p_A)] \quad (\text{for } p_A < p_{A.A} < 1). \quad (1)$$

They also defined a degree of randomness as

$$D = p_{A.A}/p_A \quad (\text{for } 0 < p_{A.A} < p_A), \quad (2)$$

noting that complete disorder is defined by $D = 1$ as well as by $S = 0$. In every case $p_A < 0.5$. Cesari *et al.* (1961) also presented a working formula of Allegra's mixing function. For convenience, this formula can be rewritten as:

$$\Phi(s) = \frac{A(B + C)G}{(1 + C)(A^2 + CF - BG + D\cos s\phi_1 + E\cos s\phi_2)}, \quad (3)$$

where:

$$\begin{aligned} A &= q_1 + q_2, \\ B &= q_1 q_2, \\ C &= 1 - (q_1 + q_2), \\ D &= q_2[1 - (q_1 + q_2)] - q_1, \\ E &= q_1[1 - q_1 + q_2)] - q_2, \\ F &= 1 - \cos s(\phi_1 + \phi_2), \\ G &= 1 - \cos s(\phi_1 - \phi_2), \end{aligned}$$

and

$$\begin{aligned} s &= 1/d, \\ q_1 &= p_{A.A}, \\ q_2 &= p_{B.B}, \\ \phi_1 &= 2\pi d_1, \\ \phi_2 &= 2\pi d_2, \text{ and} \\ d_1 &> d_2. \end{aligned}$$

The formula takes into consideration the manner of stacking of individual layers and is valid only for infinitely extensive layer sequences. It does not allow incorporation of different scattering functions for interlamellar material; however, for the binary system of 10.1- and 7.2-Å layers in halloysite the use of Allegra's function is practical with no need for more elaborate procedures. The interstratification of hydrated and dehydrated kaolin layers is an ideal system for a systematic calculation of this function, as it does not involve significantly different structure factors. The purpose of this note is to undertake such a calculation with the aim to construct graphs which could be used for the identification of the manner in which the two layers are assembled in naturally occurring halloysites, and to establish the ratio of these layers.

RESULTS AND DISCUSSION

Allegra's function was computed for interstratification of hydrated and dehydrated kaolin layers with various degrees of randomness and segregation. Complete, intermediate, and absent randomness, as well as several levels of segregation ranging from very low to high, were evaluated. Some results for the combinations of $001_{10}/001_7$ and $003_{10}/002_7$ are illustrated by Figures 1–3. In Figures 1 and 2 the mixing function is plotted in relation to the frequency of occurrence of the two layers, expressed as the fractional proportion of the 10-Å layer. Figure 3 shows the movement of $001_{10}/001_7$ and $003_{10}/002_7$ peaks of the mixing func-

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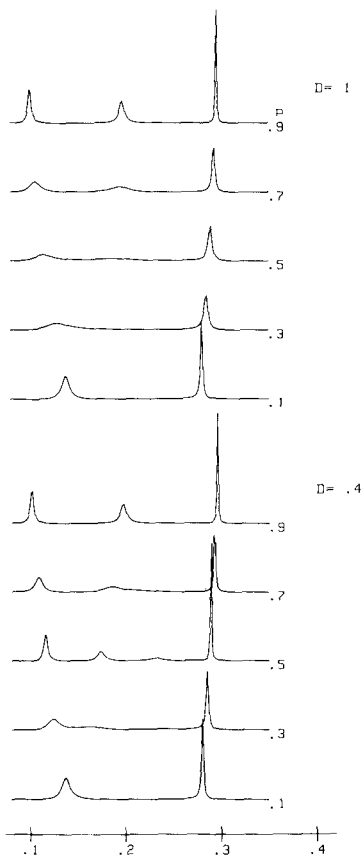


Figure 1. Allegra's mixing function of completely random (D = 1) and partially ordered (D = 0.4) interstratification of 10.1/7.2-Å layers. p = percentage content of 10.1-Å layers; the horizontal scale is 1/d.

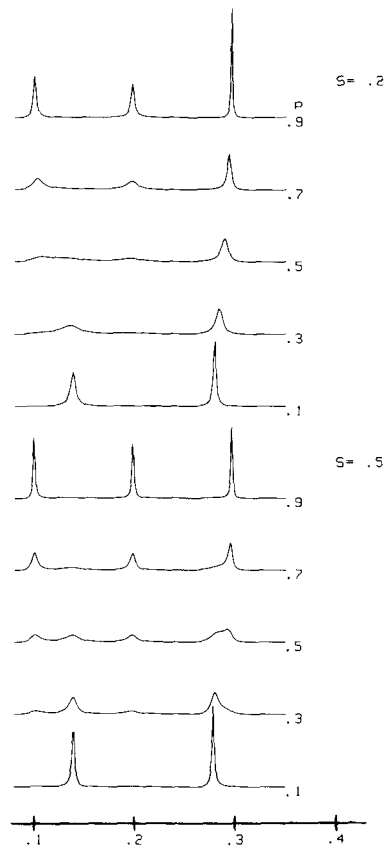


Figure 2. Allegra's mixing function for two cases of partly segregated interstratification of 10.1/7.2-Å layers. p = percentage of 10.1-Å layers; the horizontal scale is 1/d.

tion in relation to the same variable. The diagrams show that the first-order peaks, even for a moderate segregation (such as 0.2), tend to group near the spacings of the two layers, i.e., 10 and 7 Å, respectively. The peak position corresponding to the prevailing form, hydrated or dehydrated, is only slightly influenced by the presence of the other one. For high segregation, the assemblage assumes the behavior of a mechanical mixture, for all practical purposes. The random and regular combinations, where D equals 1 and 0, produce a continuous variation with p_A. The resulting curves are S-shaped, and bent in a manner that is opposite with respect to each other. The $003_{10}/002_7$ combinations appear to be continuous until the segregation 0.6. At this value, these peaks behave similarly to the first-order peaks, being near 3.6 Å for the dehydrated layer, and near 3.37 for the hydrated layer.

The mixing function can be multiplied by the appropriate form of the Lorentz-polarization factor (LP) and the squared amplitude of layer structure factor (SFL) in order to calculate diffraction from a mixed-layer assemblage. This was done for several selected cases with the aid of structure factor values computed by Cole and Lancucki (1966) and the single crystal form of the Lorentz-polarization factor. When compared with curves of Figures 1 and 2, the influence of SFL and LP is mainly in modifying the size and shape of the mixing function maxima, whereas the shift in the position of the peaks is less noticeable. Thus, when, as is often the case in clay mineralogy, strictly quantitative results are not always required, it is sufficient to compare the diffractometer traces of a material under study with peaks of the mixing function. For this application, the first step is to use curves showing peak migration with composition (Figure 3) followed by careful matching of mixing function maxima with diffraction peaks. Figure 4 shows the latter procedure. Halloysite from Wanaaring (Great Australian Basin, northwest New South Wales, Australia) was examined at three different stages of hydration and its first-order basal peaks were compared with Allegra's mixing function. A very good

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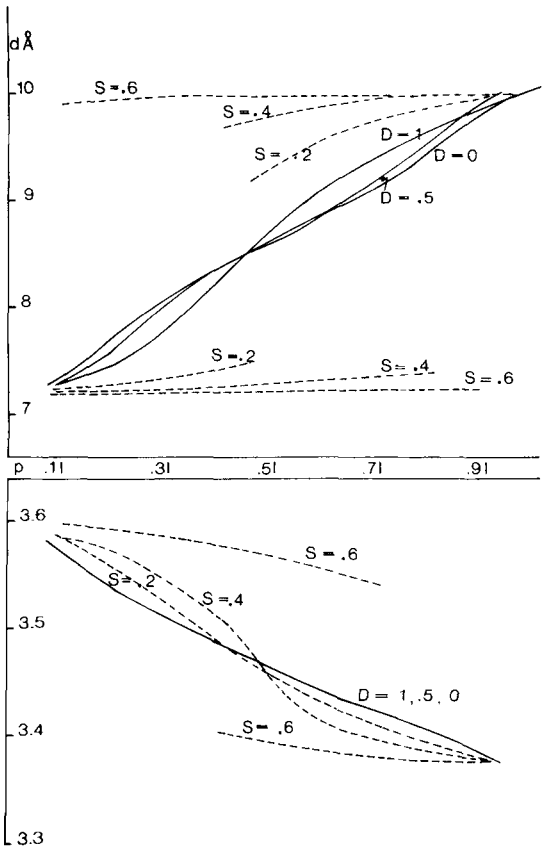


Figure 3. Migration of 001/001 and 003/002 peaks of Allegra's mixing function for interstratification of 10.1- and 7.2-Å layers with composition and the type of stacking. D = degree of randomness; S = degree of segregation; p = percentage content of 10.1-Å layers.

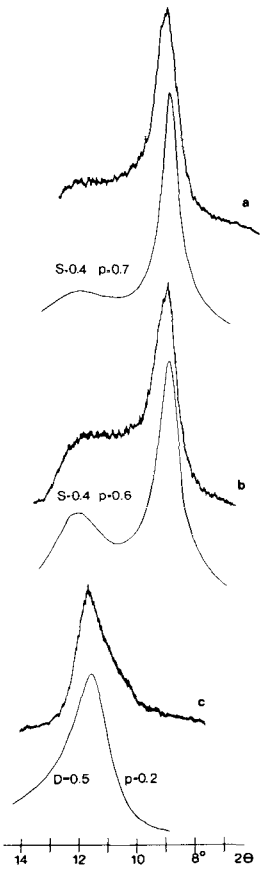


Figure 4. Comparison of diffraction patterns (CuKα) of halloysite from Wanaaring with Allegra's mixing function. Calculated curves (smooth) were normalized to match the diffraction patterns. (a) Specimen wet after washing in water; (b) specimen in the process of drying; (c) dry specimen.

match was found for wet and air-dry specimens with curves for partly segregated interstratification at S = 0.4 and the percentage content of 10.1-Å component of 0.7 and 0.6, respectively. For an almost dehydrated specimen a good match was established with a partially ordered curve (D = 0.5) for 0.2 of 10.1-Å layers.

When a rigorous, quantitative approach is desirable, an accurate modeling of diffraction maxima should be attempted. This modeling involves dealing with several problems, including the best form of LP, the number of layers in the interstratified assemblage, the correct atomic scattering factors, and the contribution of interlamellar material to SFL.

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