COMMENTS

THE FUNDAMENTAL NATURE OF ILLITE/SMECTITE MIXED-LAYER CLAY PARTICLES: A COMMENT ON PAPERS BY P. H. NADEAU AND COWORKERS

Recently, conventional transmission electron microscopy (TEM) of a regular illite/smectite (I/S) (52% illite layers) having R=1 ordering was reported by Nadeau *et al.* (1984a, 1984b). In these studies, they estimated that 79% of these clay particles were only 20 Å thick along the *c*-axis direction. A complementary TEM and X-ray powder diffraction (XRD) approach was used to show that very thin particles can still provide significant coherent diffraction by X-rays, even if the particles are less than the theoretical size limit for coherent diffraction (Brindley, 1980). To account for an apparent mixed-layer XRD pattern, Nadeau *et al.* (1984a, 1984b) suggested that interparticle diffraction occurred between these very thin (~20 Å) particles as well as between individual particles and complexes of water and/or organic molecules. In the course of these arguments, Nadeau *et al.* (1984a, 1984b) suggested that regular I/S consists of elementary illite particles 20 Å thick in the *c*-axis direction. Indeed, they suggested on the basis of these results, that randomly interstratified I/S can be regarded as two phases, smectite and illite, and that regularly interstratified I/S is a single phase of illite 20–50 Å thick (Nadeau *et al.,* 1984b). The following is an alternative interpretation of the TEM results obtained by Nadeau *et al.* (1984a, 1984b) on the regularly interstratified I/S (sample MB 235) from Canon City, Colorado). This interpretation suggests that no evidence exists for the presence of only illite particles in this sample.

LAYER COLLAPSE

High-resolution transmission electron microscopy (HRTEM) studies of I/S mixed-layer clays have shown that expanded smectite and alternating illite and smectite layers can be directly imaged along the basal direction (Yoshida, 1973; McKee and Buseck, 1978; Klimentidis and Mackinnon, 1986). Basal dimensions measured from these studies show that particle thicknesses can be many unit cells in the *c*-axis direction. A number of these studies have noted a range of basal spacings for the smectite layer, due, in part, to varia-

tions in the degree of layer collapse (Page and Wenk, 1979; Ahn and Peacor, 1985). Other studies have indicated that smectite layers completely collapse to ~10 Å (Yoshida, 1973; Eggleton, 1984; Klimentidis and Mackinnon, 1986). Kohyama *et al.* (1982) showed that untreated smectite in a water-saturated environmental cell has a typical 16-Å basal spacing; however, within 30 min of evacuation of the environmental cell, smectite layers collapsed to 12.7 Å. Collapse or partial collapse of smectite layers may be due to the length of time under vacuum or in the electron beam, cleanliness and level of vacuum, microscope operating voltage, and sample preparation techniques (e.g., heating as a result of sample removal, sample coating, or ion-milling). Thus, untreated smectite layers observed directly with an electron microscope may show a range of basal spacings between 10 and 16 Å. Similarly, mixed-layer I/S may show basal spacings between 20 and 26 Å when subjected to layer collapse through sample preparation and/or electron microscope observation.

The experimental procedures reported by Nadeau *et al.* (1984a, 1984b) for both montmorillonite and I/S utilized moderate vacuum ($<10^{-5}$ torr) and, in the case of Pt shadowing, significant temperatures. Indeed, in the procedural reference quoted, Weir *et al.* (1962) indicated that the (at the time) conventional method to determine shadow angle via latex spheres could not be used because radiant heat from the evaporator filament caused latex spheres to flatten. Clay samples which contain a significant percentage of collapsed or partially collapsed layers (such as those investigated by Nadeau *et al.,* 1984a, 1984b) may show considerable variation in basal spacing when subjected to the experimental procedures described by Weir *et al.* (1962). The values of basal spacings in clays with small crystallite thicknesses are relevant to this discussion as Weir *et al.* (1962) showed that the XRD basal spacing may be approximated by thickness measurements of the clay particle. Thus, Weir *et al.* (1962) made the reasonable assumption that particle thicknesses for allevardite specimens (~19.5 Å) are directly related to basal spac-

ings (d(001) $\approx$ 19.3 Å, *collapsed lattice*). A similar assumption relating basal spacing (collapsed or uncollapsed) to particle thickness for crystallites with Np < 5 will be adopted here. A given particle thickness may or may not take integral multiples of basal spacing, but for the work reported by Nadeau *et al.* (1984a, 1984b) where the precision is relatively low, only integral multiples of basal spacing need be considered.

The Pt shadowing technique used by Nadeau *et al.* (1984a, 1984b) to measure individual particle thicknesses has a relatively low precision. The exact value for the precision of this technique is suggested by Nadeau *et al.* (1984a) to be ±4 Å based upon the earlier work of Weir *et al.* (1962). This technique uses a low shadow angle (~11°) and collimated thermal evaporation to deposit metal particles. Recently, sophisticated shadowing techniques (Wildhaber *et al.*, 1985) and model calculations (Guckenberger, 1985) over a wide range of shadowing angle, showed that problems of interpretation of thin metal films can arise if geometrical shadowing and decoration cannot be properly distinguished. In addition, visual comparison of shadow casting results are quite subjective, and this subjectivity has prompted practitioners of the art to turn to computer-based image analysis for reliable results on surface reliefs (Chalcroft, 1985; Wildhaber *et al.*, 1985). Although the full details of the shadowing techniques used by Nadeau *et al.* (1984a, 1984b) are not immediately apparent, the precision of their particle thickness measurements and implications for their interpretation should be evaluated with care. The relative precision of the Pt shadowing technique is critical to a clear interpretation of the particle size histograms presented by Nadeau *et al.* (1984a, 1984b). This aspect is illustrated by considering two possible cases: (1) when the precision, p, is <4 Å, or (2) when p > 4 Å.

The *c*-axis particle-thickness distribution for the regular I/S from Canon City, Colorado, ranges from ~7 to ~30 Å, with the bulk of the grains measured at ~20 Å (see Figure 4b of Nadeau *et al.*, 1984a). For p > 4 Å, the size distribution data presented in Figure 4 of Nadeau *et al.* (1984a) will merely show the relative error in thickness determinations for all clay particles measured. Assuming that (1) smectite layer collapse is not significant, and (2) these samples contain only illite, particle thicknesses along the *c*-axis should only be integer multiples of the basic layer repeat, 10 Å. This repeat would correspond to individual crystallites of 1 layer, 2 layers, etc. of illite. A size distribution corresponding to integer multiples of 10 Å is not shown in any histogram presented in Figure 4 of Nadeau *et al.* (1984a). In the specific case of I/S from Canon City, Colorado, particle thicknesses appear to follow a gaussian normal distribution, apart from the slight drop in frequency values at ~13 and ~15 Å. This spread of particle thickness values from <10 to ~30 Å may

simply have been an inherent artifact of the measurement technique if the precision was greater than ~4 Å.

If the precision of the Pt shadowing technique is equal to or better than 4 Å, little evidence exists for the presence of only "20 Å fundamental *illite* particles" in sample MB 235. Again, if 2:1 silicate layers were the fundamental components of these clay particles, and if such particles had an integral number of layers, particle thickness distributions would have shown high frequency values at only 10 Å, 20 Å, 30 Å, etc., corresponding to integer multiples of the 10-Å illite layer. Alternatively, if the fundamental component of sample MB 235 was two 2:1 silicate layers, particle thickness distributions should have shown high frequency values at 20 Å, 40 Å, etc. In either case, there should not be thicknesses at non-integer values of 10 Å or 20 Å. A single peak in a particle thickness histogram at only 20 Å argues for fundamental particles of one type (perhaps two 2:1 silicate layers). Instead, for the regular I/S particles, and for the montmorillonite sample (Nadeau *et al.*, 1984a), particle size distributions showed frequency values (significantly above background) for all histogram bins recorded over the range 7 to 29 Å. [These histogram bins correspond to 2-Å intervals (Figures 4a and 4b, Nadeau *et al.*, 1984a)]. In addition, for regular I/S, the second most abundant particle thickness was in the 17–19-Å range, and additional particles with thicknesses between 21 and 25 Å were common.

For montmorillonite, the most abundant thickness was in the 11–13-Å range, whereas a significant number of particles had thicknesses between 13 and 15 Å (Figure 4a, Nadeau *et al.*, 1984a). These thickness ranges do not correspond to integer multiples of a 2:1 silicate layer structure in the *c*-axis direction. Indeed, this particle thickness distribution provides additional support for the suggestion that layer collapse has occurred in these samples if the precision of the technique is ≤4 Å.

The particle thickness distributions for both the montmorillonite and I/S samples shown in Figures 4a and 4b of Nadeau *et al.* (1984a) can be readily explained if the degree of smectite layer collapse is considered. For example, a fundamental unit of I/S has a basal spacing between ~24 and ~26 Å when water-saturated, but on collapse of the smectite layer, the basal spacing may range from ~20 to ~26 Å. The data shown in Figure 4a of Nadeau *et al.* (1984a) show just this type of thickness distribution (if the precision of measurements is considered to be ~4 Å or better). Similarly, the montmorillonite basal dimension ranges from ~16 to ~10 Å depending upon the degree of collapse of the hydrated layer. The basal spacing for an arrangement of illite and collapsed smectite is not exactly the same as two elementary layers of illite, due to the presence of interlayer cation(s) in the latter struc-

tural unit and different Al/Si ratios for illite and I/S. Again, two elementary layers of illite do not have the same basal dimension as a two-layer collapsed smectite, due to the presence of interlayer cation(s) of a different size to K in illite (Brindley, 1980). The difference in basal spacing between these three types of structural units: two-layer illite, two-layer collapsed smectite, and collapsed smectite-layer I/S, is much less than the apparent precision (~4 Å) of the platinum shadowing technique. Thus, the indirect approach used by Nadeau *et al.* (1984a, 1984b) to measure particle thicknesses cannot provide unambiguous data to infer the fundamental nature of component layers in thin I/S or montmorillonite. No direct TEM evidence exists that either the montmorillonite or I/S samples described by Nadeau *et al.* (1984a, 1984b) contain only illite particles 10 or 20 Å thick.

The apparent discrepancy in potassium content for sample MB 235 relative to muscovite could have been due to a significant smectite component. Nadeau *et al.* (1984b) suggested that if sample MB 235 consisted entirely of two 2:1 silicate layers coordinated by an interlayer of K ions, the K_2O content should have approached 5.04 wt. %. Instead, the K_2O content for sample MB 235 was 3.4 wt. %. This value represents a significant deficiency of K (even if compared to the Rotleigend illite) and suggests that neither 2:1 silicate layers coordinated by K nor fundamental illite particles occurred in significant amounts in this I/S sample. Chemical data presented by Nadeau *et al.* (1984a) support the possibility that the fundamental particles observed in MB 235 were predominantly collapsed or partially collapsed smectite-layer I/S.

CONCLUDING REMARKS

The above comments do not dispute the possibility that both montmorillonite and I/S particles are extremely thin; probably on the order of one to three layer thicknesses in the *c*-axis direction. These thicknesses are certainly less than the commonly accepted thickness (five layers) for coherent diffraction of X-rays (Brindley, 1980; Reynolds, 1980). In this case, interparticle diffraction of X-rays may be a significant factor to consider in the interpretation of X-ray powder diffraction data; however, other factors, such as type of layer stacking, the percentage of stacking faults present (even in two or three layer particles; Drits *et al.,* 1984), and variations in composition all influence the type of XRD pattern obtained from I/S particles or physical mixtures of I/S and other clays (Reynolds, 1980). It is not clear if these other factors have been considered in terms of their relative contribution to the X-ray data presented by Nadeau *et al.* (1984a, 1984b). Nevertheless, TEM and chemical data for the ordered I/S from Canon City, Colorado, do not support the suggestion

that these thin particles consist of fundamental illite particles 20 Å thick.

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