Clays and Clay Minerals, Vol. 35, No. 1, 77–79, 1987.

THE FUNDAMENTAL NATURE OF INTERSTRATIFIED ILLITE/SMECTITE CLAY PARTICLES: A REPLY

Key Words—Fundamental particles, Illite/smectite, Interstratification, Transmission electron microscopy, X-ray powder diffraction.

The basis of Mackinnon's (1986) comments concerning our papers on the fundamental nature of interstratified I/S clay particles is that the shadowing technique used by Nadeau *et al.* (1984a, 1984b) to determine particle thicknesses is relatively imprecise and that consequently the interpretation of the particle thickness data was ambiguous, particularly for a sample of regularly interstratified I/S (MB 235). In our opinion much of Mackinnon's (1986) discussion was irrelevant to the conclusions drawn in those papers and necessarily implies an unrealistic view of the nature of these thin particles as will be shown below.

Mackinnon (1986) questioned the claimed precision of ±4 Å for the measurement of particle thickness using Pt/C shadowing and transmission electron microscopy (TEM). The technique and conditions used by Nadeau *et al.* (1984a, 1984b) employed an electron beam evaporator source and a quartz film-thickness monitor. Particular care was taken in measuring the shadow angle at the target. We are confident, therefore, after measuring many particles, that a precision of ±4 Å is reliable and consistent with all the particle thickness data presented. In any event, the exact precision of the measurement was not the main concern in these studies. Nadeau *et al.* (1984a) simply stated that the histograms showed that the montmorillonite and sample MB 235 consisted primarily of particles 10 Å (Figure 4a) and 20 Å (Figure 4b) thick, respectively, which, considering the ±4 Å resolution, we believe they did.

To answer some of the more detailed criticisms of the shadowing technique, it is important to realize that the conditions and temperatures involved in the Pt/C shadowing procedure are much less severe than those encountered in other TEM preparative methods, such as ion-beam milling commonly used for lattice-image studies of clays. Mackinnon's (1986) discussion concerning the use of latex spheres and decoration features are irrelevant because latex spheres were not used by Nadeau *et al.* (1984a, 1984b) to determine shadow angle, and decoration features are only important at shadowing angles >45°. Nadeau *et al.* (1984a, 1984b) used an angle of about 10°.

Turning to interparticle diffraction and the interpretation of the thickness data reported by Nadeau *et al.* (1984a, 1984b), we maintain that interparticle diffraction is the coherent diffraction of radiation by atomic planes of adjacent parallel particles whose interfaces are capable of forming complexes with water and organic molecules. This phenomenon is important only if the particles are exceedingly thin, i.e., less than about five layers thick. Using sample MB 235 as an example to illustrate the ambiguity of our interpretation, Mackinnon asserted that if this sample contained "only illite, particle thicknesses along the *c*-axis should 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". Nowhere in our earlier papers did we refer to the existence of individual particles of illite 10 Å thick. Our view is that elementary illite particles are 20 Å thick and can only consist of two 2:1 silicate layers coordinated by a single plane of non-exchangeable potassium ions (Figure 1a). Other interpretations assume unreasonable boundary conditions as is well illustrated by Mackinnon's (1986) proposed alternatives to account for the particle thickness data relating to sample MB 235. These alternatives include collapsed smectite-layer I/S, in other words, a 20 Å-thick particle that includes both smectitic and illitic interlayers. The only way in which these interlayers could be accommodated in a 20-Å-thick particle is by assuming that the particles do not terminate on the plane of basal oxygens of the tetrahedral sheet (Figure 1b). Similarly, Mackinnon's view of a 20-Å-thick, 2-layer illite or smectite particle implies the existence of two planes of potassium or exchangeable ions and again leads to particles that do not terminate on the tetrahedral sheet (Figures 1c and 1d).

These alternative "particles" are based on a literal interpretation of the one-dimensional interstratification model, which defines the octahedral sheets as the terminations between layers. We agree that the precision of the shadowing technique used by Nadeau *et al.* (1984a, 1984b) is not adequate to differentiate between these alternatives, but such an abstract model can only be considered in the theoretical arrays of layer sequences of the one dimensional interstratified clay "crystallite." In view of the nature of the chemical bonds involved, however, this model represents a patently unreasonable boundary condition for the termination of crystals, as admitted in treatments of the

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         E+
    TTTTTTTTTT
    OOOOOOOOOO
    TTTTTTTTTT
     K   K   K
(a) TTTTTTTTTT
    OOOOOOOOOO
    TTTTTTTTTT
         E+

    uuuuuuuuuu
    TTTTTTTTTT
         E+
    TTTTTTTTTT
(b) OOOOOOOOOO
    TTTTTTTTTT
     K   K   K
    TTTTTTTTTT
    uuuuuuuuuu

    uuuuuuuuuu
    TTTTTTTTTT
     K   K   K
    TTTTTTTTTT
(c) OOOOOOOOOO
    TTTTTTTTTT
     K   K   K
    TTTTTTTTTT
    uuuuuuuuuu

    uuuuuuuuuu
    TTTTTTTTTT
         E+
    TTTTTTTTTT
(d) OOOOOOOOOO
    TTTTTTTTTT
         E+
    TTTTTTTTTT
    uuuuuuuuuu
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Figure 1. Schematic diagram of layer arrangements of (a) elementary illite particle, (b) collapsed illite/smectite, (c) two-layer illite, and (d) two-layer collapsed smectite. T = tetrahedral sheet, O = octahedral sheet, u = one half of an octahedral sheet, K = plane of nonexchangeable potassium ions in the illite layer, and E+ = plane of exchangeable cations.

interstratification model (Reynolds, 1980). Furthermore, even if the incomplete octahedral sheets of these particles could somehow join to form longer layer sequences, it would be impossible to form ideal R=1 ordering by the random joining of such particles.

To understand why Mackinnon (1986) advances such a proposal, the reader should recall that one-dimensional models, which have been generally used to interpret the 001 X-ray powder diffraction (XRD) profiles and TEM lattice-fringe images of illitic clays, assume that the clay is composed of interstratified illite/smectite (I/S) "crystallites" many layers thick. Therefore, the selection of symmetry centers and layer terminations is somewhat arbitrary. Such a premise is common for the selection of the unit cell, which is often chosen as a matter of convenience for making mathematical calculations. This procedure is acceptable as long as the boundary conditions are insignificant, such as in crystals which are sufficiently thick so as to be considered "infinite." Nadeau *et al.* (1984a, 1984b, 1984c, 1985) as well as Wilson and Nadeau (1985) and Nadeau (1985) demonstrated, however, that for many diagenetic illitic clays the individual crystals are generally less than five and often only 2–3 layers in thickness. For these minerals, the boundary conditions predominate, in some minerals, to the extreme. Therefore, the layer terminations cannot be chosen arbitrarily.

The boundary condition assumed by Nadeau *et al.* (1984a), that the particles terminate on the plane of basal oxygens of the tetrahedral sheet whose surface charge is balanced by exchangeable cations, represents the only viable interpretation of the analytical data. As a consequence of the interparticle diffraction phenomenon, the interfacial adsorption of exchangeable cations and water/organic molecules between adjacent particles within aggregates is perceived by XRD as smectite interlayers. From this perspective it is not necessary to consider "smectite layer collapse" to rationalize the analytical results. By using the theoretical XRD data which shows 52% illite layers having R=1 type ordering (Nadeau *et al.*, 1984a, p. 70) and the chemistry data for the Ba-saturated specimen which show comparable amounts of nonexchangeable and exchangeable cations (Figure 5b, Nadeau *et al.*, 1984a), in conjunction with the TEM thickness data (Figure 4b, Nadeau *et al.*, 1984a), we can state, unambiguously, that sample MB 235 consisted primarily of elementary illite particles. Furthermore, in having about 60% of the K_2O content of muscovite per illite layer, sample MB 235 is similar to illitic clays in general (Środoń and Eberl, 1984; Nadeau and Bain, 1986). Thus, Mackinnon's (1986) statement ". . . the indirect approach used by Nadeau *et al.* (1984a, 1984b) to measure particle thickness cannot provide unambiguous data to infer the fundamental nature of . . . I/S" also fails to take account of the fact that Nadeau *et al.* (1984a,

https://doi.org/10.1346/CCMN.1987.0350111 Published online by Cambridge University Press

1984b) based their conclusion on the theoretical and experimental XRD data and the chemical data, in addition to the TEM thickness data.

The Macaulay Institute for Soil Science
Aberdeen, Scotland
United Kingdom

P. H. NADEAU
M. J. WILSON
W. J. MCHARDY
J. M. TAIT

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(Received 17 December 1985; accepted 9 September 1986; Ms. 1479B)