Clays and Clay Minerals, Vol. 37, No. 6, 542–546, 1989.

ILLITE/SMECTITE FROM GULF COAST SHALES: A REAPPRAISAL OF TRANSMISSION ELECTRON MICROSCOPE IMAGES[1]

JUNG HO AHN[2] AND DONALD R. PEACOR[3]

[2] Department of Geology, Arizona State University, Tempe, Arizona 85287

[3] Department of Geological Sciences, The University of Michigan
Ann Arbor, Michigan 48109

Abstract—Transmission electron microscope (TEM) images of mixed-layer illite/smectite (I/S) from Gulf Coast shales obtained earlier by the authors have been reexamined by comparing them with the calculated images of G. D. Guthrie and D. R. Veblen. Ordered two-layer periodicity was not detected in the 1750- and 2450-m depth samples, for which X-ray powder diffraction (XRD) showed 20% and 40% illite randomly interstratified in I/S, respectively. Two-layer periodicities that occur in images of the 5500-m depth sample were inferred to reflect ordered I/S. XRD data for the same sample imply the presence of 80% illite in R1-ordered I/S. The two-layer periodicities were observed in slightly overfocused images, consistent with the image calculations of Guthrie and Veblen, with strong dark fringes inferred to correspond to smectite interlayers. Two-layer periodicities were observed only in small domains of a few of the images, consistent with the requirement of special orientation of layers, which varies continuously over a wide range. The lack of more frequent observations of ordered periodicities in TEM images may reflect the lack of the special observation conditions and chemical heterogeneity of illite and smectite layers. Ordered mixed-layering may exist in those specimens for which XRD indicates such ordering, in contrast to the previous interpretation of the authors.

Key Words—Illite/smectite, Lattice-fringe images, Periodicity, Transmission electron microscopy, X-ray powder diffraction.

INTRODUCTION

Transmission electron microscopy (TEM) has been used to obtain lattice-fringe images of mixed-layer illite/smectite (I/S) by many investigators (e.g., Lee *et al.*, 1985; Ahn and Peacor, 1986a; Klimentidis and Mackinnon, 1986; Yau *et al.*, 1987; Huff *et al.*, 1988). Although 001 lattice fringes of 2:1 phyllosilicates are easily imaged using samples for which X-ray powder diffraction (XRD) patterns show mixed layering of illite and smectite, individual layers of illite or smectite cannot be unambiguously identified. Differences in contrast or interlayer spacing between fringes are generally non-existent or so subtle as to be non-diagnostic under normal imaging conditions (Ahn and Peacor, 1986a).

A major cause of the ambiguity is the dehydration and collapse of smectite interlayers in the electron microscope, giving rise to a layer thickness of about 10 Å (Ahn and Peacor, 1986a). Because illite layers also have a 10-Å spacing, collapsed smectite and illite layers cannot be differentiated on the basis of 001 interplanar spacings. Attempts to use intercalating organic agents, such as laurylamine hydrochloride, to prevent layer collapse give rise to ambiguous results (Yoshida, 1973; Lee and Peacor, 1986; Bell, 1986). Although Vali and Koster (1986) imaged various mixed-layer clays containing intercalated octadecylammonia ions, individual smectite or illite layers were still not unambiguously differentiated.

Ahn and Peacor (1986a) obtained TEM lattice-fringe images of ion-milled specimens of Gulf Coast shales, which had been shown by XRD to contain I/S (Hower *et al.*, 1976). Using the same TEM instrumental conditions, they also obtained lattice-fringe images of rectorite which showed 20-Å periodicity, inferred to reflect 1:1 ordered I/S (Ahn and Peacor, 1986b), as had previously been reported by McKee and Buseck (1978), implying that the lack of such periodicity in images of Gulf Coast I/S reflected a lack of ordering. From observations of two types of 2:1 layer silicates, each having a characteristic texture, Ahn and Peacor (1986a) suggested that I/S may not be the dominant phase in those Gulf Coast shales. Furthermore, they suggested that differences in TEM and XRD interpretations were at least in part artifacts caused by disarticulation and reconstitution of specimens prepared for XRD.

Guthrie and Veblen (1989) recently showed that lattice-fringe images of ordered I/S should display features that reflect the ordering only under certain special experimental conditions. They calculated images using factors corresponding to the JEM 100C TEM instrument, which is similar to the JEM 100CX TEM instrument used by Ahn and Peacor (1986a, 1986b). The

[1] Contribution 460 from the Mineralogical Laboratory, Department of Geological Sciences, The University of Michigan, Ann Arbor, Michigan 48109.

https://doi.org/10.1346/CCMN.1989.0370606 Published online by Cambridge University Press

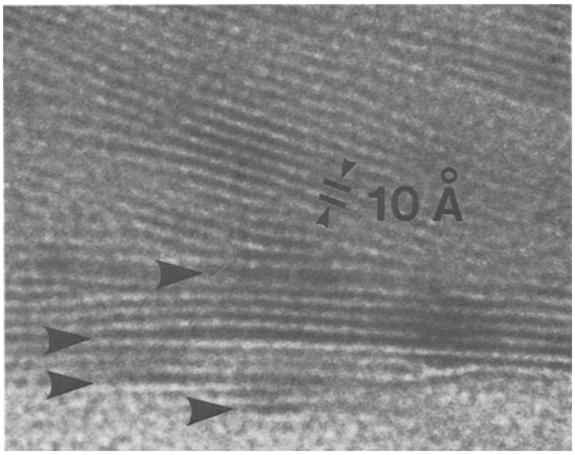

Figure 1. Lattice-fringe image of mixed-layer illite/smectite from the 2450-m depth sample. Although wider dark fringes (indicated by arrows) can be identified, layer periodicities consistent with X-ray powder diffraction data are not identified.

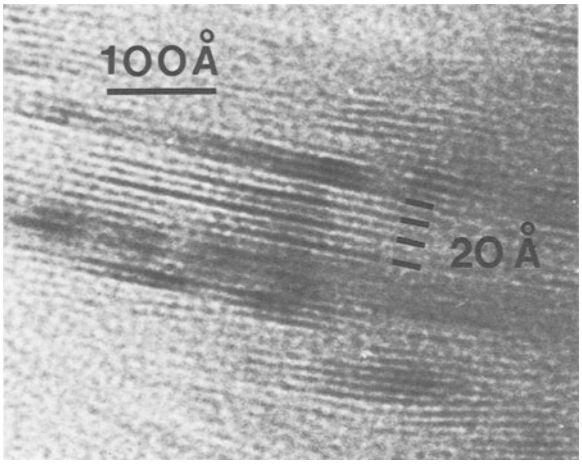

Figure 2. Lattice-fringe image of mixed-layer illite/smectite from the 5500-m depth sample. Several units of two-layer periodicities occur in part of the crystals, but such periodicities become indistinct if the fringes are traced along the layer.

results of Guthrie and Veblen suggested that ordering could be detected, and they prescribed the conditions for observation. This development has led to the reinterpretation of the TEM images of I/S obtained earlier by Ahn and Peacor (1986a). Subtle differences in contrast that define periodicities, which may reflect ordering of I/S, have subsequently been found in some of the overfocused images of specimens for which XRD implied R1 ordering. This paper describes the reinterpreted images and discusses their significance.

SPECIMENS AND EXPERIMENTAL TECHNIQUES

The specimens used as sources for TEM images were shale cuttings from 1750-, 2450-, and 5500-m depths from the Case Western Reserve University (CWRU) Gulf Coast 6 well. These were chosen for TEM study by Ahn and Peacor (1986a) to bracket the transition from smectite to illite, as defined by the XRD and chemical data of Hower *et al.* (1976). The transition was defined by an increase in the fraction of illite layers in the I/S. The three samples corresponded to 20%, 40%, and 80% illite layers, respectively; only the 5500-m sample exhibited R1 ordering, as detected by XRD.

The sample preparation and experimental methods were described by Ahn and Peacor (1986a). Images were obtained using the JEOL JEM-100CX scanning-transmission electron microscope (STEM). All lattice-fringe images were obtained by using an objective aperture that included the 00*l* reflections within the range of 003. Because lattice fringe images of detrital micas commonly display fringe periodicities due to polytypism that resemble periodicities due to I/S ordering, images of such micas were excluded, based on the criteria described by Ahn and Peacor (1986a).

REEXAMINATION OF LATTICE-FRINGE IMAGES

Ahn and Peacor (1986a) described two kinds of lattice-fringe images: (1) straight fringes that had relatively constant contrast, were relatively defect-free, and had a constant spacing of ~10 Å. They reported that the analytical electron microscopy (AEM) data were compatible with illite. The fringes of this phase were interpreted to correspond to packets of illite, and that interpretation is unchanged. (2) Curved ("wavy") fringes that were discontinuous and had many layer terminations. These fringes had variable contrast and an apparent range of lattice-fringe spacings. Most of the spacings were as small as 10 Å, but some were larger. The AEM data were reported to be compatible with a smectite-like phase. This material, within which the illite occurred as packets of layers, was interpreted to be smectite. It is this material that is the subject of the present paper.

XRD patterns of the 1750-m depth sample showed the I/S to be randomly interstratified and to contain 20% illite layers. Such material is characteristic of the pre-transition stage of burial diagenesis of Gulf Coast shales (Hower *et al.*, 1976). Reexamination of the lattice-fringe images indicated no evidence of I/S ordering. The lattice-fringe images have variable layer contrast and a range of spacings, even along the same layer, as well as other characteristics as originally described by Ahn and Peacor (1986a). Individual layers could not be interpreted as consisting of either illite or smectite.

Figure 1 is a typical lattice-fringe image obtained from the 2450-m sample, for which XRD data imply 40% illite layers in randomly interstratified I/S, and which represents an intermediate transition state. Some

https://doi.org/10.1346/CCMN.1989.0370606 Published online by Cambridge University Press

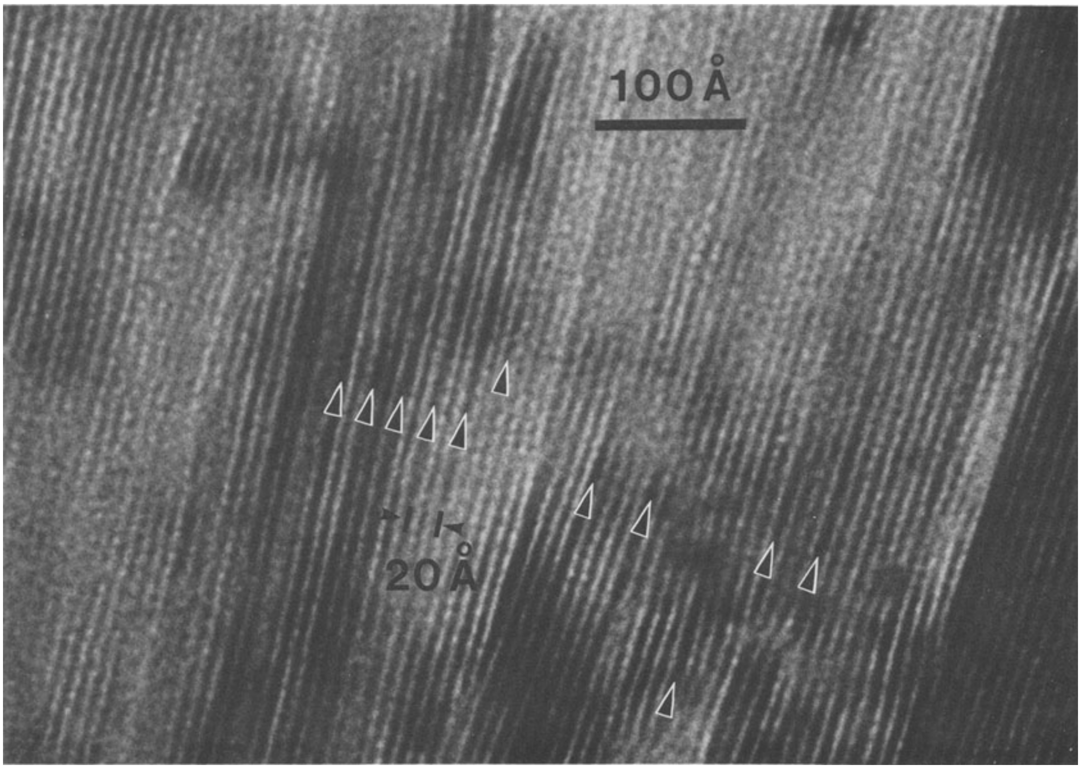

Figure 3. Lattice-fringe image of mixed-layer illite/smectite from the 5500-m depth sample. Wider dark fringes (indicated by arrows) may occur near the positions of smectite interlayers. Well-defined two-layer periodicities are also present.

fringes are wider and darker than others, as indicated by arrows in Figure 1 and are limited to local areas of a given image. No multi-layer periodicity was detected in wide, dark fringes, compared with fringes that were less dark and more narrow.

The 5500-m depth sample was shown by XRD to contain 80% illite layers in R1 ordered I/S. Most lattice-fringe images exhibited no periodic contrast differences between alternate fringes, and they resembled the images from specimens from shallower depths. Some images locally exhibited two-layer periodicity, however, as shown in Figure 2. The periodicity was the result of wider, darker fringes alternating with less dark and narrower fringes. Such periodicity typically occupied only small areas of an image and faded along the trace of a given fringe. Figure 3 shows an unusually fine example of an image that contains more extended two-layer periodicities, although even in this image the two types of fringes cannot easily be differentiated in some areas.

DISCUSSION

Guthrie and Veblen (1989) showed that differences in contrast between illite and smectite layers occurred at slightly overfocused conditions. The images shown in Figures 1–3 were obtained under such conditions. Guthrie and Veblen showed that wider and darker fringes superimpose on or near the position of the smectite interlayers and that narrower and less dark fringes were close to the illite interlayer. These relations imply that fringes having the contrast differences appearing in Figures 2 and 3 may correspond to illite and smectite interlayers.

Although distinct layer periodicities consistent with XRD data were identified based on the differences in fringe contrast in the 5500-m depth sample, periodic changes in contrast between adjacent fringes were difficult to discern in images of smectite-rich shallower samples. Contrast differences could, indeed be discerned in such samples in selected layers, but such differences were more subtle than those in Figures 2 and 3, and contrast changes between layers were no more apparent than changes along layers. Where periodic contrast differences were noted, especially in samples in which the XRD data implied ordering of I/S, the contrast differences were reasonably well characterized; however, in disordered sequences it has not yet been possible to characterize individual fringes as corresponding to either illite or smectite layers.

Clearly, defined periodicities are common only in parts of the TEM images, raising the question of their existence in the areas that do not exhibit two-layer periodicities. Guthrie and Veblen (1989) showed that the two-layer periodicity is more easily observed if the

https://doi.org/10.1346/CCMN.1989.0370606 Published online by Cambridge University Press

layers are slightly tilted relative to the incident beam. A change in orientation of the layers in the plane of the images is then evident through their "wavy" nature, and such variable orientation may be present in the third dimension. Thus, even where ordering exists over the entire area of a given image, it should be detectable in only limited areas of images. The presence of contrast in only limited areas of the fringes of Figures 2 and 3 in particular and in all images from the 5500-m depth sample in general does not imply that I/S ordering was restricted only to those areas. Indeed, the data imply that ordering may be much more common than is directly observed in the lattice-fringe images; the full extent of such ordering cannot now be assessed by TEM techniques.

The question remains, however, as to why periodic, two-layer fringe contrast was invariably observed by Ahn and Peacor (1986b) in samples of rectorite, given that the imaging conditions were equivalent to those used for the Gulf Coast samples. The lack of defects, the presence of homogeneity in the TEM images, and the high quality of the XRD patterns all imply that the rectorite consisted of highly ordered, homogeneous crystals of substantial size, compared with the I/S from the Gulf Coast. The degree of chemical (and structural) differences between illite and smectite 2:1 layers and interlayers are critical factors in promoting contrast differences. The contrast differences in simulated images as calculated by Guthrie and Veblen (1989) were a result of the chemical differences between interlayers and the tetrahedral sites, with atomic coordinates being identical in all 2:1 layers. A greater difference in chemistry, or differences in atomic coordinates (the latter are an inevitable function of chemical differences) will result in enhanced contrast between fringes. The ease of observing ordered images in rectorite was thus due to its highly ordered, defect-free structure compared with the general heterogeneity of I/S in shales, which gives rise to averaging of the differences between illite and smectite.

Ahn and Peacor (1986a) found that the compositions of both smectite and illite appeared to vary over significant ranges; they implied that chemical heterogeneity (and resultant minor adjustments in atom coordinates) must have existed over domains of either illite or smectite. Indeed, such heterogeneity can be reasonably expected both along and between layers of either illite or smectite. Chemical and structural heterogeneity were further implied by the presence of abundant defects and the curvature of layers of I/S. Such features would tend to minimize contrast differences, compared with the calculated images and, if combined with variable layer orientation, adequately account for the difficulty in observing ordering in sedimentary I/S, compared with calculated images or those of rectorite.

Although the observation of ordered I/S is compatible with XRD data, the possibility remains that periodic contrast differences were caused by two-layer polytypism, as demonstrated by Guthrie and Veblen (1989). Although I/S showing 2-layer polytypism was not identified in the Gulf Coast specimens, random stacking of illite and smectite layers could have locally produced two-layer polytypes, by analogy with randomly produced intergrowth relations in pyriboles (Veblen and Buseck, 1980). The periodicity in contrast of lattice-fringe images must be interpreted cautiously, if the stacking relations are not known.

Contrast differences in TEM images consistent with ordering of I/S in samples for which XRD implied ordering of illite and smectite layers have now been directly observed by several investigators: Hansen and Lindgreen (1987) observed two-layer periodicities in I/S in North Sea shales; Veblen *et al.* (1990) utilized the Philips 420 TEM to observe IS and ISII ordering in shales and bentonites; other studies in this laboratory, using the Philips CM 12 to study ion-milled samples of Gulf Coast I/S, have noted contrast in images of the kind described in the present paper; Ahn *et al.* (1988) used the JEOL 4000EX HRTEM to observe ordering in I/S from bentonites; and other studies in this laboratory have examined ion-milled samples of I/S resulting from near-surface alteration of micaceous slates using a Philips CM-12 STEM.

Such observations of ordered periodicities, combined with Guthrie and Veblen's (1989) results, which showed that TEM observations commonly fail to detect ordering present in mixed-layer sequences, suggest that XRD data (e.g., Reynolds and Hower, 1970; Nadeau *et al.*, 1984c) may reflect the true general arrangement of the I/S in the original rock, despite treatments that cause the I/S to disarticulate into units as thin as individual layers. High-resolution TEM studies of specimens that were not disaggregated (Ahn *et al.*, 1988) showed that I/S consists of translation-periodic crystals that are larger than the "fundamental particles" of Nadeau *et al.* (1984a, 1984b). Ahn and Peacor (1986a, 1986b) pointed out that the disarticulation and reconstitution that occur during preparation of specimens for XRD studies may cause layer sequences to be altered; the sequences detected by XRD would therefore be different than those observed by TEM in samples that had not been disarticulated. Ahn and Peacor (1986b) directly observed cleavage in rectorite, suggesting that layers separate along the expandable interlayer. Therefore, if separation occurs much more readily only along expandable interlayers, packets of layers are expected to be reconstituted preferentially along the same expandable interlayers, resulting in little change in the one-dimensional sequence of illite and smectite layers. Some change in sequences must occur, of course, but the specific amount of change is yet to be determined. Nevertheless, the TEM data imply that the sequences as determined by XRD in treated specimens apparently reflect the average layer sequences in untreated rock.

SUMMARY AND CONCLUSIONS

Two-layer periodicities were observed in some TEM images of Gulf Coast I/S that had been obtained under slightly overfocused conditions, in agreement with the image calculations of Guthrie and Veblen (1989) and consistent with IS (R1) ordering, as indicated by XRD data. The regions showing two-layer periodicities occur over only limited areas of an image and become indistinct when traced along layers, reflecting change in orientation of layers. Such contrast was not observed for shallow specimens for which XRD data implied <50% illite layers in a randomly interstratified sequence. Individual illite or smectite layers were not identified in images of such material. Although periodic contrast in lattice-fringe images may represent ordered mixed layering of I/S, caution must be used due to ambiguities caused by polytypism or stacking faults. The interpretations of XRD patterns of I/S, even though based on disaggregated and rearticulated samples, are not inconsistent with TEM observations of non-disarticulated samples.

ACKNOWLEDGMENTS

We are grateful to D. R. Veblen for making available the report of the image calculations and to P. R. Buseck for reviewing the manuscript. This work was supported by NSF grants EAR87-08529 to P. R. Buseck, and EAR86-04170 to D. R. Peacor.

REFERENCES

Ahn, J. H., Buseck, P. R., and Reynolds, R. C. (1988) Stacking sequences of mixed-layer illite/smectite: HRTEM imaging: in *Program with Abstracts, 25th Annual Meeting of The Clay Minerals Society, Grand Rapids, Michigan, 1988,* 73.

Ahn, J. H. and Peacor, D. R. (1986a) Transmission and analytical electron microscopy of the smectite-to-illite transition: *Clays & Clay Minerals* **34,** 165–179.

Ahn, J. H. and Peacor, D. R. (1986b) Transmission electron microscope data for rectorite: Implications for the origin and structure of "fundamental particles": *Clays & Clay Minerals* **34,** 180–186.

Bell, T. E. (1986) Microstructure in mixed-layer illite/smectite and its relationship to the reaction of smectite to illite: *Clays & Clay Minerals* **34,** 146–154.

Guthrie, G. D. and Veblen, D. R. (1989) High-resolution transmission electron microscopy of mixed-layer illite/smectite: Computer simulations: *Clays & Clay Minerals* **37,** 1–11.

Hansen, P. L. and Lindgreen, H. (1987) Structural investigations of mixed-layer smectite-illite clay minerals from North Sea oil rocks: in *Proc. 45th Annual Meeting, Electron Microsc. Soc. Amer.,* G. W. Bailey, ed., San Francisco Press, San Francisco, 374–375.

Hower, J., Eslinger, E. V., Hower, M. E., and Perry, E. A. (1976) Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence: *Geol. Soc. Amer. Bull.* **87,** 725–737.

Huff, W. D., Whiteman, J. H., and Curtis, C. D. (1988) Investigation of a K-bentonite by X-ray powder diffraction and analytical transmission electron microscopy: *Clays & Clay Minerals* **36,** 83–93.

Klimentidis, R. E. and Mackinnon, I. D. R. (1986) High-resolution imaging of ordered mixed-layer clays: *Clays & Clay Minerals* **34,** 155–164.

Lee, J. H., Ahn, J. H., and Peacor, D. R. (1985) Textures in layered silicates: Progressive changes through diagenesis and low temperature metamorphism: *J. Sed. Petrol.* **55,** 532–540.

Lee, J. H. and Peacor, D. R. (1986) Expansion of smectite by laurylamine hydrochloride: Ambiguities in transmission electron microscope observations: *Clays & Clay Minerals* **34,** 69–73.

McKee, T. R. and Buseck, P. R. (1978) HRTEM observation of stacking and ordered interstratification in rectorite: in *Electron Microscopy 1978, Vol. 1,* J. M. Sturgess, ed., Microscopical Society of Canada, Toronto, Ontario, 272–273.

Nadeau, P. H., Wilson, M. J., McHardy, W. J., and Tait, J. M. (1984a) Interparticle diffraction: A new concept for interstratified clays: *Clay Miner.* **19,** 757–769.

Nadeau, P. H., Wilson, M. J., McHardy, W. J., and Tait, J. M. (1984b) Interstratified clays as fundamental particles: *Science* **225,** 923–925.

Nadeau, P. H., Tait, J. M., McHardy, W. J., and Wilson, M. J. (1984c) Interstratified XRD characteristics of physical mixtures of elementary clay particles: *Clay Miner.* **19,** 67–76.

Reynolds, R. C., Jr. and Hower, J. (1970) The nature of interlayering in mixed-layer illite/montmorillonite: *Clays & Clay Minerals* **18,** 25–36.

Vali, H. and Koster, H. M. (1986) Expanding behavior, structural disorder, regular and random irregular interstratification of 2:1 layer-silicates studied by high-resolution images of transmission electron-microscopy: *Clay Miner.* **21,** 827–859.

Veblen, D. R. and Buseck, P. R. (1980) Microstructures and reaction mechanisms in biopyriboles: *Amer. Mineral.* **65,** 599–623.

Veblen, D. R., Guthrie, G. D., Livi, K. J. T. (1990) High resolution transmission electron microscopy and electron diffraction of mixed-layer illite/smectite: Experimental results. *Clays & Clay Minerals* **38,** 1–13.

Yau, Y.-C., Peacor, D. R., and McDowell, S. D. (1987) Smectite to illite reactions in Salton Sea Shales: A transmission and analytical electron microscopy study: *J. Sed. Petrol.* **57,** 335–342.

Yoshida, T. (1973) Elementary layers in the interstratified clay minerals as revealed by electron microscopy: *Clays & Clay Minerals* **21,** 413–420.

(Received 9 December 1988; accepted 7 April 1989; Ms. 1861)