

TRIOCTAHEDRAL SMECTITE AND INTERSTRATIFIED CHLORITE/SMECTITE IN JURASSIC STRATA OF THE CONNECTICUT VALLEY

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Abstract—Trioctahedral smectite and regularly interstratified chlorite/smectite in strata of the East Berlin Formation of the Connecticut Valley are largely restricted to black shale and gray mudstone deposited in alkaline, perennial lakes. The precursor of the mixed-layer clay appears to have been a smectite. Alkaline lake waters and inherited pore waters rich in magnesium favored the transformation of smectite to mixed-layer chlorite/smectite by fixation of brucitic interlayers into the smectite unit structure. Gray mudstones containing the mixed-layer chlorite/smectite are invariably underlain by magnesium-rich black shale—a possible source of Mg for the clay mineral transformations. The black shale is composed predominantly of Mg-rich trioctahedral smectite of probable authigenic origin.

Key Words—Alkaline lake, Chlorite, Interstratification, Magnesium, Mudstone, Shale, Smectite.

INTRODUCTION

Mixed-layer chlorite/smectite is being reported with increasing frequency in sedimentary rocks, and it seems likely that the mineral is more common than previously recognized (e.g., Dunoyer de Segonzac, 1970; Blatter *et al.*, 1973; Weaver and Pollard, 1975, p. 114; Almon *et al.*, 1976). Velde (1977) suggested that such corrensite-like minerals may be abundant in sedimentary rocks, but that they are often simply overlooked and, hence, seldom reported in the literature. Likewise, the purported scarcity of trioctahedral smectite in sedimentary rocks has also been questioned. After finding the mineral as a principal constituent of shales in the Green River Formation, Dyni (1976) stated that the abundance of trioctahedral smectite in sediments of continental closed basins may be greater than otherwise thought.

In an investigation of the clay mineralogy of sedimentary sequences in the Connecticut rift valley, both trioctahedral smectite and mixed-layer chlorite/smectite were identified in lacustrine strata of the East Berlin Formation (Early Jurassic age). The minerals occur in black shale and gray mudstone deposited in large, alkaline perennial lakes that intermittently covered the tropical rift valley floor. This paper reports on the geologic occurrence of these minerals, characterizes their mineralogy and chemistry, proposes models for their origin, and briefly discusses the paleoenvironmental implications of their presence in such rocks.

GEOLOGIC SETTING

The geology of the Connecticut Valley and the stratigraphy of the rock units were discussed by April (1980). The East Berlin Formation is sandwiched between the Holyoke and Hampden lava units and con-

sists of a 145–450-m thick sequence of fluvial and lacustrine deposits. Based on work by Hubert *et al.* (1976, 1978), rock units can be assigned to (1) a floodplain depositional system consisting of sediments deposited in stream channels, floodplains (overbank silts and muds), and shallow, oxidizing, temporal lakes; or (2) a perennial lake system composed of gray siltstone-mudstone and black shale representing, respectively, the shallow and deeper portions of the lake. The latter units occur in symmetrical cycles of gray mudstone–black shale–gray mudstone; the cycles record the periodic waxing and waning of the rift valley lakes. The areal extent of the lake(s) probably exceeded 4700 km², and water depths were tens of meters. At least four lake-cycle sequences, some better exposed than others, have been recognized in East Berlin strata.

SAMPLING AND ANALYTICAL METHODS

Sixty-two samples of lacustrine gray mudstone and black shale were collected at 8 localities in the Connecticut Valley. About half of the gray mudstones and all of the black shales were taken from four perennial lake-cycle sequences within the East Berlin Formation. The remaining samples (all gray mudstones) were collected from the Shuttle Meadow and Portland Formations and the Turners Falls Sandstone. Sampling localities SMR, P, TS, and C are about 15 km south of Hartford, Connecticut, and MTSA, HD, and PC are 5 km north of Holyoke, Massachusetts. Locality TFD is in Turners Falls, Massachusetts.

A detailed account of sample preparation procedures and analytical techniques for clay mineralogy and chemistry was given by April (1978, 1980). For the <1- μ m fraction of each sample, 5 diffraction patterns were obtained: (1) air-dried, (2) ethylene glycol-solvated, (3)

Table 1. Whole rock and clay mineralogy of the <1- μ m fraction of gray mudstones and black shales.

Sample number ¹	Whole rock mineralogy ^{2,3}	Clay mineralogy ^{3,5}	Comment ⁴
Gray Mudstone			
SM-4-SMR	Q, P, D	Ch, I, S	
SM-5-SMR	P, D, Q	Ch, I, S (?)	
SM-6-SMR	P, D, Q	I, Ch	
SM-7-SMR	P, D, Q	I, Ch, S	
SM-8-SMR	Q, P, Cc	I, Ch	
SM-9-SMR	Q, P, D, Cc	I, Ch	
SM-10-SMR	Q, P, D	I, Ch	
SM-11-SMR	Q, P, D, Cc	I, Ch, S (?)	
SM-12-SMR	Q, P, D, Cc	I, Ch	
SM-13-SMR	Q, P, Cc	I, Ch	
SM-14-SMR	Q, P, Cc	I, Ch	
SM-2-P	Q, P, Cc, D	I, Ch, S	
EB-4-C	Q, D, P, Py	C/S, I, Ch	upper
EB-7-C	Q, P, D, A, Py	I, Ch	upper
EB-10-C	Q, P, K, D, Py	I, Ch, Ec	lower
EB-11-C	Q, P, K, D	I, Ch, C/S	upper
EB-14-C	Q, P, D, A, K	I, Ch, Ec (?)	lower
EB-20-C	Q, P, D, A, Py	C/S, I, Ch	upper
EB-21-C	Q, D, P, K, A, Py	C/S, I, Ch	upper
EB-22-C	Q, D, P, K, Py	C/S, I, Ch	upper
EB-23-C	Q, D, P, K, Py	C/S, I, Ch	upper
EB-1-TS	Q, D, P, K	C/S, I, Ch	upper
EB-3-TS	Q, D, K, Py, P	I, S, Ch, Ec (?)	lower
EB-5-TS	Q, D, K	I, Ch	lower
EB-7-TS	Q, P, D	C/S, I, Ch	upper
EB-1-PC	Q, P, D, Py	Ch, I	lower
EB-2-PC	Q, P, D, K, Cc, Py	I, Ch, S	lower
EB-5-PC	Q, D, P, K	I, C/S, Ch	upper
EB-7-PC	Q, P, Cc, D	I, Ch, S (?)	lower
EB-10-PC	Q, D, P, K	C/S, I, Ch	upper
EB-11-PC	Q, D, P, K, Py	C/S, I, Ch (?)	upper
EB-12-PC	Q, P, K	C/S, I	upper
EB-1-MTSA	Q, D, P, K, A	C/S, I, Ch	upper
CS-2-HD	Q, P, Cc	Ch, S, I	
CS-3-HD	Q, P, Cc	Ch, I, S	
CS-4-HD	P, D, Q, Py	I, Ch, S	
CS-5-HD	P, D, Q	I, C/S, Ch, S (?)	
CS-6-HD	Q, D, P, Py	I, Ch, Ec	
CS-7-HD	Q, D, P, A, Py	I, Ch, S	
CS-8-HD	Q, D, P, A	I, Ch, Ec (?)	
CS-10-HD	Q, P, D	I, Ch, S (?)	
TF-5-TFD	D, Q, P	I, S, Ch	
TF-7-TFD	P, D, Q	I, S, Ch	
TF-8-TFD	Q, P	Ch, I, S, Ec (?)	
TF-9-TFD	Q, P, D, Py	I, Ch	
TF-10-TFD	Q, P, D, Py	I, Ch, S	
TF-11-TFD	Q, P, D, Py	I, Ch, S	
TF-12-TFD	Q, P, D	I, S, Ch	
Black Shale			
EB-5-C	Q, D, P, Py	I, Ch, S	
EB-8-C	Q, D, P, A, M	I, S, Ch	upper gray-blk. transition
EB-9-C	Q, D, P, K	S, I, I/S	
EB-12-C	Q, D, P, K, M	S, I, I/S, Ch (?)	upper gray-blk. transition
EB-13-C	Q, D, P, K, Py	S, I, I/S	
EB-15-C	Q, D, P, K	S, I	
EB-2-TS	Q, D, P	S, I	
EB-4-TS	Q, D, P, K, M	S, I	
EB-6-TS	Q, D, P, M	I, S, Ch, I/S	
EB-3-PC	Q, D, P, Py	S, I, Ch	

Table 1. Continued.

Sample number ¹	Whole rock mineralogy ^{2,5}	Clay mineralogy ^{2,5}	Comment ⁴
EB-4-PC	Q, D, P, K, Py	S, I, Ch	
EB-9-PC	Q, D, P, K	I/S, I, S, Ch	
EB-13-PC	Q, P, K	S, I, I/S	
EB-2-MTSA	Q, D, K, P	S, I, Ch	

¹ SM = Shuttle Meadow Formation; EB = East Berlin Formation; CS = Portland Formation (Chicopee Shale); TF = Turners Falls Sandstone.

² Q = quartz; P = plagioclase; K = potassium feldspar; D = dolomite; Cc = calcite; Py = pyrite; A = analcime; M = magnesite.

³ I = illite; Ch = chlorite; S = smectite; C/S = interstratified chlorite/smectite; I/S = interstratified illite/smectite; Ec = expandable chlorite.

⁴ Describes the relative stratigraphic position of East Berlin gray mudstone to the central black shale of the lake-cycle sequences.

⁵ Minerals listed in order of approximate relative abundance.

K-saturated, (4) heated to 350°C, and (5) heated to 550°C. When necessary, magnesium-saturated, glycerol-solvated specimens were prepared (Walker, 1961) to distinguish between high- and low-charge swelling phases (i.e., vermiculite and smectite). Selected samples were treated with 1 N HCl (80°C) to test for the presence of kaolinite. Illite polytypes were determined by the method of Velde and Hower (1963). The whole rock mineralogy of each sample was determined using standard X-ray powder diffraction (XRD) techniques (Table 1). Thin sections of selected samples were also prepared for petrographic microscope examination and electron microprobe analyses.

RESULTS

Clay mineralogy and chemistry of the gray mudstone

The clay mineralogy of the lacustrine gray mudstone is dominated by illite and chlorite (Figure 1, Table 1). Illite is present in all samples. Polytype determinations and $d(060)$ spacings at 1.50–1.51 Å show that the mineral is composed predominantly of dioctahedral 1Md (low temperature) illite. Chlorite was identified in every sample but one and is a trioctahedral, magnesium-rich variety as indicated by $d(060) \sim 1.54$ Å and the intensities and positions of basal (00 l) reflections (Brindley, 1961). Regularly interstratified, well-crystallized, mixed-layer chlorite/smectite occurs almost exclusively in East Berlin gray mudstone contiguous with and stratigraphically above central black shale beds (Table 1). These gray mudstone units are thus referred to as upper gray mudstone. The mineral is characterized by a distinct superlattice reflection at ~ 29 Å which shifts to ~ 31 Å upon ethylene glycol treatment. The superlattice is poorly defined or nonexistent in two samples containing the mineral, suggesting the presence of a more poorly ordered form with higher proportions of randomly interstratified layers.

Trace to minor amounts of discrete smectite and expandable chlorite are present in about half of the samples, but in the East Berlin Formation these phases appear to be restricted to the gray mudstone below the central black shale beds (henceforth, the lower gray mudstone). The expandable chlorite shows a 14-Å reflection that broadens to 14.5–15.0 Å after glycolation, but remains at 13.8–14.0 Å after heating to 550°C. The “expandable chlorite” phase may possibly be a mixed-layer chlorite/expandable-layer clay with truly random interstratification (Suchecky *et al.*, 1977).

Diffraction patterns of the $<1\text{-}\mu\text{m}$ fraction of East Berlin upper gray mudstone samples show well- to poorly ordered, mixed-layer chlorite/smectite as the predominant clay mineral with subordinate amounts of 1 Md illite and discrete chlorite. Samples EB-11-PC and EB-12-PC, upper gray mudstones from two different lake-cycle sequences, were further size fractionated. The $<0.5\text{-}\mu\text{m}$ fraction of both contained a relatively pure interstratified clay mineral with trace amounts of illite (Figure 2). The diffraction patterns for sample EB-11-PC (not shown) are essentially identical with those of sample EB-12-PC. The air-dried and glycolated samples display a superlattice peak at ~ 28.5 Å, shifting to ~ 31 Å with rational higher orders shown to $d(009)$. Upon magnesium saturation and glycerol treatment, a well-defined peak giving a first order basal spacing of ~ 32 Å appears as the result of regularly alternating 14-Å and 18-Å layers. The swelling layers partially collapse to ~ 12.5 Å with potassium saturation and totally collapse upon heating to 350°C and 550°C; the 24-Å superlattice peak is now the result of the regular interstratification of 10-Å collapsed swelling layers and 14-Å chlorite. The behavior of the swelling layers is characteristic of smectite rather than vermiculite (Harward *et al.*, 1969).

A strong $d(060)$ reflection at 1.54 Å for both samples suggests a trioctahedral nature for at least one of the 2:1 silicate layers in the unit structure. The chemical

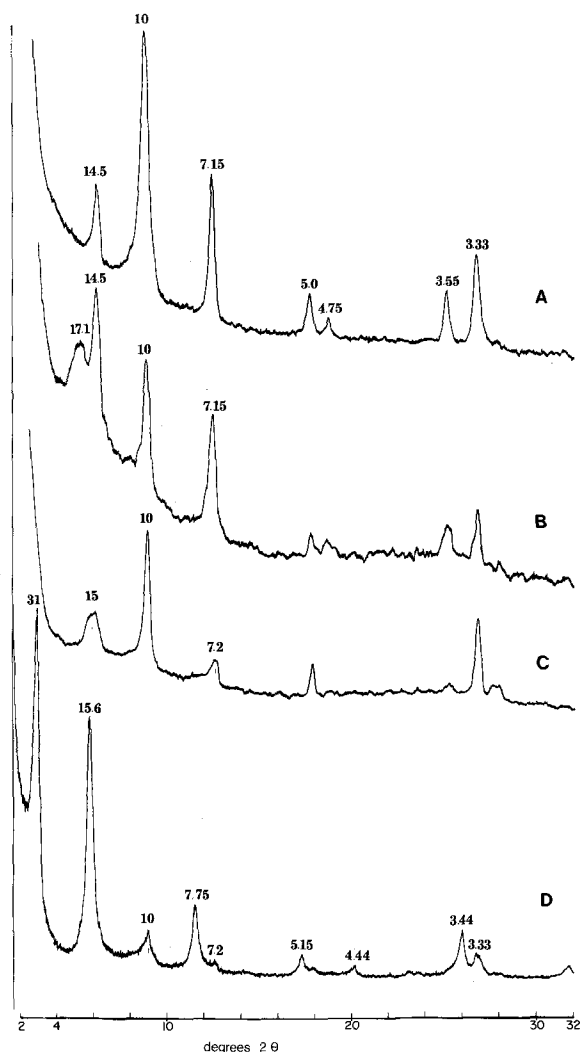


Figure 1. X-ray powder diffraction patterns of glycolated <1-μm fraction samples of some gray mudstones. (A) Typical illite + chlorite assemblage; (B) Illite + chlorite + smectite assemblage; (C) Illite + chlorite + expandable chlorite assemblage; (D) Interstratified chlorite/smectite + illite + minor chlorite assemblage. (CuKα radiation)

data now presented indicate that both layers are trioctahedral.

A chemical analysis of a relatively pure, <0.5-μm fraction of sample EB-12-PC is listed in Table 2. Before recasting the analysis into a structural formula, corrections were applied for the presence of minor amounts of illite by assuming all of the K in the chemical analysis to be from illite (April, 1980). The composition of the illite was assumed to be close to that of the "Interlake illite," a 1Md dioctahedral illite characterized by Hower and Mowatt (1966). The structural formula for the mixed-layer chlorite/smectite calculated on the basis of 20 oxygens + 10 (OH) or 50 equivalents is shown be-

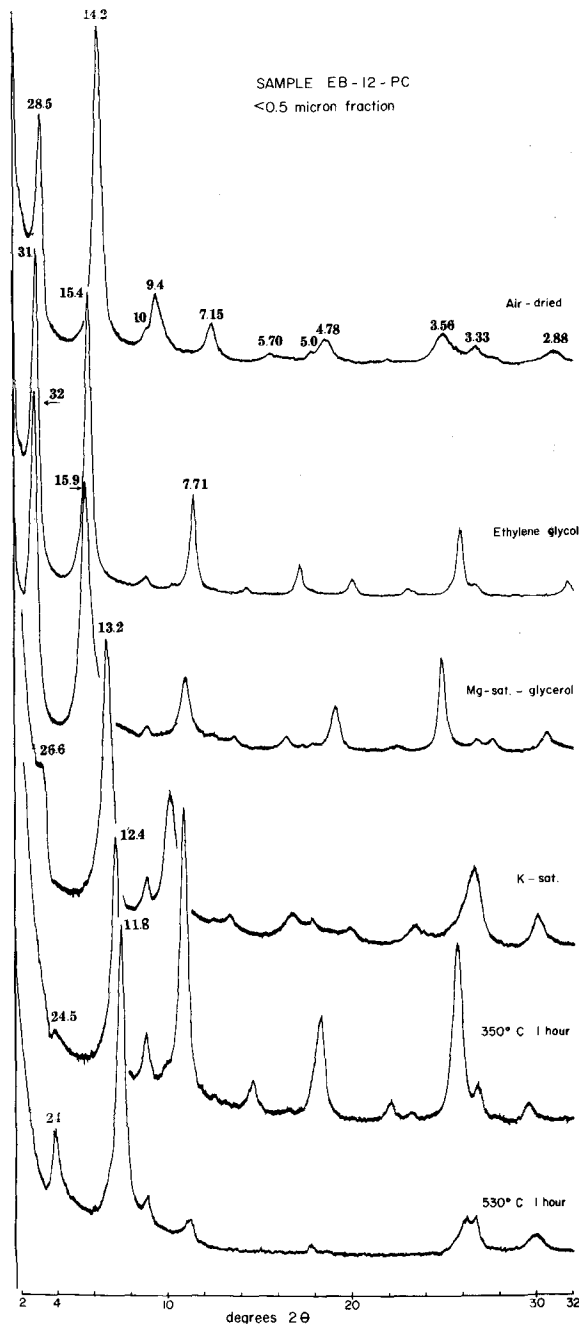


Figure 2. X-ray powder diffraction traces of the <0.5-μm fraction of sample EB-12-PC, an upper gray mudstone. (CuKα radiation)

low. TiO₂ was considered a separate phase and is therefore not included in the structural formula.

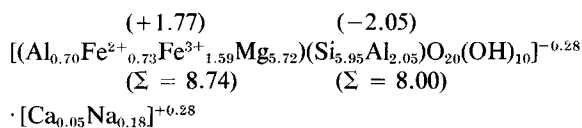


Table 2. Chemical analyses of the $<0.5\text{-}\mu\text{m}$ fraction of sample EB-12-PC and the $<1\text{-}\mu\text{m}$ fraction of sample EB-13-PC.

Oxides	Sample EB-12-PC		Sample EB-13-PC	
	Wt. %	Wt. % after illite subtraction ¹	Wt. %	Wt. % after illite subtraction ¹
SiO ₂	41.59	39.04	51.64	49.76
Al ₂ O ₃	18.25	15.32	16.10	8.53
Fe ₂ O ₃	10.64	13.86	9.46	13.61
FeO	4.43	5.57	—	—
MgO	19.80	25.23	18.63	26.70
MnO	0.20	—	0.38	0.58
CaO	0.23	0.30	0.16	0.24
Na ₂ O	0.54	0.68	0.42	0.58
K ₂ O	2.12	—	3.34	—
TiO ₂	0.94	—	0.85	—
Total	98.74	100.00	100.98	100.00

¹ Illite composition based on the chemical analysis of the $<0.5\text{-}\mu\text{m}$ fraction of the Interlake illite of Hower and Mowatt (1966).

The calculated total unit structure charge is -0.28 equivalents/unit cell ($1/2$ unit cell chlorite + $1/2$ unit cell smectite). It is reasonable that this charge deficiency arises principally from the swelling layers, with the value 0.28 equivalents/unit cell being well within the range of $0.20\text{--}0.40$ equivalents per 10 oxygen + 2(OH), characteristic of smectites. These results support the XRD data for an interstratified chlorite/smectite. Also, because the octahedral cation population is 8.74 per 20 oxygen + 10(OH), both the chlorite and smectite layers are nearly trioctahedral (ideally, 9 cations per 20 oxygen + 10(OH) are expected if both chlorite and smectite are trioctahedral). As mentioned above, the trioctahedral nature of the unit structure is supported by the presence of strong $d(060)$ reflections at 1.54 \AA .

Clay mineralogy and chemistry of the black shale

Black shale from the East Berlin Formation contains the clay-mineral assemblage smectite + illite \pm (minor) chlorite \pm mixed-layer illite/smectite. Illite and smectite show $d(060)$ reflections near 1.50 \AA and 1.52 \AA and are, respectively, dioctahedral and trioctahedral. Diffractograms also display weak reflections at $\sim 1.54\text{ \AA}$ when chlorite is present suggesting that the mineral is trioctahedral. The positions of first order and non-integral (00ℓ) reflections in diffractograms of a number of air-dried and ethylene glycol treated samples indicate the presence of a mixed-layer illite/smectite (Reynolds and Hower, 1970). A slight asymmetry of the 10-\AA reflection toward low angles (higher d -spacing) in some diffractograms suggests the presence of mixed-layer illite/smectite with $<10\text{--}20\%$ expandable layers. Other samples contain essentially 100% expandable layers with a small percentage of illite layers randomly interstratified (Figure 3). Discrete illite in all samples

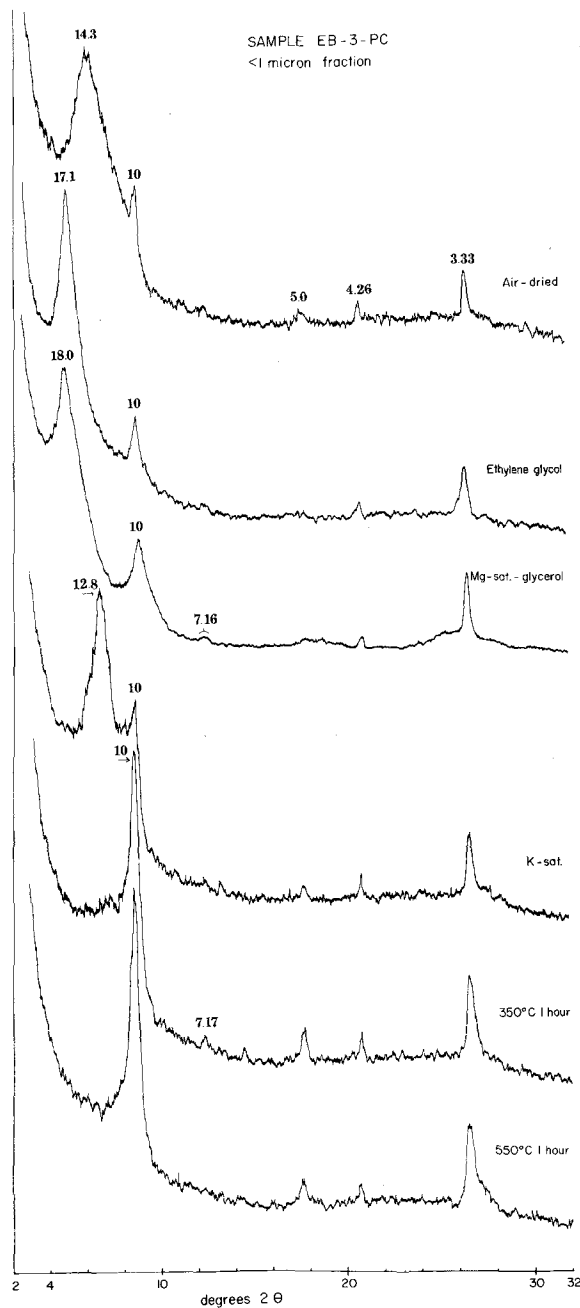
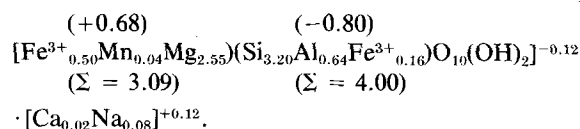


Figure 3. X-ray powder diffraction traces of the $<1\text{-}\mu\text{m}$ fraction of sample EB-3-PC, a black shale from the East Berlin Formation. The shale contains a clay-mineral assemblage of trioctahedral smectite + illite + (trace amounts of) chlorite. (CuK α radiation)

precluded attempts to determine precisely the degree and nature of the interstratification.

The chemical analysis of the $<1\text{-}\mu\text{m}$ fraction of sample EB-13-PC from lake-cycle sequence 1 which contains smectite and minor amounts of illite and mixed-layer illite/smectite (but no chlorite) is listed in Table

2. In recasting the analysis into a structural formula, it was assumed that all of the K in the chemical analysis belongs to illite (as both discrete and mixed-layer illite) and that the average composition of the illite is close to that of the "Interlake illite." Accordingly, 35% of the <1- μm fraction is illite and the rest smectite. The structural formula calculated on the basis of 10 oxygens + 2 (OH) is shown below:



The above formula should be regarded cautiously because it lacks data for ferrous iron. Nonetheless, the trioctahedral nature of the mineral and the predominance of magnesium in octahedral sites are evident. The composition and calculated structural formula suggest that this East Berlin mineral is saponite (Weaver and Pollard, 1975, p. 77–83). Supporting evidence includes: (1) the degree of Al–Si substitution that results in a high negative charge on the tetrahedral sheet; (2) the cation occupancy in the octahedral sheet near 3.00; (3) the positive charge of the octahedral sheet; and (4) an 060 reflection near 1.52 Å. Although the total structural unit charge of 0.12 equivalents is more typical of stevensite (Faust and Murata, 1953), the data compiled by Dyni (1976) on the distribution of structural charge for trioctahedral smectites show that values as low as 0.10 equivalents have been reported for saponites. It is concluded, therefore, that the mineral is saponite. The necessity of assigning some Fe^{3+} to tetrahedral sites to bring the cation occupancy of the tetrahedral sheet to 4.00 suggests a similarity between this mineral and diabantite—a fibrous variety of saponite reported by Cailière and Hénin (1951).

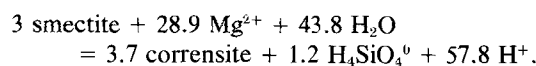
DISCUSSION

Trioctahedral smectite occurs in gray mudstone in all formations in the Connecticut Valley. It is present in minor amounts in the East Berlin lower gray mudstone and it is the predominant clay mineral in the central black shale of the lake-cycle sequences. However, smectite is conspicuously absent or rare in the mixed-layer chlorite/smectite-bearing upper gray mudstone. These observations suggest that most original smectite in the upper gray mudstone altered to a mixed-layer phase sometime during and/or after deposition of the lacustrine sediments. The following questions, however, must be answered: (1) What conditions prevailed during deposition and burial of the upper gray mudstone that favored the formation of mixed-layer chlorite/smectite; and (2) Why is this mineral restricted to the upper gray mudstone in the East Berlin lake-cycle sequences?

According to Hubert *et al.* (1976), sedimentary struc-

tures, such as ripple marks, dolomite concretions, mudcracks, and dinosaur footprints, indicate that the upper gray mudstone was deposited in shallow water, possibly in isolated bays and pools, during periods of relative drought and falling lake levels. Dolomite laminae, analcime, traces of gypsum, and rare molds of halite and possibly glauberite in these beds support the contention that the mudstone was deposited in alkaline, hard-water lakes with high concentration of Mg^{2+} , Ca^{2+} , Na^+ , HCO_3^- , and SO_4^{2-} . Under these conditions the formation of authigenic smectite is favored (cf. Millot, 1970; Weaver *et al.*, 1976; Dyni, 1976). With extended evaporation of the lake waters during deposition of the upper gray muds, however, conditions would eventually shift to favor mixed-layer chlorite/smectite over smectite. Almon *et al.* (1976) showed that authigenic corrensite (i.e., mixed-layer chlorite/smectite) can form under hyposaline conditions where pH values range from 7.5 to 8.8 and $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios are about 10 to 50. Grim *et al.* (1960) reported a range of mixed-layer clays of the corrensite-type associated with an evaporite sequence and noted that their stability was dependent upon pH and magnesium activity.

As the activity of Ca^{2+} in the East Berlin lake waters increased as evaporation proceeded, calcite or Mg-calcite (laminae) would begin to precipitate. As a result, pH, Na^+ , and Mg^{2+} activities and the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio would rise in the increasingly alkaline lake waters. A possible reaction for the alteration of smectite to an "ideal corrensite" under these conditions was given by Weaver and Beck (1977, p. 195), based on thermodynamic values calculated by the method of Tardy and Garrels (1974) and Fe-free ideal mineral compositions:



Analcime may have precipitated when pH values of 9 or 10 were reached in the lake or sediment pore waters. Hay (1966) reported the precipitation of analcime directly from strongly alkaline (pH = 9.70), sodium carbonate brines in Lake Natron, Tanzania. Continued removal of Na^+ and Ca^{2+} with further evaporation of the lake waters would have ultimately produced conditions favorable for the formation of Mg-hydroxy (brucitic) layers (Carstea *et al.*, 1970). The lack of typical evaporite mineral assemblages in the gray mudstone, however, indicates that such conditions were probably not attained. Mixed-layer chlorite/smectite formation in the upper gray muds, therefore, likely began in the depositional environment and continued during burial as alkaline, magnesium-rich pore waters continued to react with the sediment.

A possible explanation for the absence of mixed-layer chlorite/smectite in the lower gray mudstone is that the requisite aqueous chemistry of the lake and pore waters was not achieved due to changes in the paleo-

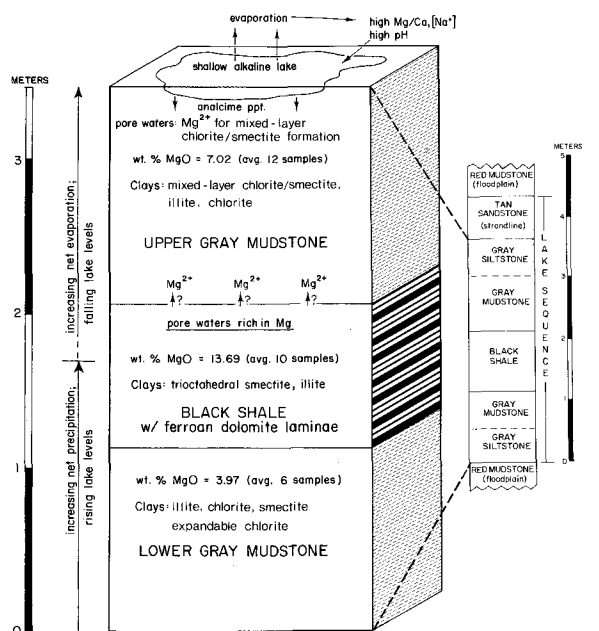


Figure 4. Summary schematic diagram showing the clay mineralogy and chemistry of the gray mudstone and black shale in the lake-cycle sequences. Mixed-layer chlorite/smectite occurs in the upper gray mudstone. Magnesium for its formation may have been supplied by (1) inherited lake pore waters and (2) upward migration of interstitial water during compaction of the black mud. Weight percent MgO values are for whole rock samples.

climate. The relative stratigraphic position of the lower gray mudstone in the lake-cycle sequences implies deposition during periods of increasing precipitation and rising lake levels. These periods of relative wetness were characterized by lake expansion and lower water alkalinity and ionic strength, and culminated with the deposition of the central black shale beds. The paucity of analcime in the lower gray mudstone also suggests that net evaporation was lower. Conditions, therefore, precluded both direct precipitation of analcime and the aggradation of smectite to mixed-layer chlorite/smectite.

A corollary of the above model is that the lake-cycle sequences in the East Berlin Formation are primarily the result of climatic rather than tectonic influences. The symmetric lithological cycles of gray mudstone-black shale-gray mudstone are actually asymmetric with respect to their chemistry and mineral assemblages. Oscillations in the paleoclimate caused periodic fluctuations in net evaporation over precipitation and were, therefore, a major factor controlling the formation of analcime and mixed-layer chlorite/smectite in the gray mudstone of shallow lacustrine origin.

A second interpretation of the restricted occurrence of mixed-layer chlorite/smectite involves the movement of Mg-rich pore water from the black muds into

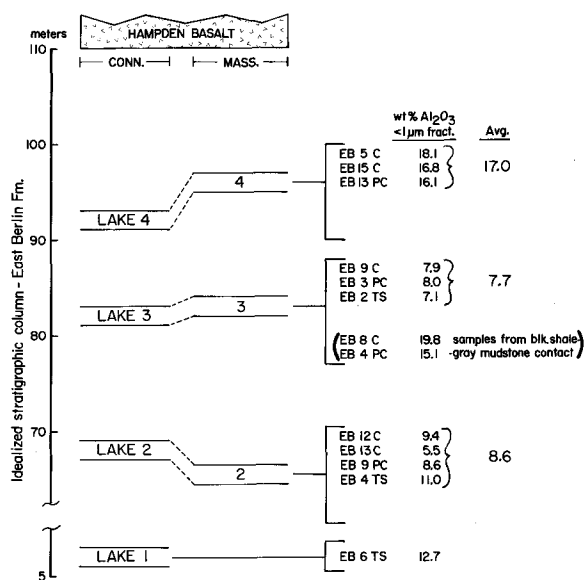


Figure 5. Alumina content of the $<1\text{-}\mu\text{m}$ fraction of black shales from four East Berlin lake-cycle sequences. Sample suites EB-C and EB-TS were collected in Connecticut, and EB-PC in Massachusetts.

the overlying gray muds. Quartz, dolomite, magnesite, feldspar, and pyrite constitute the whole rock mineralogy of the black shales along with a clay-mineral assemblage dominated by Mg-rich trioctahedral smectite. The average whole rock MgO content of 10 black shale samples is given in Figure 4. As expected from the mineralogy, magnesium concentrations are relatively high; pore waters in equilibrium or near equilibrium with the black muds were no doubt highly magnesium-rich as well. During burial and on compaction of the black muds, upward movement of pore waters and constituent ions in response to dewatering and concentration gradients may have provided a source of magnesium to the overlying upper gray muds. As shown in Figure 4, the average magnesium content of the upper gray mudstone is approximately twice that of the lower gray mudstone underlying the black shale beds. The influx of magnesium would favor the aggradation of smectite to mixed-layer chlorite/smectite, whereas smectite would persist in the lower gray mudstone having lower magnesium concentrations. Interestingly, mixed-layer chlorite/smectite is rare in lacustrine gray mudstone sampled from other formations in the Connecticut Valley (see Table 2). These beds are not usually associated with contiguous black shales and contain mineral assemblages similar, in most instances, to those in the East Berlin lower gray mudstone.

Saponite in the black shale probably formed as an authigenic precipitate. Dyni (1976) and Bradley and Fahey (1962) suggested that trioctahedral smectite (i.e., hectorite and stevensite) in the lacustrine deposits of

the Green River Formation formed authigenically in response to magnesium-rich pore waters. A similar origin was suggested by Papke (1970, 1972) and Droste (1961) for trioctahedral smectite (i.e., saponite) in playa lake sediments. As discussed above, pore waters in the East Berlin black muds contained high concentrations of magnesium early after burial as evidenced by: (1) the complete conversion of original Mg-calcite laminae to dolomite, and (2) the occurrence of magnesite in the black shale (Figure 4). Also, the presence of dolomite-cored magnesite crystals in which magnesite replaced dolomite suggests that Mg^{2+}/Ca^{2+} ratios in the pore waters increased with burial and eventually exceeded 40 (Müller *et al.*, 1972). Whether saponite formed as a direct precipitate or by the transformation of a precursor clay cannot be determined. There is no evidence, however, indicating a detrital origin for the smectite.

Some data show that the clay mineralogy of the black shale may differ in the four lake-cycle sequences. Attempts to calculate smectite structural formulae for three chlorite-free samples from lake sequences 2 and 3 failed when the illite subtraction procedure could not be completed because of insufficient amounts of Al_2O_3 (relative to K_2O) in chemical analyses. The same problem occurred when calculations were carried out using an illite composition with the lowest reported Al_2O_3/K_2O ratio for naturally occurring illites (Weaver and Pollard, 1975). As shown in Figure 5, the average Al_2O_3 content of the $<1\text{-}\mu\text{m}$ fraction of black shale is substantially higher in lake sequence 1 than in lake sequences 2, 3, and 4. These results suggest that the chemistry of the 10-Å mineral in lake sequences 2 and 3 may differ considerably from "normal" or "average" dioctahedral illite. In addition, smectite in the black shale of lake sequences 2 and 3 (and 4?) may be a Mg-rich, Al-poor variety (e.g., stevensite). Unfortunately, with the limited data presently available, the nature and identity of these minerals remains problematic.

Finally, although the black shales are highly enriched with magnesium, they contain a clay-mineral assemblage dominated by Mg-rich trioctahedral smectite and no mixed-layer chlorite/smectite. Therefore, as suggested here and by others (e.g., Grim *et al.*, 1960; Weaver and Pollard, 1975, p. 116; Almon *et al.*, 1976; Weaver and Beck, 1977, p. 210; Velde, 1977, p. 113), physical processes—in this case evaporitic conditions—controlling pH and the ionic concentration and strength of lake and pore waters played an important role in governing the formation of mixed-layer chlorite/smectite in the sedimentary environment.

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Резюме—Триоктаэдрический смектит и регулярно внутринапластованный хлорит/смектит в пласте формации Восточного Берлина в Долине Коннектикута ограничены, в основном, до черной сланцеватой глины и серой иловатой глины, осажденных в щелочных непересыхающих озерах. Смектит кажется предшественником смешанно-слоистой глины. Воды щелочных озер и наследственные пористые воды, богатые в магний, способствовали преобразованию смектита в смешанно-слоистый хлорит/смектит путем фиксации бруцитовых промежуточных слоев в элементарную структуру смектита. Черные сланцеватые глины, богатые в магний—возможные источники магния, используемые для преобразования глинистых минералов—неизменно располагаются под серыми иловатыми глинами, содержащими смешанно-слоистый хлорит/смектит. Черная сланцеватая глина, в основном, состоит из богатого в магний триоктаэдрического смектита, вероятно, аутигенного начала. [E.C.]

Resümee—Trioktaedrischer Smektit und regelmäßige Chlorit/Smektit-Wechselagerungen sind in den Schichten der East Berlin Formation des Connecticut Valley hauptsächlich auf schwarzen Schieferton und grauen Tonstein beschränkt, die in alkalischen permanenten Seen abgelagert sind. Der Vorläufer der Wechselagerung scheint ein Smektit gewesen zu sein. Alkalische Seewässer und Mg-reiche Porenwässer begünstigten die Umwandlung des Smektit in die Chlorit/Smektit-Wechselagerung, indem brucitische Zwischenlagen in die Smektit-Struktur eingebaut wurden. Unter den grauen Tonsteinen, die die Chlorit/Smektit-Wechselagerung enthalten, findet sich immer ein Mg-reicher schwarzer Schieferton, der eine mögliche Mg-Quelle für die Tonmineralumbildung ist. Der schwarze Schieferton besteht vor allem aus Mg-reichem trioktaedrischem Smektit mit wahrscheinlich authigener Entstehung. [U.W.]

Résumé—La smectite trioctaèdre et la chlorite/smectite régulièrement interstratifiée dans les lits de la formation East Berlin de la vallée du Connecticut sont pour la plupart restreintes au shale noir et à l'argilite grise déposés dans des lacs alcalins perpétuels. Le précurseur de l'argile à couches mélangées semble avoir été une smectite. Les eaux alcalines du lac et les eaux héritées des pores, riches en magnésium, ont favorisé la transformation de la smectite en chlorite/smectite à couches mélangées par la fixation d'intercouches brucitiques dans la structure unitaire de la smectite. On trouve invariablement des shales noirs riches en magnésium, une source possible de Mg pour les transformations de minéral argileux, sous des argilites grises contenant la chlorite/smectite à couches mélangées. Le shale noir est composé surtout de smectite trioctaèdre riche en Mg et probablement d'origine authigénique. [D.J.]