

The conversion of smectite to illite during diagenesis: evidence from some illitic clays from bentonites and sandstones

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ABSTRACT. Diagenetic illitic clays from seven North American bentonites of Ordovician, Devonian, and Cretaceous ages and from three subsurface North Sea sandstones of Permian and Jurassic ages have been examined by X-ray diffraction (XRD) and transmission and scanning electron microscopy (TEM and SEM). XRD indicates that the clays from the bentonites are randomly and regularly interstratified illite/smectites (I/S) with 30-90% illite layers, whereas the clays from the Jurassic and Permian sandstones are regularly interstratified I/S, with 80-90% illite layers, and illite respectively. TEM of shadowed materials shows that randomly interstratified I/S consists primarily of mixtures of elementary smectite and 'illite' particles (10 and 20 Å thick respectively) and that regularly interstratified I/S and illite consist mainly of 'illite' particles 20-50 Å thick and > 50 Å thick respectively. Regularly interstratified I/S from bentonites and sandstones are similar with regard to XRD character and particle thickness distribution. These observations can be rationalized if the interstratified XRD character arises from an interparticle diffraction effect, where the smectite interlayers perceived by XRD, result from adsorption of exchangeable cations and water or organic molecules at the interfaces of particles generally < 50 Å thick. A neoformation mechanism is proposed by which smectite is converted to illite with increasing depth of burial in sedimentary rocks, based on dissolution of smectite particles and the precipitation/growth of 'illite' particles occurring within a population of thin phyllosilicate crystals.

KEYWORDS: smectite, illite, diagenesis, clays, bentonite, sandstone.

RECENT studies of some diagenetic interstratified illite/smectite (I/S) clays based on complementary use of transmission electron microscopy (TEM) and X-ray diffraction (XRD) have shown that the smectite layers detected by XRD actually represent the interfaces between particles consisting of only 1-3 silicate layers in thickness (McHardy *et al.*, 1982; Nadeau *et al.*, 1984a, b). Furthermore, the latter studies demonstrate that randomly interstratified I/S can be synthesized from mixed suspensions of elementary smectite and 'illite'

particles (10 Å and 20 Å thick respectively). The interstratified XRD phenomenon of these materials is thus an interparticle diffraction effect where water and organic molecules are adsorbed on the smectite-like interfaces within aggregates of thin phyllosilicate crystals. One objective of the present study is to assess the application of these concepts to illitic clays from bentonites and sandstones in greater detail.

Illitic clays in bentonites are currently accepted as being the products of a transformation process by which smectite layers, in response to increasing Al^{3+} for Si^{4+} tetrahedral substitution, collapse about selectively adsorbed interlayer K^+ ions thus forming illite layers (Hower *et al.*, 1976; Hoffman and Hower, 1979). The diagenetic conversion of smectite to illite is considered to be of general importance in the clay petrology of pelitic sediments. (Nadeau and Reynolds, 1981a; Eslinger and Sellars, 1981). In contrast, diagenetic illitic clays in sandstones are accepted as being the products of neoformation, i.e. precipitated from solution (Wilson and Pittman, 1977; Güven *et al.*, 1980). These clays are of great interest to the petroleum industry because of their deleterious effects on production from hydrocarbon reservoirs (Gray and Rex, 1966; Stalder, 1973; Pallatt *et al.*, 1984). The current situation is, therefore, that illitic clays in bentonites and sandstones are accepted as being formed during diagenesis but by different mechanisms, namely transformation in the case of bentonites and neoformation in the case of sandstones. Therefore, a second objective of this paper is to evaluate these hypotheses in the light of new experimental and analytical evidence.

Materials and methods. Ten samples of illitic clays (Table I) were Na-saturated and washed free of chloride. The < 0.1 µm fraction of samples WWB, CCB, NCB, and DIB and the < 0.2 µm fractions of SFB, MAG, LPB, RAN, TGB, and ROT were then isolated by centrifuga- tion. Sedimented aggregates of the suspensions were

Table I.

Sample Description		
Sample	Type/Location	Mineralogy
WVB	Cretaceous Bentonite Westwater, Utah (Sample MB 405; Nadeau, 1980)	Randomly Interstratified I/S (30% illite layers)
CCB	Cretaceous Bentonite Canon City, Colorado (Sample MB 235; Nadeau, 1980)	Regularly Interstratified I/S (50% illite layers)
NCB	Cretaceous Bentonite New Castle, Colorado (Sample MB 297; Nadeau, 1980)	Regularly Interstratified I/S (60% illite layers)
SFB	Ordovician Bentonite St. Francois Mtns., Missouri (Sample from R.C. Reynolds)	Regularly Interstratified I/S (80% illite layers)
MAG	Jurassic Sandstone Magnus Field, North Sea Basin (McHardy <i>et al.</i> , 1982)	Regularly Interstratified I/S (80% illite layers)
LPB	Cretaceous Bentonite Las Piedras, Colorado (Sample MB 912; Nadeau 1980)	Regularly Interstratified I/S (80% illite layers)
DIB	Cretaceous Bentonite Dillon, Colorado (Sample MB 312; Nadeau, 1980)	Regularly Interstratified I/S (80% illite layers)
RAN	Jurassic Sandstone Rannoch Fm. North Sea Basin	Regularly Interstratified I/S (90% illite layers)
TGB	Devonian Bentonite Tioga Fm. Mohawk Valley, New York (Sample T1; Welden, 1966)	Regularly Interstratified I/S (90% illite layers)
ROT	Ferrian Sandstone Rotliegend Fm. Southern North Sea Basin	Illite

prepared on glass slides, ethylene glycol vapour solvated, and examined by XRD on a Philips 2 kW diffractometer using Fe-filtered Co-K α radiation, 1° divergence and anti-scatter slits, and a 0.2 mm receiving slit. The XRD patterns were interpreted using the data of Reynolds and Hower (1970) and Reynolds (1980) as a standard reference.

For TEM examination, the suspensions were diluted and spread over a piece of freshly cleaved mica, dried, shadowed with Pt at an angle of about 10° (the precise angle being measured for each sample) and coated with carbon. The shadowed carbon film was then floated on water and picked up on electron microscope grids. The shadow lengths of 30–84 particles per sample were measured from micrographs. Knowing the shadowing angle, the shadowing direction and the micrograph magnification, the particle thickness (± 2 to ± 4 Å) was calculated from the measured shadow length.

SEM examination was conducted on critical point dried (CPD) samples of preserved cores of MAG, RAN, and ROT. The method involves the replacement of pore fluids from the preserved core material first by methanol and finally by liquid CO₂ (McHardy *et al.*, 1982). Drying is accomplished within a pressure apparatus at temperatures above the critical point of CO₂ (32°C). The importance of CPD preparations of preserved core material for SEM clay morphological examination is discussed by Pallatt *et al.* (1984).

Results. Representative SEM micrographs from the CPD sandstone materials (fig. 1) demonstrate the filamentous or 'hairy' morphology of the illitic clay particularly in sample MAG at high magnification (fig. 1*b*) and in RAN and ROT (fig. 1*c–f*). The delicate morphology of the clay indicates its diagenetic neoformed nature. This view is supported by observations of the clay growing on euhedral quartz overgrowths (fig. 1*a* and *b*), on grain boundaries, and around grain-to-grain contacts (fig. 1*e* and *f*). The morphological similarities of MAG and ROT are evident but the ROT material is significantly larger and more robust.

Micrographs from shadowed samples (fig. 2) show the overall thin, platy, and lath-like habit of the particles. Generally, a lath-like habit is more common in the sandstone clays (fig. 2*c, e, g*) whereas a plate-like habit is more common in bentonites. The notable exceptions are bentonite SFB which has a prominent lath-like habit (fig. 2*d*), and samples CCB, TGB, and NCB which have lath-like particles present in subordinate amounts. The particle thickness distribution data of the < 0.1 μm or < 0.2 μm fractions and the XRD traces for ethylene glycol solvated samples of the same

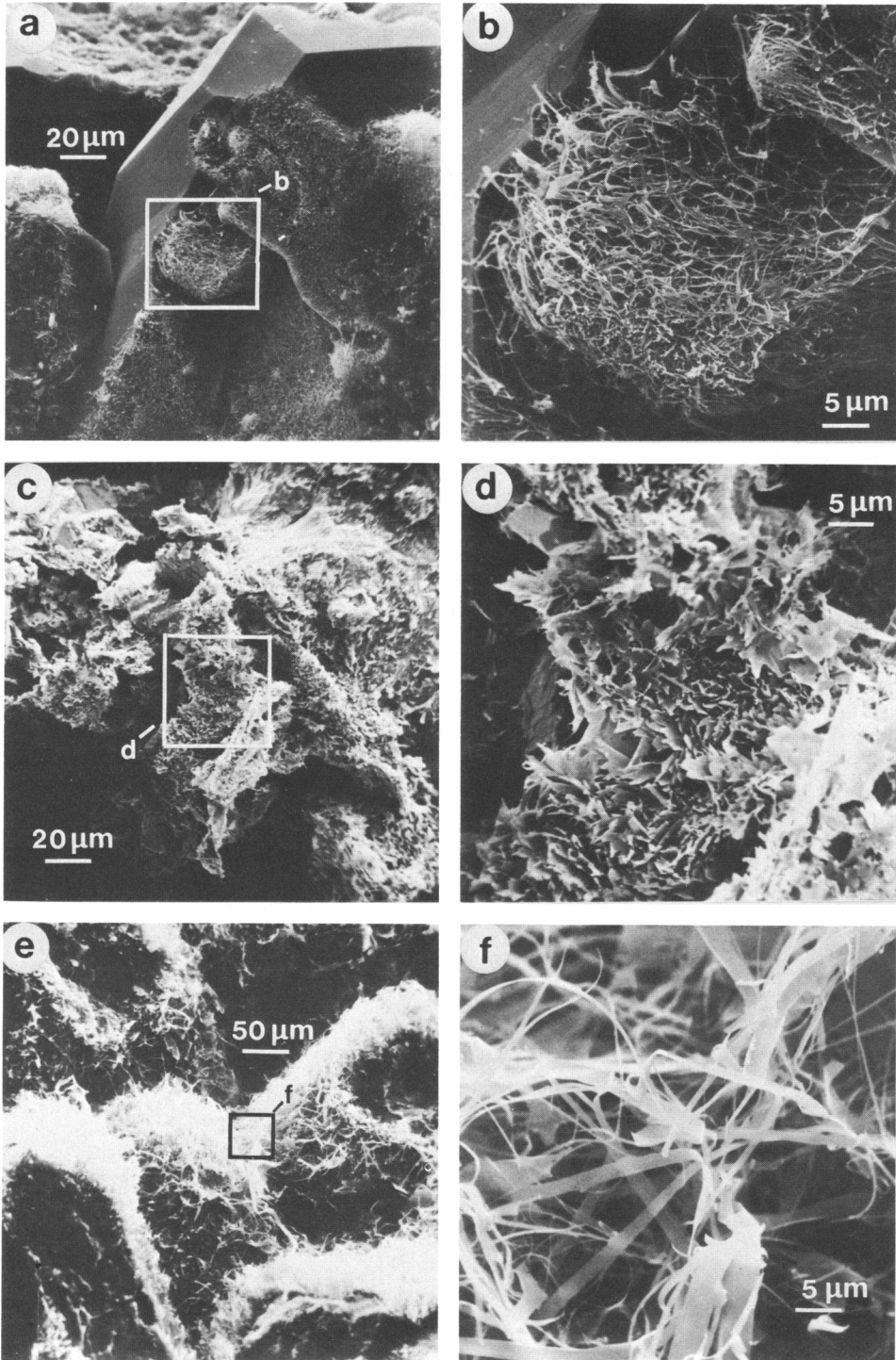


FIG. 1. Scanning electron micrographs of critical point dried preserved core samples of (a, b) MAG, (c, d) RAN, and (e, f) ROT.

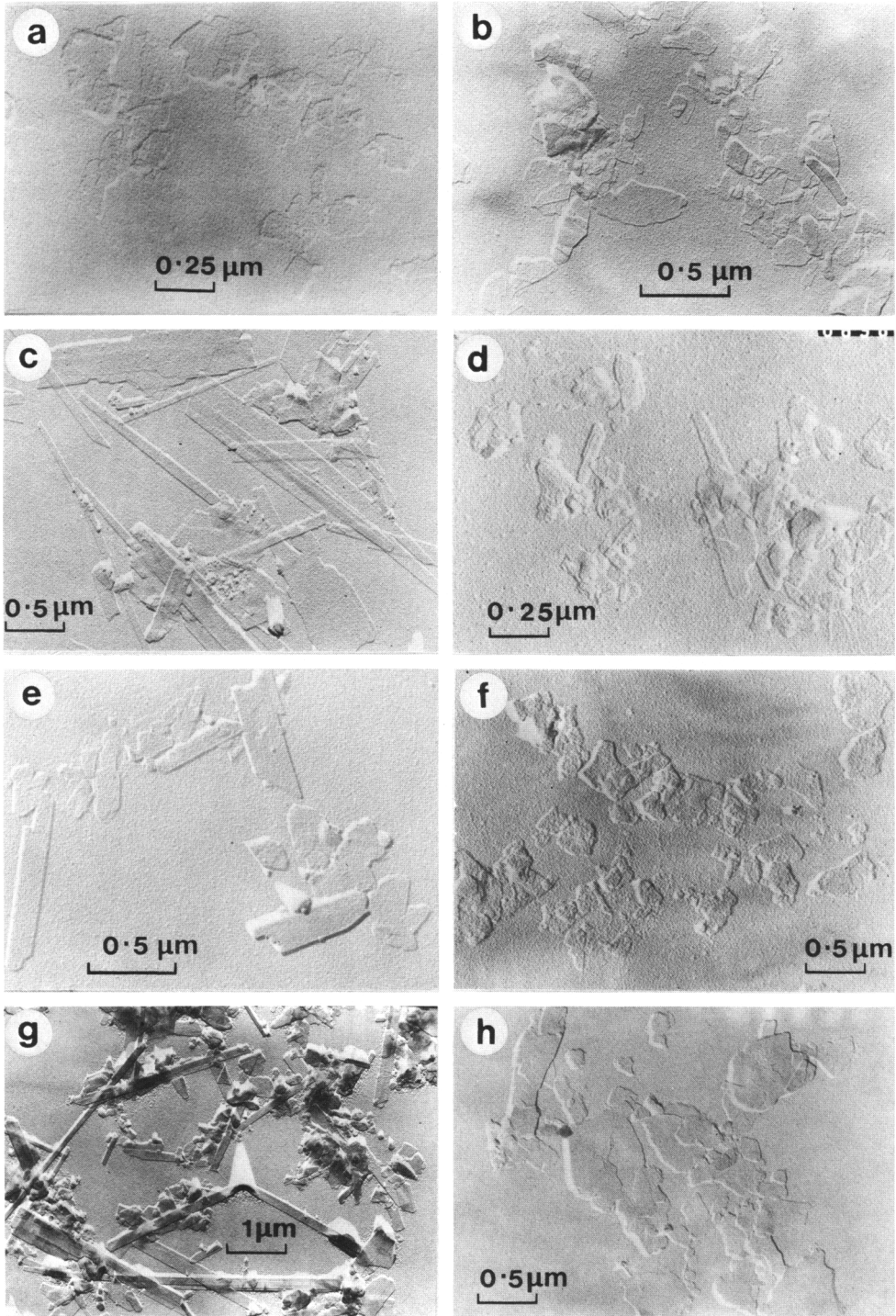


FIG. 2. Transmission electron micrographs of Pt/C shadowed fine clay fractions of (a) WWB, (b) NCB, (c) MAG, (d) SFB, (e) RAN, (f) DIB, (g) ROT, and (h) TGB.

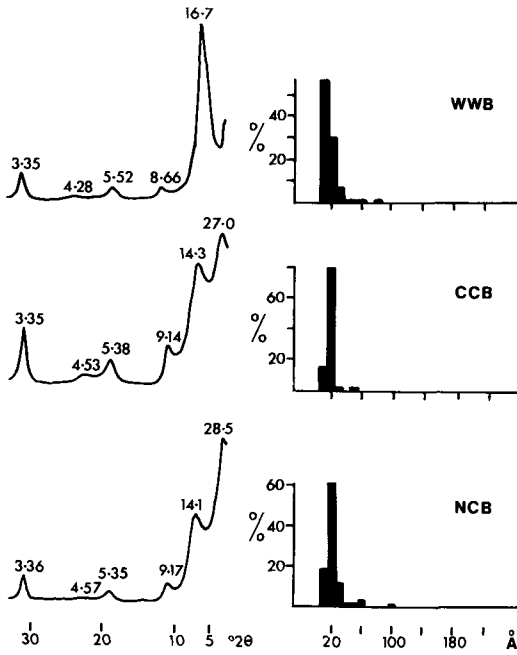


FIG. 3. X-ray diffraction patterns of ethylene glycol sedimented aggregates and particle thickness histograms of fine clay fractions of samples WWB, CCB, and NCB.

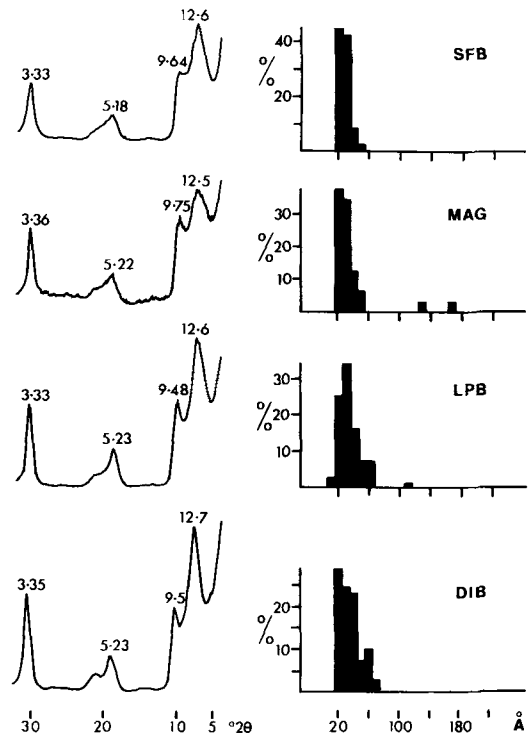


FIG. 4. X-ray diffraction patterns of ethylene glycol sedimented aggregates and particle thickness histograms of fine clay fractions of samples SFB, MAG, LPB, and DIB.

sample are shown in figs. 3, 4, and 5. The data show a consistent, overall increase in particle thickness with increasing percent illite layers. Sample WWB (fig. 3), a randomly interstratified I/S with 30% illite layers, is primarily composed of particles 10–20 Å thick. Samples CCB and NCB (fig. 3) are IS (nearest neighbour) type regularly interstratified I/S clays with 50 and 60% illite layers respectively, and are relatively homogeneous populations of 80 and 60% 20 Å thick particles respectively. Long range ordered materials from samples SFB, MAG, LPB, and DIB (fig. 4) are IIS-type regularly interstratified I/S with approximately 80% illite layers, and are primarily composed of 20–40 Å thick particles. Long range ordered materials from samples RAN and TGB (fig. 5) are IIIS or Kalkberg-type regularly interstratified I/S with 90% illite layers, and are primarily composed of particles 30–50 Å thick. Sample ROT yields a conventional illite XRD pattern (fig. 5) and is primarily composed of particles > 50 Å in thickness.

Discussion. The relationship between XRD patterns and particle thickness distribution data demonstrates that the concept of inter-particle diffraction proposed by Nadeau *et al.* (1984a, b) is applicable to diagenetic illitic clays from both bentonites and sandstones. Sample WWB is par-

ticularly noteworthy. Its XRD pattern is closely similar to that produced from a mixed-suspension of CCB and < 0.1 μm fraction of Na-saturated Wyoming montmorillonite in a 1 : 1 ratio by weight (Nadeau *et al.* 1984a, fig. 1b). The mixed suspension was shown to be composed essentially of elementary smectite and 'illite' particles, 10 and 20 Å thick respectively, in complete agreement with the particle thickness data for sample WWB (fig. 3). Likewise, the data for samples CCB and NCB (fig. 3) demonstrate that IS-type regularly interstratified I/S is composed primarily of elementary 'illite' particles 20 Å thick, so that the tendency for the regularly alternating IS layer sequence can be explained by interparticle diffraction, the smectite layers actually being the interfaces between the elementary illite particles. As discussed by Nadeau *et al.* (1984a, b), the thickness data for the IIS and IIIS type indicate that these samples do not consist of a completely homogeneous population of 30 and 40 Å thick particles respectively, but show a somewhat broader thickness distribution. This material can, perhaps, be best described as consisting of thin 'illite' particles 20–50 Å thick. It may be noted

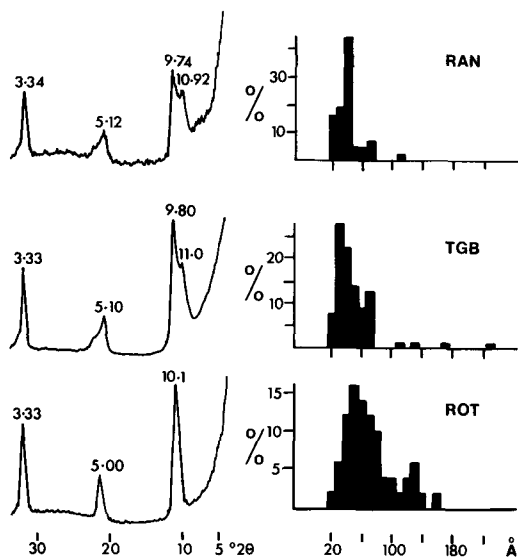


Fig. 5. X-ray diffraction patterns of ethylene glycol sedimented aggregates and particle thickness histograms of fine clay fractions of samples RAN, TGB, and ROT.

that both bentonite and sandstone materials, show a similar relationship between XRD and particle thickness distribution, e.g. compare SFB/MAG (fig. 4) and RAN/TGB (fig. 5). It may be added that this interparticle diffraction phenomenon rationalizes analytical inconsistencies sometimes noted in the literature (cf. Wilson and Pittmann, 1977; Velde and Weir, 1979) between SEM/TEM observations and XRD, where illitic material lacking any morphological indications of smectite are identified by XRD as interstratified I/S.

The above findings could have profound implications with regard to the mechanism by which smectite converts to illite during diagenesis. The diagenetic formation of illite and interstratified I/S was established by Hower and Mowatt (1966) and Perry and Hower (1970). A layer-by-layer mechanism, was developed by which smectite layers are converted to illite layers (Hower *et al.*, 1976) within individual crystallites. In part, this proposal was based on the mathematically modelled XRD character of these clay minerals (Reynolds and Hower, 1970). The data presented here and by Nadeau *et al.* (1984a, b) shows that the assumptions of crystal thickness used in the theoretical XRD calculations are not necessarily applicable. The XRD character of these materials can be better explained by an interparticle diffraction effect from exceedingly thin phyllosilicate 'crystals' present in various types and proportions.

Although it could be objected that the methods

of preparation for TEM examination have cleaved pre-existing interstratified clay crystals along smectite interlayers, this possibility is regarded as unlikely because the XRD character of the fine fractions is not adversely affected by such treatments and is not significantly different from that of the coarser fractions. Furthermore the XRD and TEM data were obtained from the same materials prepared in the same manner. In addition, SEM examination of the illitic clays in the undisturbed sandstone materials show no morphological evidence of interstratification. It has also been suggested that a layer-by-layer smectite to illite transformation mechanism operating within an interstratified clay crystal should produce primarily IS and IIS layer sequences (cf. Brown, 1984). Furthermore, Środón and Ebenl (1984) have emphasized the IS and ISS layer sequences in the modelling of XRD of illitic clays similar to those studied here. If this were the case, and the particles examined by TEM here were cleaved from pre-existing interstratified crystals along smectite interlayers, then this hypothesis predicts that the resulting particles should be predominantly 20 and 40 Å thick showing few 30, 50, 60, and 70 Å thick particles. This type of distribution is clearly not supported by the TEM data.

The above observations indicate that an alternative, neoformation mechanism for the diagenetic formation of illite, as is currently accepted for sandstones, can also be proposed for bentonites. Such a mechanism is summarized on fig. 6. The precipitation of 20 Å thick 'illite' particles in intimate association with smectite particles produces materials which yield randomly interstratified I/S. As smectite dissolves and/or thin illite is precipitated, the percent illite layers in the randomly interstratified I/S detected by XRD increases until smectite particles are no longer dominant (< 20% of total particles). The XRD character of interstratified I/S then appears to become ordered, > 50% illite layers. If the population is sufficiently homogeneous in 20 Å thick particles the XRD pattern is rectorite-like. As illite particles of greater thickness are precipitated, or grown from thinner ones, the percent illite layers detected by XRD continues to increase. Once the illite particles become sufficiently thick (> 50 Å) the XRD intensities are essentially the product of intraparticle diffraction and smectite layers are no longer detected by XRD. The typical 10 Å spacing of illite with a 001 series of basal reflections then becomes apparent.

The mechanism outlined on fig. 6 shows a starting composition of smectite, which would be expected for bentonites. If, as may be the case in many sandstones, the initial precipitation of thin 'illite' occurs in the absence of smectite particles, the

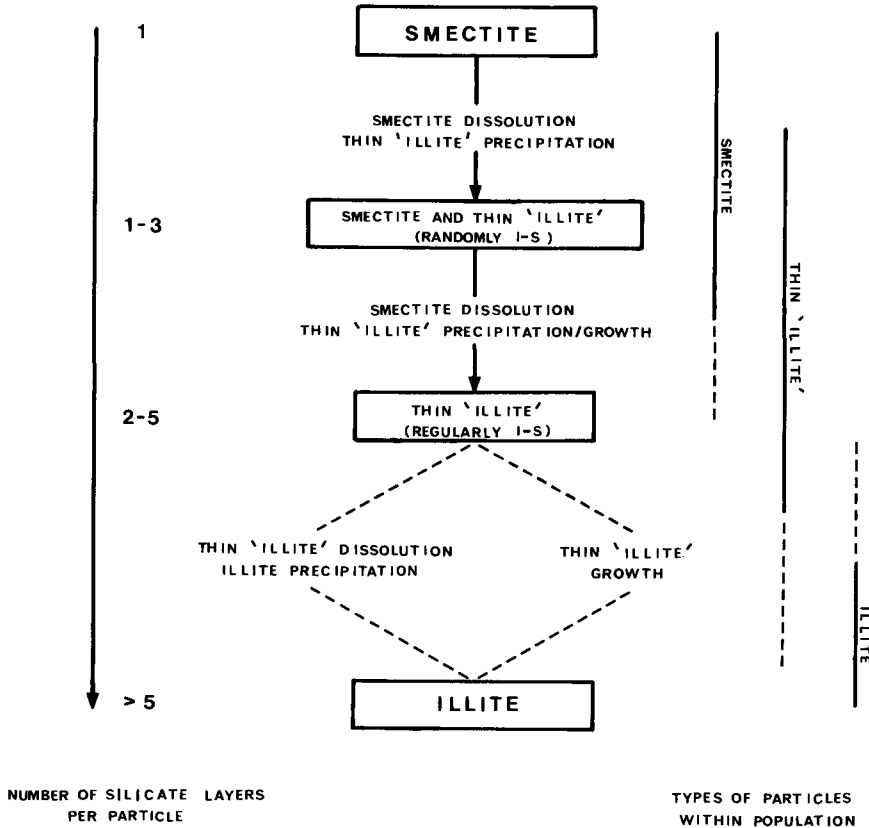


FIG. 6. Proposed neoformation mechanism for the conversion of smectite to illite in bentonites.

XRD character of this material would be that of regularly interstratified I/S and further diagenetic precipitation/growth of thicker illite particles would alter the XRD character accordingly. It is conceivable therefore that the simultaneous precipitation of thin 'illite' in bentonites and sandstones could result in clay mineral assemblages with different XRD characters, that is randomly interstratified I/S and regularly interstratified I/S respectively. Such a rationale may also explain the discrepancy between the composition of interstratified I/S bentonites and enclosing shales reported in the literature (Schultz, 1978; Nadeau and Reynolds, 1981b). The discrepancy, where the percent smectite layers is greater in the bentonites than in the shales, could arise from the fact that bentonites contain a larger number of smectite particles than the shales.

It is evident that the neoformation mechanism proposed here for bentonites could also be valid generally for the formation of illitic clays in pelitic sedimentary sequences. It is to be hoped that future

research will address this important geochemical problem by the complementary use of both TEM and XRD techniques as employed here.

Conclusions. The relationship between the XRD character and particle thickness distribution data of diagenetic illitic clays is consistent with the concept of interparticle diffraction. Illitic clays from bentonites as well as sandstones are similar in this respect, suggesting that they are products of the same processes occurring within sediments during diagenesis. A neoformation mechanism is proposed for the diagenetic conversion of smectite to illite in bentonites. This model views illitic clays as populations of extremely small phyllosilicate crystals precipitated from solution, the XRD character being determined by the types and proportions of particles present.

It should be noted that this investigation has not considered the surface layer charge of the particles, nor any asymmetry of charge distribution across the 2:1 layers, as suggested by Brown, 1984.

Research into such aspects requires precise chemical analysis on mineralogically pure materials, and future work should consider this important issue.

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REFERENCES

- Brown, G. (1984) In: *Clay Minerals: Their Structure, Behaviour and Use*, Phil. Trans. Roy. Soc. Lond. A 311 (L. Fowden, R. M. Barrer, and P. B. Tinker, eds.), 221-40.
- Eslinger, E., and Sellars, B. (1981) *J. Sedim. Petrol.* **51**, 203-16.
- Gray, D. H., and Rex, R. W. (1966) *Clays Clay Minerals*, **14**, 355-66.
- Güven, N., Hower, W. F., and Davies, D. K. (1980) *J. Sedim. Petrol.* **50**, 761-6.
- Hoffman, J., and Hower, J. (1979) In: *Aspects of Diagenesis* SEPM Spec. Publ. 26 (P. A. Scholle and P. R. Schluger, eds.), 55-79.
- Hower, J., and Mowatt, T. C. (1966) *Am. Mineral.* **51**, 825-54.
- Eslinger, E. V., Hower, M. E., and Perry, E. A. (1976) *Geol. Soc. Am. Bull.* **87**, 725-37.
- McHardy, W. J., Wilson, M. J., and Tait, J. M. (1982) *Clay Minerals*, **17**, 23-39.
- Nadeau, P. H. (1980) Ph.D. thesis, Dartmouth College, Hanover, New Hampshire, USA.
- and Reynolds, R. C. (1981a) *Nature*, **294**, 72-4.
- (1981b) *Clays Clay Minerals*, **29**, 249-59.
- Tait, J. M., McHardy, W. J., and Wilson, M. J. (1984a) *Clay Minerals*, **19**, 67-76.
- Wilson, M. J., McHardy, W. J., and Tait, J. M. (1984b) *Clay Minerals*, **19**, 757-69.
- Pallatt, N., Wilson, M. J., and McHardy, W. J. (1984) *J. Petroleum Technology*, **36**, 2225-7.
- Perry, E. A., and Hower, J. (1970) *Clays Clay Minerals*, **18**, 165-77.
- Reynolds, R. C. (1980) Pp. 249-303. In: *Crystal Structures of Clay Minerals and their X-ray Identification* (G. W. Brindley and G. Brown, eds.). Mineralogical Society, London.
- and Hower, J. (1970) *Clays Clay Minerals*, **18**, 25-36.
- Schultz, L. G. (1978) *U.S. Geol. Surv. Prof. Pap.* 1064-A, 28 pp.
- Šrodón, J., and Ebenl, D. D. (1984) In *Micas* (S. W. Bailey, ed.). *Mineral. Soc. Am.* 495-544.
- Stalder, P. J. (1973) *Geologie Mijnb.* **52**, 217-20.
- Velde, B., and Weir, A. H. (1979) Pp. 395-404. In: *Proc. Int. Clay Conf., Oxford, 1978* (M. M. Mortland and V. C. Farmer, eds.). Elsevier, Amsterdam.
- Welden, C. M. (1966) M.Sc. thesis, Brown University, Providence, Rhode Island, USA.
- Wilson, M. D., and Pittman, E. D. (1977) *J. Sedim. Petrol.* **47**, 3-31.

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