REGULARLY INTERSTRATIFIED CHLORITE/VERMICULITE IN CONTACT METAMORPHOSED RED BEDS, NEWARK GROUP, CONNECTICUT VALLEY

Richard H. April

Department of Geology, Colgate University, Hamilton, New York 13346

Abstract—A regularly interstratified chlorite/vermiculite occurs in red beds of the East Berlin Formation (Early Jurassic age) in the Connecticut Valley. The mineral is restricted to a 2.5-m wide zone of contact metamorphosed strata adjacent to and underlying the Hampden Basalt. Chemical and X-ray powder diffraction data indicate that the chlorite/vermiculite formed in response to lava-induced elevated temperatures and the availability of magnesium in the muds during and shortly after emplacement of the lava flow. Near the contact, hydrothermal fluids originating from the lava and from the synchronal weathering of basalt fragments by superheated pore waters provided a source of Mg. Further from the contact, magnesium was primarily derived from the thermal dissociation of dolomite. K_2O concentrations and the distribution of clay minerals in the red mudstone suggest that the interstratified chlorite/vermiculite formed from pre-existing illite or vermiculite as potassium was released and brucitic sheets were incorporated into interlayer positions.

Key Words—Chlorite, Contact metamorphism, Hydrothermal, Mixed-layer, Red beds, Vermiculite.

INTRODUCTION

General

This paper is concerned with the nature and possible origin of a regularly interstratified chlorite/vermiculite in hydrothermally altered red beds of the East Berlin Formation (Early Jurassic age) in the Hartford Basin of the Connecticut Valley. Regularly interstratified clay minerals as the result of hydrothermal alteration were previously reported by a number of authors including Blatter *et al.* (1973), Shimoda (1969), Harvey and Beck (1962), and Sudo *et al.* (1954). Other authors, notably Eberl (1978), Velde (1972, 1977a), and Iiyama and Roy (1963), showed experimentally that hydrothermal treatment of natural clay minerals can produce regularly interstratified mixed-layer clays.

The interstratified clay mineral in the East Berlin red beds is found in a 2.5-m wide zone of strata underlying the Hampden Basalt. Chemical and X-ray powder diffraction data indicate that the mineral formed as an alteration product in the sediments during and shortly after emplacement of the Hampden lava flow. The purpose of this paper is to: (1) characterize the mineralogy and chemistry of the interstratified clay mineral; (2) describe its geologic occurrence; and (3) propose a model that explains its formation in the red beds.

Corrensite-type clay minerals

The term corrensite was proposed by Lippmann (1954) to describe a mixed-layer clay mineral with regularly alternating layers of chlorite and swelling chlorite. Since then, the terms corrensite, corrensitic material, and corrensite-like have been employed to describe a variety of genetically similar magnesium-rich mixed-layer clay minerals in rocks with a spectrum of lithologies and modes of origin. These clays consist of regular, or nearly regular, interstratifications of chlorite with swelling chlorite, smectite, or vermiculite (e.g., Early *et al.*, 1956; Bradley and Weaver, 1956; Lippmann, 1956; Peterson, 1961; Blatter *et al.*, 1973; Almon *et al.*, 1976; Ross and Kodama, 1976). In this report the term corrensite-type clay is used in a general sense to describe an ordered 1:1 interstratification of chlorite with a hydrated, interlayer clay mineral.

Mechanisms controlling the formation of corrensite-type clay minerals are not yet fully understood. Although it is generally recognized that magnesium plays an important role, few papers on the occurrence of corrensite-type clay minerals in sedimentary rocks actually document the source of the magnesium. Hydrothermal fluids, alkaline lake waters, pore waters, and the decomposition of pre-existing mineral phases and volcanic glasses have often been suggested, but less often demonstrated, as primary sources of the magnesium. In terms of the actual mechanics of formation of corrensite-type clays, two distinct, although rather general models, can be distilled from the literature: an aggrading model and a degrading model, both of which are briefly described below.

The aggrading model, as synthesized from information in Weaver and Pollard (1975), Carstea *et al.* (1970), Basset (1959), Wyart and Sabatier (1966), Dunoyer de Segonzac (1970), and Shover (1964), assumes that the initial clay material is a 2:1 layer silicate, such as smectite or vermiculite. When exposed to a diagenetic or metasomatic environment rich in magnesium, the mineral may aggrade by random fixation of Mg-hydroxy (brucitic) sheets in the interlayer space. Bond strength differences, changes in the OH bond angles, and development of asymmetric charge distributions in the structure causes fixation to become ordered and results
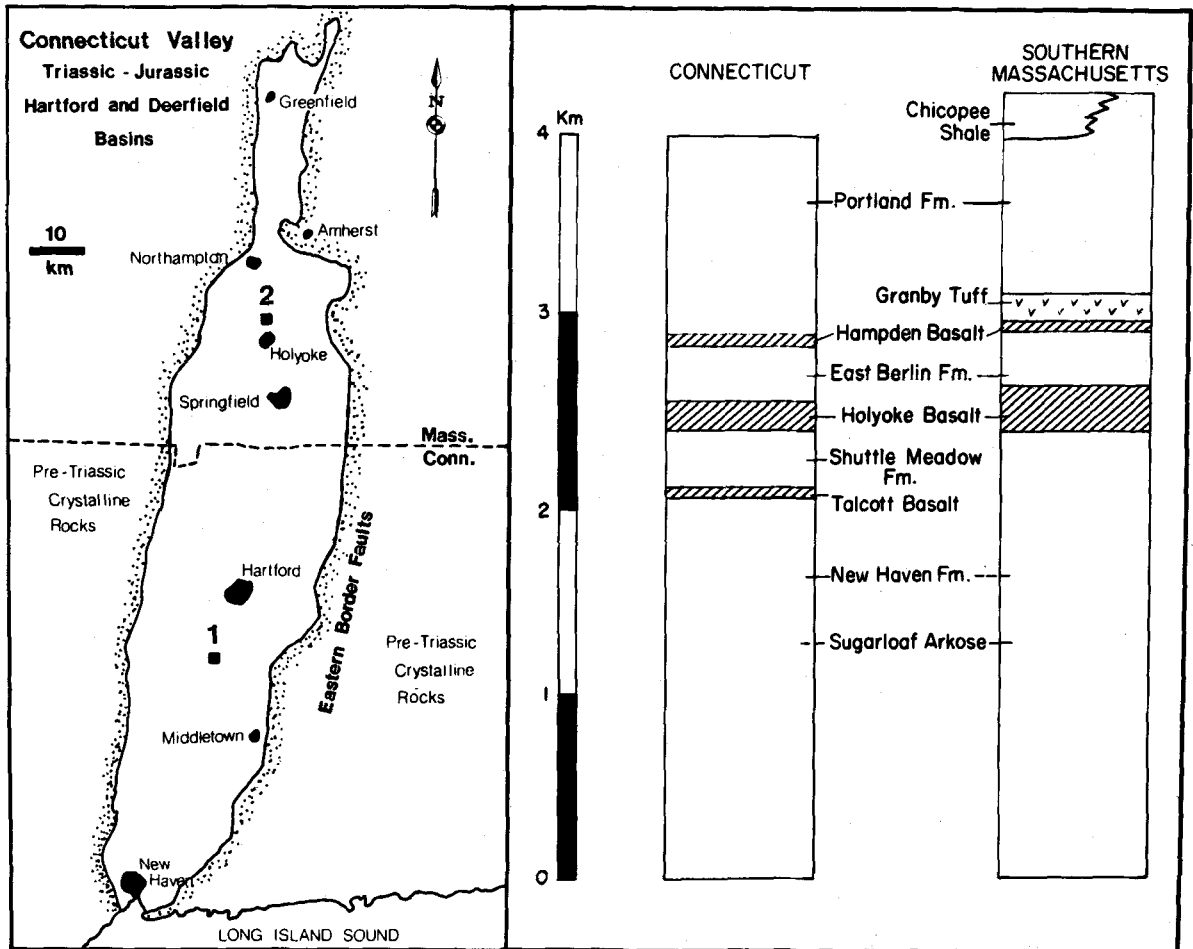
1

Figure 1.   Stratigraphy of the Newark Group in the Hartford Basin of Connecticut and southern Massachusetts. Sampling localities are shown on the index map.

in regular alternations of 2:2 (chlorite) and 2:1 (smectite or vermiculite) layers. The final product is a 1:1 regular, or nearly regular, interstratified chlorite/smectite or chlorite/vermiculite. Dunoyer de Segonzac (1970) stated that corrensite might be an intermediate product in the transformation of illite to chlorite by Mg fixation, implying that rather than a true expandable phase, the initial 2:1 layer silicate template could be a degraded illite from which potassium is removed.

The degrading model differs from the aggrading model in that the parent material is usually a chlorite (Bradley and Weaver, 1956; Jackson, 1963; Johnson, 1964; Post and Janke, 1974; Ross, 1975; Ross and Kodama, 1976). Structural disruption of interlayer brucitic sheets by weathering or oxidation may cause selective removal of alternate interlayers as a result of asymmetries in charge distributions within the 2:1 layers. Ross and Kodama (1976) showed that chlorites with intermediate Fe^{2+} contents (brunsvigites) are most likely to alter to a regularly interstratified chlorite/vermiculite. This

model seems to be directed more toward explaining the genesis of interstratified chlorite/vermiculite rather than chlorite/smectite. Biotite, hypersthene, plagioclase, and hornblende have also been reported by Sarkisyan and Kotelnikov (1972, p. 347) to alter to interstratified chlorite/vermiculite. Mechanisms controlling these processes are very poorly understood.

In addition, recent work by Velde (1977a) involving clay mineral transformations at elevated pressures (2 kbar) and temperatures ($>300°C$) indicates that the formation of corrensite-type clay minerals during burial metamorphism may be controlled by the R^{3+} (i.e., Al^{3+} and/or Fe^{3+}) content of the initial clay mineral assemblage.

GEOLOGIC SETTING

The Hartford Basin is a north–south trending trough ~170 km long and 8–35 km wide in Connecticut and central Massachusetts. The rocks in the basin consist of terrestrial deposits interlayered with basalt flows and

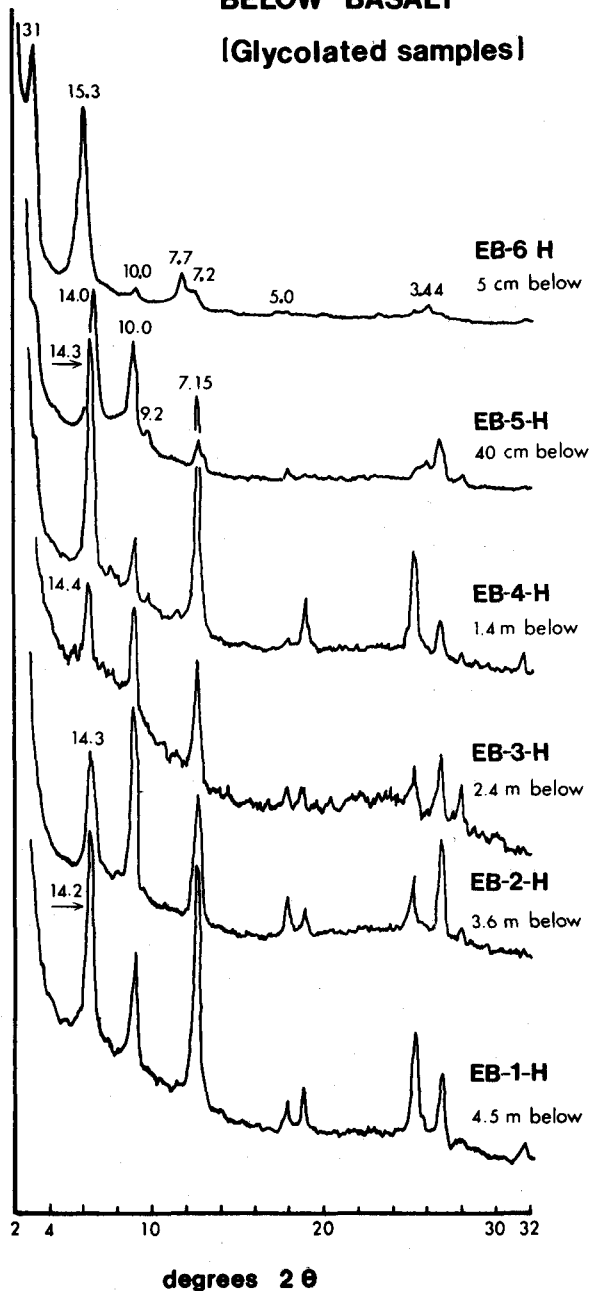## RED MUDSTONES
BELOW BASALT
[Glycolated samples]

Figure 2. X-ray powder diffraction patterns of East Berlin red mudstone glycolated samples EB–1–H to EB–6–H taken in a traverse below the Hampden Basalt in Massachusetts. A well-defined superlattice peak at 31 Å in sample EB–6–H gives way to less defined superlattice reflections with distance from the contact. (CuKα radiation.)

volcaniclastics whose total thickness is about 4 km (Figure 1). The East Berlin Formation, which is sandwiched between the Holyoke and Hampden lava units, consists of a 145–450 m thick sequence of fluvial and lacustrine rocks. Based on work by Hubert et al. (1976) and Reed (1976), rock units in the East Berlin Formation 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 lake environments; or (2) a perennial lake system composed of gray siltstone-mudstone and black shale representing, respectively, the shallow and deeper portions of the lake.

SAMPLING AND EXPERIMENTAL TECHNIQUES

Red mudstone samples of the East Berlin Formation were collected in traverses away from the overlying Hampden Basalt at two well-exposed localities nearly 100 km apart (Figure 1). Samples were washed with distilled/demineralized water, coarse crushed, and washed again to remove artificially created clay-size material. The rock fragments were repeatedly sonified and then treated with a buffered (pH = 5.0) NaOAc-HOAc solution to dissolve carbonates (Jackson, 1976). The material was subsequently washed several times to remove all salts. The <1-μm fraction, and for selected samples the <0.5-μm fraction, was centrifugally separated and oriented on ceramic plate mounts according to the method of Kinter and Diamond (1956).

Diffractograms were obtained with a Diano (G.E.) XRD-5 diffractometer using Ni-filtered CuKα radiation. Patterns were obtained at scanning rates of 2° and 0.4° 2θ/min using a 1° divergence slit, a medium resolution soller slit, and a 0.1° receiving slit. The voltage and amperage were adjusted accordingly for maximum intensity. Cholesterol [d(010) = 33.6 Å and d(020) = 16.8 Å] was used to calibrate the instrument for accurate measurement of the d-values of superlattice reflections (Brindley and Wan, 1974; Kittrick, 1960).

An ETEC automated electron microprobe was utilized to obtain chemical analyses. A modified version of Fabbi's (1972) method was used to prepare samples. Each sample was ignited at 950°C for 1 hr, weighed, mixed with a lithium tetraborate flux, and fused in a graphite crucible at 950°C for 15 min. The resulting glass bead was cooled, reground in a tungsten carbide ball mill, and refluxed for 20 min to insure homogeneity of the bead. No measurable volatilization problems were encountered. The glass bead was carefully cracked and several chips mounted in epoxy, polished, and coated with carbon for wide-beam ($\sim$25 μm) microprobe analysis. Accuracy of the results was determined by analyzing a suite of U.S. Geological Survey standards (AGV–1, BCR–1, GSP–1, and G–2) prepared in the same manner. Matrix corrections were applied to raw data using a modified version of Bence and Albee's (1968) iterative correction routine. Ferrous iron (FeO) determinations were made using the dichromate titration method of Shapiro (1975).
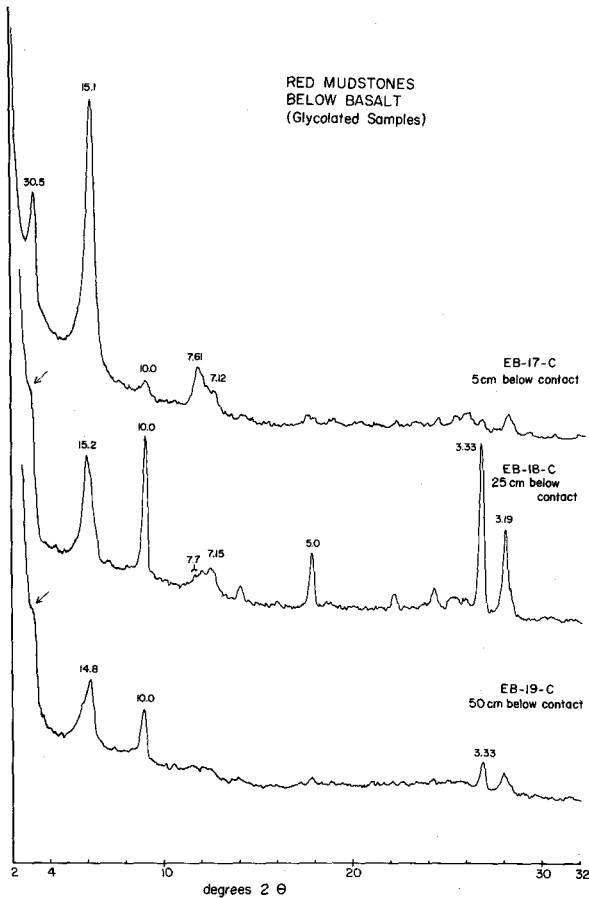
Figure 3. X-ray powder diffraction patterns of East Berlin red mudstone glycolated samples EB–17–C to EB–19–C taken in a traverse below the Hampden Basalt in Connecticut. Another sample from this traverse (diffraction pattern not shown) taken 4.5 m from the contact contains the clay-mineral assemblage illite + chlorite. (CuKα radiation.)

RESULTS

Chlorite/vermiculite in the red beds

Six red mudstone samples were collected in a traverse at locality 2 at points from 5 cm to 4.5 m below the Hampden Basalt. Figure 2 shows that only in sample EB–6–H, collected immediately beneath the contact, is a well-ordered, interstratified clay mineral predominant. The imperfect superlattice peak in the diffractogram of sample EB–5–H (40 cm below the contact) indicates the presence of a more poorly ordered interstratified clay. As shown by the relative intensity of the 10-Å peak, illite is a major constituent of the <1-μm fraction. Further from the overlying basalt (samples EB–4–H to EB–1–H), the samples contain illite and chlorite. Upon close inspection, however, the diffraction patterns of samples EB–4–H and EB–3–H show a slight offset in the rising background near 3° 2θ. This peak, along with weak, rational order (001) peaks, in-
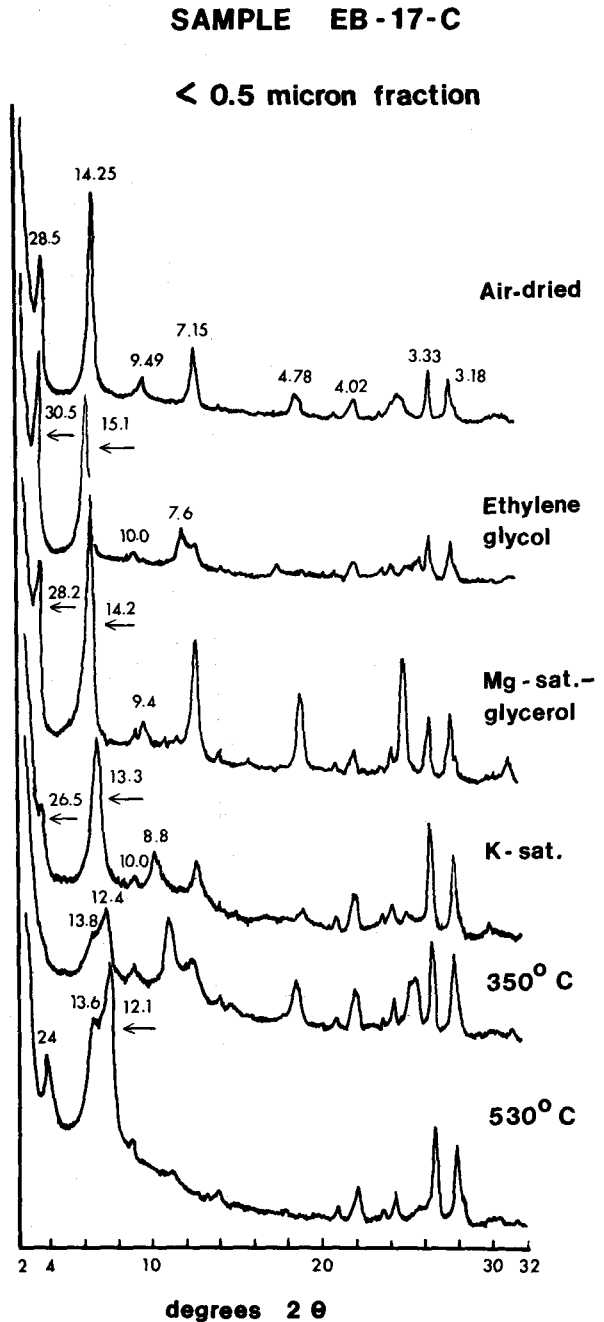

Figure 4. X-ray powder diffraction traces of the <0.5-μm fraction of sample EB–17–C taken 10 cm below the Hampden Basalt–red mudstone contact. Quartz and feldspar peaks result mainly from the ceramic tile in unavoidably thin mounts. (CuKα radiation.)

dicate the presence of some mixed-layering which could not be detected in the remaining samples of the traverse.

Four samples were collected at locality 1, 0.10, 0.25, 0.50, and 4.5 m below the basalt–mudstone contact. Diffraction patterns indicate a well-ordered interstrat-

Table 1.   Chemical analyses of the <0.5-μm fraction of sample EB–6–H.

Oxides	Wt. %	Wt. % after illite subtraction[1]
SiO_2	39.79	39.45
Al_2O_3	14.97	14.16
Fe_2O_3	20.26	21.97
FeO	9.12	9.85
MgO	12.30	13.15
MnO	0.04	—
CaO	0.67	0.73
Na_2O	0.64	0.68
K_2O	0.62	—
TOTAL	99.51	99.99

[1] Illite composition based on the chemical analysis of the <0.5-μm fraction of the Interlake illite of Hower and Mowatt (1966).

ified clay mineral dominating the <1-μm fraction of the baked mudstone adjacent to the contact (Figure 3). With increasing distance from the contact a more poorly ordered interstratified clay mineral plus relatively greater amounts of illite and chlorite comprise the bulk of the <1-μm fraction. Sample EB–2–C taken 4.5 m from the contact contains only the assemblage illite + chlorite. X-ray diffraction data suggest that small departures from perfect 1:1 ordering of the interstratified layers lead to the rapid deterioration of the superlattice reflection in air-dried mounts.
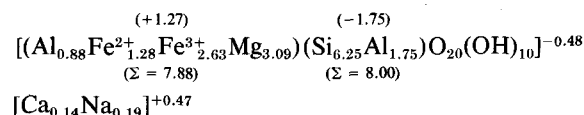
Specimens EB–6–H and EB–17–C collected from directly beneath the Hampden Basalt were further size fractionated. The <0.5-μm fraction of sample EB–6–H contained a relatively pure interstratified clay mineral, whereas that of sample EB–17–C contained minor amounts of quartz and plagioclase. Figure 4 is a series of diffractograms for sample EB–17–C. The diffractograms of sample EB–6–H (not shown) are similar. The pattern for the air-dried sample clearly shows the presence of a superlattice peak at ~28.5 Å with rational higher orders shown to d(00·10) at 2.84 Å. Upon glycolation, the sample expands giving a d(001) reflection at ~30.5 Å. These data indicate a well-ordered, 1:1 interstratification of a 14-Å phase and a 14.5-Å phase which swells to 16.5–17 Å with glycol. Failure of the swelling layers that expanded with glycol to expand upon Mg saturation and treatment with glycerol confirms characteristics more akin to vermiculite than to smectite (Walker, 1961). Potassium saturation in 1 N KCl for 24 hr apparently causes only a partial collapse of the vermiculite layers (1 water layer) to give 12.5- and 14-Å alternating units and a corresponding superlattice at ~26.5 Å. Expansion of the swelling layers with ethylene glycol and partial contraction with K saturation suggests a low layer charge on the vermiculite (Walker, 1961). Heating at 350° and 530°C for 1 hr leads to complete collapse of the vermiculite to about 10 Å.

A superlattice peak at 23.8 Å indicates the regular alternation of 13.8-Å chlorite and 10-Å vermiculite layers.

Chemistry

A chemical analysis was obtained for the relatively pure <0.5-μm fraction of sample EB–6–H (Table 1). 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. The assumption appears justified because: (1) the amount of K in the chemical analysis is low and quantitatively accounts for the small amount of illite recognized in the X-ray diffraction pattern; and (2) literature analyses of regularly interstratified chlorite/vermiculite, or chlorite/smectite minerals, contain minor amounts of K (usually <0.5 %), and even this is commonly attributed to contaminating illitic or micaceous material.

The composition of the illite in sample EB–6–H was assumed to be close to that of the <0.5-μm fraction of the "Interlake illite," a 1 Md dioctahedral illite characterized by Hower and Mowatt (1966). The structural formula for the mixed-layer clay mineral calculated on the basis of 20 oxygens + 10 (OH) or 50 equivalents is shown below. TiO_2 was considered a separate phase and therefore is not included in the structural formula.

$$[(\overset{(+1.27)}{Al_{0.88}Fe^{2+}_{1.28}Fe^{3+}_{2.63}Mg_{3.09}})\underset{(\Sigma = 8.00)}{(\overset{(-1.75)}{Si_{6.25}Al_{1.75}})}O_{20}(OH)_{10}]^{-0.48}$$
$$\underset{(\Sigma = 7.88)}{}$$

$$[Ca_{0.14}Na_{0.19}]^{+0.47}$$

The calculated total structural lattice charge is −0.48 equivalents/unit cell (½ unit cell chlorite + ½ unit cell vermiculite). Assuming that the charge deficiency arises principally from the swelling units, this value corresponds to a charge of 0.48 equivalents per 10 oxygen + 2 (OH) on the swelling layer. This value is outside of the range of 0.20–0.40 equivalents per 10 oxygens + 2 (OH) characteristic of low-charge smectites (Hower and Mowatt, 1966). Taken alone, the charge could be interpreted as arising from either a high-charge smectite or low-charge vermiculite. As already described, the X-ray diffraction data support the latter.

The octahedral population of 7.88 cations/unit cell is slightly less than the ideal of 8 for a 1:1 regularly interstratified, trioctahedral chlorite/dioctahedral vermiculite. The low value may result from concomitant vacancies in octahedral sites of the chlorite phase. Ross and Kodama (1976) showed that the oxidation of Fe^{2+} is important in the alteration of chlorite to regularly interstratified chlorite/vermiculite causing a loss of Fe and other cations from octahedral sites and thereby increasing octahedral vacancies in both the chlorite and the alteration product. Certainly the high Fe_2O_3 content

Table 2. Chemical trends in red mudstone below Hampden Basalt, Connecticut and Massachusetts localities.

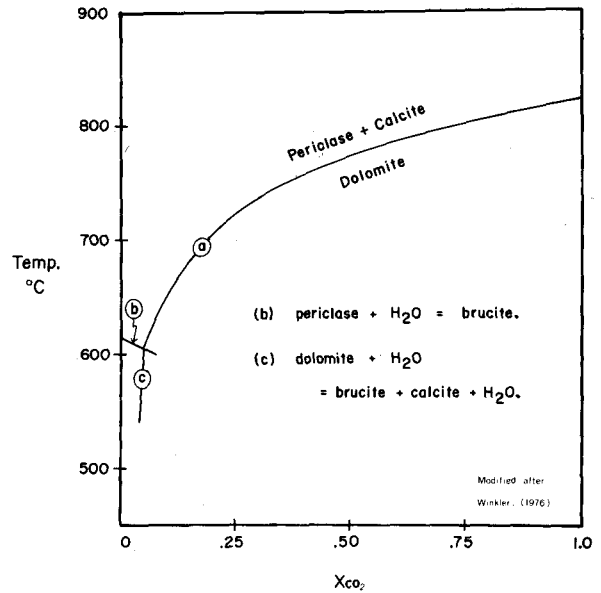| Sample (distance below basalt) | Locality 1—Connecticut | | | |
	Wt. % MgO whole rock	Wt. % CaO whole rock	Wt. % K₂O <1-μm fraction	K₂O/ Al₂O₃ whole rock
EB–17–C (5–10 cm)	3.16	11.24	0.63	0.050
EB–18–C (25 cm)	2.60	5.22	1.24	0.051
EB–19–C (50 cm)	1.57	2.33	1.87	0.079
EB–2–C (4.5 m)	3.05	5.11	3.69	0.210
Average for red beds of East Berlin Formation	2.30	3.53	3.04	
	Locality 2—Massachusetts			
EB–6–H (5 cm)	8.46	2.79	0.77	0.152
EB–5–H (40 cm)	1.51	1.79	2.93	0.191
EB–4–H (1.4 m)	2.61	2.38	2.63	0.201
EB–3–H (2.4 m)	0.35	8.32	3.49	0.150
EB–2–H (3.6 m)	0.97	1.54	4.37	0.184
EB–1–H (4.5 m)	2.30	0.93	3.14	0.188

Figure 5. Phase diagram showing the isobaric equilibrium curve for the thermal dissociation of dolomite at a total fluid pressure of 1 kbar (after Winkler, 1976). X_{CO_2} is the mole fraction of CO_2 in the fluid phase consisting of $CO_2 + H_2O$. Dedolomitization may occur at temperatures as low as 550°C.

of sample EB–6–H suggests Fe^{3+} in the octahedral sites of both the chlorite and vermiculite phases.

DISCUSSION

Origin of the interstratified chlorite-vermiculite

The restricted occurrence of the 1:1 regularly interstratified chlorite/vermiculite in the East Berlin floodplain red mudstone in a 2.5-m wide zone adjacent to the lowest Hampden lava flow precludes an origin strictly by inheritance, or low temperature aggradation or degradation. Rather, it is likely that the mineral formed as a result of the physicochemical conditions brought about by emplacement of the lava flow.

A crucial step in explaining the occurrence of the interstratified chlorite/vermiculite is determining the source of magnesium. Table 2 presents whole rock analyses of MgO and CaO for red mudstone samples in both traverses. Mg concentrations are greatest adjacent to the basalt. At locality 1, Mg decreases away from the contact over a total distance of 50 cm. At locality 2, after a sharp decrease in the Mg concentration 40 cm from the contact, the remaining samples show no discernible trend as a function of distance. The data suggest that in a 40–50-cm contact zone, Mg was derived from the overlying basalt, possibly from hydrothermal solutions. These solutions may have resulted from synchronal weathering of basalt fragments incorporated in the upper few centimeters of the floodplain sediments. The unusually high Fe and Mg concentrations of sample EB–6–H taken 5 cm below the basalt may be relicts of the *in situ* weathering of these basalt fragments by su-

perheated pore waters. The disturbed, convoluted texture of the sample and the presence of steam tubes and vesicles at the basalt-mudstone interface support this hypothesis.

As presented, the chemical analyses indicate no influx of Mg beyond 50 cm from the contact, results which are consistent with the idea that the generation of large quantities of hydrothermal fluids from a basalt flow is unlikely. However, interstratified chlorite/vermiculite occurs to a distance ~2.5 m from the basalt, albeit, with increasing distance from the contact the mineral is more poorly ordered and less abundant, requiring a second source of Mg.

In the zone containing the mixed-layer chlorite/vermiculite, dolomite and ferroan dolomite are conspicuously absent, whereas they are abundant as concretions, isolated rhombs, and pore-filling cement in the floodplain red mudstone. Also, calcite, in the absence of dolomite, is abundant in the 2–3 m directly below the Hampden Basalt filling veins, vesicles, and pores and as pseudomorphs after dolomite rhombs (see also, Chapman, 1965; Reed, 1976). Reed (1976) concluded that this calcite is a late stage precipitate from calcium-rich pore waters derived from the weathering of the highly fractured overlying basalt. As shown in Table 2, the CaO values at locality 1 indicate a downward flux of Ca^{2+} tapering off at a depth of ~50 cm. At locality 2, the CaO values suggest that no influx from the basalt occurred. Therefore, only a small part of the calcite in
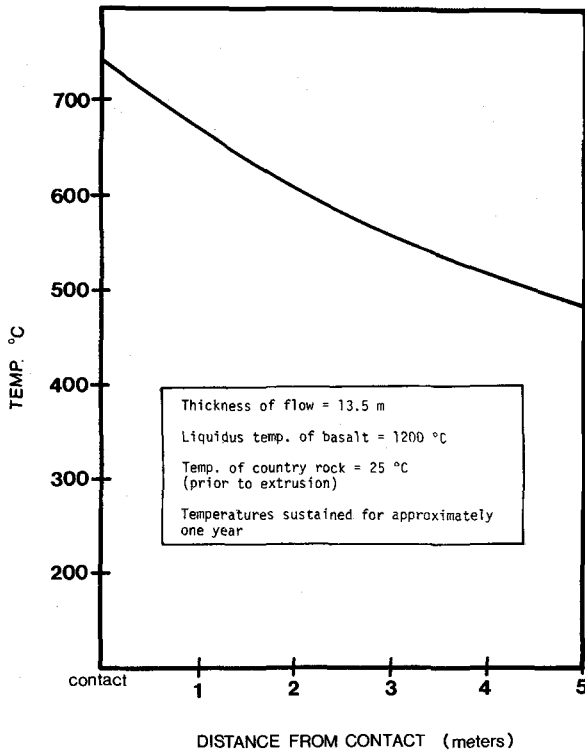
Figure 6.   Calculated curve for the thermal gradient in the red muds beneath the Hampden Basalt lava flow (after Jaeger, 1957, and Winkler, 1965). Temperatures were sustained in the red muds for approximately one year.
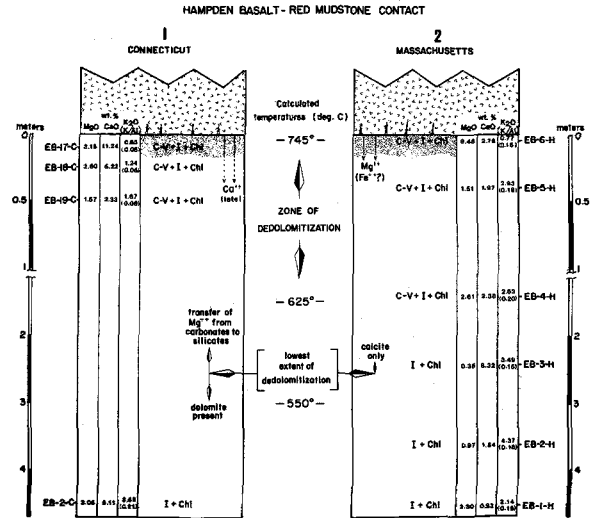

Figure 7.   Schematic summary diagram of the contact of the Hampden Basalt with mudstone depicting the clay mineralogy and chemistry of the rocks. MgO, CaO, and K/Al (K$_2$O/Al$_2$O$_3$) values are from whole rock analyses whereas K$_2$O values are for the <1-μm fraction of the samples. Dedolomitization supplied magnesium to the system for the formation of interstratified chlorite/vermiculite up to a distance 2.5 to 3.0 m below the basalt. The shaded region adjacent to the basalt shows the extent of the baked zone observable in the field.

the red mudstone below the contact can be due to late stage precipitation from basalt-derived Ca-rich waters. Instead, most of the calcite probably formed by the incongruent dissociation of dolomite (dedolomitization)—a phenomenon commonly associated with dolomite-bearing rocks subjected to magma-induced elevated temperatures (Faust, 1949). Dedolomitization also results in the evolution of Mg-rich (hydrothermal) solutions and it is suggested that these provided Mg for the formation of interstratified chlorite/vermiculite at distances >50 cm from the basalt–red mudstone contact.

Figure 5 is a phase diagram modified from Winkler (1976, after data by Metz) showing the isobaric equilibrium curve for the thermal dissociation of dolomite at a total fluid pressure (P$_f$) of 1 kbar. Implicit in the diagram and as stated by Winkler, the dissociation of dolomite is favored in shallow contact metamorphic aureoles where X$_{CO_2}$ and total P$_f$ values remain low. The thermal gradient in the red muds during and after emplacement of the lava flow can be estimated from work of Jaeger (1957) and Winkler (1965) on igneous intrusives. The basal Hampden Basalt flow is ~13.5 m thick (Chapman, 1965). If the extrusion temperature of the basalt was approximately 1200°C, the red muds in immediate contact with the basalt could have been heated

to 745°C. Temperatures 1.5 m from the basalt probably were close to 625°C; at 3 m, 550°C; and at 7 m, 400°C (Figure 6). These temperatures were probably sustained in the red muds for approximately one year.

From Figures 5 and 6, it is estimated that dedolomitization was possible to a depth of about 3 m below the basalt. If the subsequent compaction of the sediment during burial is considered, one observes—as expected from the calculations—the effects of dedolomitization in the red mudstone to a distance 2–3 m from the basalt. The temperature attained at a particular distance from the basalt controlled the nature of the stable Mg-bearing phase in the red muds (Figure 5). Brucite may have been incorporated *in toto* into interlayer positions or brucite and periclase may have dissolved and reprecipitated as a brucitic interlayer.

As shown in Figures 2, 3, and 7, the regularly interstratified chlorite/vermiculite adjacent to the Hampden Basalt is succeeded by a more poorly ordered chlorite/vermiculite within ~50 cm. The mineral is abundant and well-ordered (1) where the temperature was higher and (2) where greater amounts of Mg were available by weathering of basalt fragments and from Mg-rich hydrothermal solutions. Further from the contact, less Mg was released by the dissociation of dolomite, accounting for the lower abundance and poorly ordered nature of the mixed-layer clay. The availability of Mg at progressively greater distances from the basalt becomes a function of temperature rather than of dolomite abun-

dance. At ~3 m from the basalt, illite + chlorite is the stable clay-mineral assemblage as (1) the temperature was below 550°C and (2) dedolomitization was negligible.
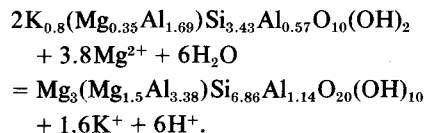
Although the source of Mg seems clear in light of the chemical evidence, the actual mechanism for the formation of the interstratified chlorite/vermiculite in the red muds remains problematic. It has been proposed that an interstratified chlorite/vermiculite can result from the removal of alternate brucitic sheets from a parent chlorite subjected to weathering (see, e.g., Bradley and Weaver, 1956; Johnson, 1964). Ross and Kodama (1976) suggested that oxidation of structural Fe^{2+} in the interlayer hydroxide sheets of the chlorite also plays a critical role in the formation of this mixed-layer mineral.

Although this mechanism appears valid for chlorites subjected to low-temperature weathering and oxidation, it is unlikely to have operated in the environment of the red muds below the basalt. One reason is that slightly reducing rather than oxidizing conditions are indicated by the extensive conversion of hematite to magnetite in the red mudstone. The loss of hematite can be observed as a color change from red to gray or grayish-purple in the contact rocks up to a distance of 25–50 cm below the basalt. Reducing conditions may also, in part, explain the high Fe content of the interstratified chlorite-vermiculite as solutions were enriched in Fe^{2+} with the reduction of hematite and the dissociation of ferroan dolomite. Kossovskaya (1972) found that corrensite-type clay minerals associated with basalts have higher iron contents relative to those in evaporitic deposits. It should be pointed out, however, that reducing conditions were restricted to the baked zone directly beneath the basalt. Further from the contact, oxidizing conditions prevailed as evidenced in thin section by hematite and iron oxide coatings on grains and the absence of magnetite. This is of particular importance in light of Velde's (1977a) experimental data which suggest that both R^{3+} ions (e.g., Fe^{3+}) and R^{2+} ions (e.g., Fe^{2+} and Mg^{2+}) must be available for corrensite formation.

Secondly, with the dissociation of dolomite, Mg, probably in the form of brucite, was made readily available for incorporation into layer silicate structures. With transfer of Mg from carbonates to silicates, it would again appear that an aggrading rather than degrading mechanism was operative.

There is some chemical as well as mineralogical evidence to suggest that the interstratified chlorite/vermiculite formed at the expense of illite. Although illite is the dominant clay mineral in the East Berlin red mudstone (April, 1978), only trace to minor amounts of illite occur in samples containing well-ordered 1:1 chlorite/vermiculite. Weaver and Beck (1977) suggested the following hypothetical reaction for converting illite to a corrensite-type clay mineral in a Mg-rich sedimentary environment (Fe not considered):

$$2K_{0.8}(Mg_{0.35}Al_{1.69})Si_{3.43}Al_{0.57}O_{10}(OH)_2$$
$$+ 3.8Mg^{2+} + 6H_2O$$
$$= Mg_3(Mg_{1.5}Al_{3.38})Si_{6.86}Al_{1.14}O_{20}(OH)_{10}$$
$$+ 1.6K^+ + 6H^+.$$

This reaction requires an external source of Mg and results in the destruction of illite and the release of K and H. Further evidence that the removal of interlayer K from mica structures produces mixed-layer interstratified clays was given by Sawhney (1977).

Table 2 shows that K concentrations are relatively low in the <1-μm fraction of samples EB–6–H and EB–17–C, both containing a well-ordered interstratified chlorite/vermiculite. Similarly, in the <1-μm fraction of red mudstone sampled at locality 1, K systematically decreases toward the basalt as the abundance and degree of ordering of the chlorite/vermiculite increase. The K concentrations of the <1-μm fraction are directly related to the proportion of illite in these samples. If the illite content remained relatively constant during deposition of the red muds the interstratified clay mineral may have formed by the aggradation of illite. Furthermore, whole rock K_2O values suggest that as K was released from illite, it was removed from the system and did not subsequently react to form another silicate mineral (e.g., K-feldspar).

Somewhat less likely, but a possibility nevertheless, is that the trend in K values reflects the preserved chemistry of a paleosol profile—one which developed on the floodplain prior to extrusion of the basalt flow. K concentrations in the <1-μm fraction of the red mudstone as well as K_2O/Al_2O_3 ratios in whole rock samples increase with distance from the basalt contact (Figure 7, Table 2). These trends suggest K^+ leaching in a soil horizon as illite (mica or biotite) alters to vermiculite (Al is assumed to be conserved in the weathering process). With this process operating in the floodplain sediments, vermiculite should then have been a major constituent of the clay fraction in near-surface soils. With extrusion of the basalt flow and the subsequent availability of Mg, aggradation of vermiculite, rather than illite, resulted in the formation of the interstratified chlorite/vermiculite. Unfortunately, there is no evidence to support the idea that vermiculite was once widespread in the floodplain sediments, for only trace to minor amounts now occur in the East Berlin red mudstone. It may be plausibly inferred, however, that burial metamorphic reactions involving uptake of K or Mg converted most of this vermiculite to illite or chlorite, respectively.

The presence of minor quantities of chlorite in most samples containing an interstratified chlorite/vermiculite may have resulted from the non-equivalence and

segregation of Mg^{2+} and Fe^{2+} (Velde, 1977b) as temperatures in the red muds dropped with cooling of the basalt. From experimental studies, Velde (1977a) suggested that chlorite in the assemblage illite + corrensite + dioctahedral mixed-layer clay + chlorite may form as Fe, in preference to Mg, enters its structure. This paragenesis could take place only if the initial bulk chemical composition of the system was Fe^{2+}-rich and if both Fe^{2+} and Mg^{2+} were abundant. As already discussed, these conditions were likely to have been present in the red muds below the basalt.

Finally, a number of red mudstone samples were collected from other formations in the Hartford Basin. In several samples from red mudstone lying directly above and in contact with the Holyoke Basalt, no interstratified clay minerals are present; the samples contain the typical red mudstone clay-mineral assemblage of illite + chlorite. One sample, collected 0.5 m below the contact between the Shuttle Meadow Formation and the overlying Holyoke Basalt (see stratigraphic column, Figure 1) contains a well-developed, regularly interstratified chlorite/vermiculite. Two lacustrine mudstone samples taken much further from the contact contain illite + chlorite + minor smectite. Interestingly, although different rock types comprise this traverse, chemical trends, especially those for MgO and K_2O, are similar to those described for the traverses in the East Berlin Formation.

SUMMARY

Regularly interstratified chlorite-vermiculite occurs in East Berlin floodplain red mudstone directly beneath the Hampden Basalt. Chemical and X-ray powder diffraction data indicate that the mineral formed in response to lava-induced elevated temperatures in the floodplain sediments and the availability of Mg during and shortly after emplacement of the lava flow. To a distance ~50 cm from the basalt-sediment contact, hydrothermal solutions emanating from the lava flow and fluids generated by superheated pore waters and the *in situ* weathering of basalt fragments provided a source of Mg. Further from the contact, to a distance 3 m from the basalt, Mg was derived primarily from the thermal dissociation of dolomite. Calcite present in this zone is a byproduct of dedolomitization. Based on phase equilibria, the calculated thermal gradient in the muds, and the inferred low mole fraction of CO_2 in the fluid phase, brucite appears to have been a stable Mg-bearing mineral in the contact zone during metamorphism. Uptake of brucitic sheets into interlayer positions by a pre-existing 2:1 layer silicate led to the formation of an interstratified chlorite/vermiculite. K_2O trends in both the whole rock and <1-μm fractions as well as the clay mineralogical data indicate that illite or vermiculite was the silicate precursor.

REFERENCES

April, R. H. (1978) Clay mineralogy and geochemistry of the Triassic-Jurassic sedimentary rocks of the Connecticut Valley: Ph.D. Dissertation, Univ. Massachusetts, Amherst, 206 pp.

Almon, W. R., Fullerton, L. B., and Davies, D. K. (1976) Pore space reduction in Cretaceous sandstones through chemical precipitation of clay minerals: *J. Sediment. Petrology* **46**, 89–96.

Bassett, W. A. (1959) The geology of vermiculite occurrences: *Clays & Clay Minerals* **10**, 61–69.

Bence, A. E. and Albee, A. L. (1968) Empirical correction factors for the electron microanalysis of silicates and oxides: *J. Geol.* **76**, 382–403.

Blatter, C. L., Roberson, H. E., and Thompson, G. R. (1973) Regularly interstratified chlorite–dioctahedral smectite in dike-intruded shales, Montana: *Clays & Clay Minerals* **21**, 207–212.

Bradley, W. F. and Weaver, C. E. (1956) A regularly interstratified chlorite-vermiculite clay mineral: *Amer. Mineral.* **41**, 497–504.

Brindley, G. W. and Wan, H. M. (1974) Use of long-spacing alcohols and alkanes for calibration of long spacings from layer silicates, particularly clay minerals: *Clays & Clay Minerals* **22**, 313–317.

Carstea, D. D., Harward, M. E., and Knox, E. G. (1970) Formation and stability of hydroxy-Mg interlayers in phyllosilicates: *Clays & Clay Minerals* **18**, 213–222.

Chapman, R. W. (1965) Stratigraphy and petrology of the Hampden basalt in Central Connecticut: State Geological and Natural History Survey of Connecticut, Report no. 3, 38 pp.

Dunoyer de Segonzac, G. (1970) The transformation of clay minerals during diagenesis and low-grade metamorphism—a review: *Sedimentology* **15**, 281–346.

Early, J. W., Brindley, G. W., McVeagh, W. J., and Vanden Heuvel, R. C. (1956) A regularly interstratified montmorillonite-chlorite: *Amer. Mineral.* **41**, 258–267.

Eberl, D. D. (1978) Reaction series for dioctahedral smectites: *Clays & Clay Minerals* **26**, 327–340.

Fabbi, B. P. (1972) A refined fusion X-ray fluorescence technique and determination of major and minor elements in silicate standards: *Amer. Mineral.* **57**, 237–245.

Faust, G. T. (1949) Dedolomitization, and its relation to a possible derivation of a magnesium-rich hydrothermal solution: *Amer. Mineral.* **34**, 789–823.

Harvey, R. D. and Beck, C. W. (1962) Hydrothermal regularly interstratified chlorite-vermiculite and tobermorite in alteration zones at Goldfield, Nevada: *Clays & Clay Minerals* **9**, 343–354.

Hower, J. and Mowatt, T. C. (1966) The mineralogy of illites

and mixed-layer illite/montmorillonites: *Amer. Mineral.* **51**, 825–854.

Hubert, J. G., Reed, A. A., and Carey, P. J. (1976) Paleo-geography of the East Berlin Formation, Newark Group, Connecticut Valley: *Amer. J. Sci.* **276**, 1183–1207.

Iiyama, J. T. and Roy, R. (1963) Controlled synthesis of heteropolytypic (mixed-layer) clay minerals: *Clays & Clay Minerals* **10**, 4–22.

Jackson, M. L. (1963) Interlayering of expansible layer silicates in soils by chemical weathering: *Clays & Clay Minerals* **11**, 29–46.

Jackson, M. L. (1976) *Soil Chemical Analysis—Advanced Course:* 2nd ed., Madison, University of Wisconsin, Dept. Soil Sci., 895 pp.

Jaeger, J. C. (1957) The temperature in the neighborhood of a cooling intrusive sheet: *Amer. J. Sci.* **255**, 306–318.

Johnson, L. J. (1964) Occurrence of regularly interstratified chlorite-vermiculite as a weathering product of chlorite in a soil: *Amer. Mineral.* **49**, 556–572.

Kinter, E. B. and Diamond, S. (1956) A new method for preparation and treatment of oriented-aggregate specimens of soil clays for X-ray diffraction analysis: *Soil. Sci.* **81**, 111–120.

Kittrick, J. A. (1960) Cholesterol as a standard in the X-ray diffraction of clay minerals: *Soil. Sci. Soc. Amer. Proc.* **24**, 17–20.

Kossovskaya, A. G. (1972) Genetic types and paragenetic associations of minerals of the corrensite group: International Clay Conf., preprints, v. **1**, 341–342.

Lippmann, F. (1954) Über einen Keuperton von Zaiserweiher bei Maulbronn: *Heidelb. Beitr. Mineral. Petrogr.* **4**, 130–134.

Lippmann, F. (1956) Clay minerals from the Röt Member of the Triassic near Göttingen, Germany: *J. Sediment. Petrology* **26**, 125–139.

Peterson, M. N. A. (1961) Expandable chloritic clay minerals from Upper Mississippian carbonate rocks of the Cumberland Plateau in Tennessee: *Amer. Mineral.* **46**, 1245–1269.

Post, J. L. and Janke, N. C. (1974) Properties of "swelling" chlorite in some Mesozoic formations of California: *Clays & Clay Minerals* **22**, 67–77.

Reed, A. A. (1976) Stratigraphy, depositional environments and sedimentary petrology of the Lower Jurassic East Berlin Formation, central Connecticut: Univ. Massachusetts, Amherst, M.S. Thesis, 175 pp.

Ross, G. J. (1975) Experimental alteration of chlorites into vermiculites by chemical oxidation: *Nature* **255**, 133–134.

Ross, G. J. and Kodama, H. (1976) Experimental alteration of a chlorite into a regularly interstratified chlorite-vermiculite by chemical oxidation: *Clays & Clay Minerals* **24**, 183–190.

Sarkisyan, S. G. and Kotelnikov, D. D. (1972) Genesis and thermodynamic stability of dioctahedral and trioctahedral mixed-layer minerals in sedimentary rocks: International Clay Conf., preprints, v. **1**, 343–352.

Sawhney, B. L. (1977) Interstratification in layer silicates: in *Minerals in Soil Environments,* J. B. Dixon and S. B. Weed, eds., Soil Sci. Soc. Amer., Madison, Wisconsin, 948 pp.

Shapiro, L. (1975) Rapid analysis of silicate, carbonate, and phosphate rocks—revised edition: *U.S. Geol. Surv. Bull.* **1401**, 76 pp.

Shimoda, S. (1969) New data for tosudite: *Clays & Clay Minerals* **17**, 179–183.

Shover, E. F. (1964) Clay-mineral–environment relationships in Cisco (Upper Pennsylvania) clays and shales, North-Central Texas: *Clays and Clay Minerals, Proc. 12th National Conf.,* 1963, 431–443.

Sudo, T., Takahashi, H., and Matsui, H. (1954) Long spacing of 30 Å from a fireclay: *Nature* **173**, 161.

Velde, B. (1972) Phase equilibria for dioctahedral expandable phases in sediments and sedimentary rocks: *Int. Clay Conf. Proc.,* Madrid, 235–248.

Velde, B. (1977a) A proposed phase diagram for illite, expanding chlorite, corrensite and illite-montmorillonite mixed-layered minerals: *Clays & Clay Minerals* **25**, 264–270.

Velde, B. (1977b) *Clays and Clay Minerals in Natural and Synthetic Systems:* Developments in Sedimentology, v. 21, Elsevier Scientific Publ. Co., Amsterdam, 218 pp.

Walker, G. F. (1961) Vermiculite minerals: in *The X-ray Identification and Crystal Structures of Clay Minerals,* G. Brown, ed., Mineralogical Society, London, 297–324.

Weaver, C. E. and Beck, K. C. (1977) *Miocene of the S.E. United States—A Model for Chemical Sedimentation in a Peri-Marine Environment:* Developments in Sedimentology, v. 22: Elsevier Scientific Publ. Co., Amsterdam, 234 pp.

Weaver, C. E. and Pollard, L. D. (1975) *The Chemistry of Clay Minerals:* Developments in Sedimentology, v. 15: Elsevier Scientific Publ. Co., Amsterdam, 213 pp.

Winkler, H. G. F. (1965) *Petrogenesis of Metamorphic Rocks:* Springer-Verlag, New York, 220 pp.

Winkler, H. G. F. (1976) *Petrogenesis of Metamorphic Rocks,* 4th ed.: Springer-Verlag, New York, 334 pp.

Wyart, J. and Sabatier, G. (1966) Synthèse hydrothermale de la corrensite: *Bull. Groupe Fr. Argiles* **18**, 33–40.

Резюме—Обычно переслаивающийся хлорит-вермикулит встречается в красных слоях формации Восточный Берлин (ранняя Юра) в Коннектикутской Долине. Этот минерал находится только в зоне контактного метаморфизма шириной 2,5 мили в отложениях, прилегающих к Базальту Хампден и подстилающих его. Химические анализы и данные порошкового метода рентгеноструктурного анализа показывают, что хлорит-вермикулит образовался в результате повышенных температур, вызванных лавой, и присутствия магния в грязях во время и сразу после соприкосновения с потоком лавы. Около контакта гидротермальные жидкости, образующиеся в лаве и в результате одновременного выветривания базальтовых обломков перегретыми поровыми водами, служили источником магния. Дальше от контакта магний высвобождался в основном в результате термальной диссоциации доломита. Концентрации K₂O и распределение глинистых минералов в красном аргиллите позволяют заключить, что переслаивающийся хлорит-вермикулит образовался из существующего уже иллита или вермикулита при высвобождении калия и включении бруситовых листов в межслойное пространство. [N. R.]

Resümee—Eine regelmäßige Chlorit-Vermiculit Wechsellagerung kommt in den Rotschichten der East Berlin Formation (frühjurassisches Alter) im Connecticut Valley vor. Das Mineral ist auf eine 2,5 m breite kontaktmetamorphe Schicht beschränkt, die unmittelbar unter dem Hampden Basalt liegt. Chemische und Röntgendiffraktometer-Daten deuten darauf hin, daß die Chlorit-Vermiculit Wechsellagerung gebildet wurde, weil bedingt durch die Lava die Temperaturen erhöht waren, und im Schlick Magnesium während und kurz nach der Platznahme des Lavastroms zur Verfügung stand. Nahe dem Kontakt wurde Magnesium von hydrothermalen Lösungen geliefert, die von der Lava selbst stammen und die bei der gleichzeitig stattfindenden Veränderung von Basaltbruchstücken durch überhitzte Porenwässer entstehen. Weiter vom Kontakt entfernt stammt das Magnesium vor allem von der thermischen Dissoziation von Dolomit. Die K_2O-Konzentrationen und die Tonmineralverteilung in den Rotschichten deuten darauf hin, daß die Chlorit-Vermiculit Wechsellagerung aus Illit oder Vermiculit gebildet wurden, indem Kalium herausgelöst wurde, und Brucitschichten in die Zwischenschichtpositionen eingebaut wurden. [U. W.]

Résumé—Une chlorite-vermiculite régulièrement interstratifiée est trouvée dans les lits rouges de la East Berlin Formation (d'âge bas-Jurassique) dans la vallée du Connecticut. Le minéral est restreint à une zone de 2,5 m de largeur de couches métamorphosées au contact adjacentes à et sous le Hampden Basalt. Les données chimiques et de diffraction aux rayons-X indiquent que la chlorite-vermiculite a été formée en réponse à des températures élevées dues à la lave et à la présence de magnésium dans les boves pendant et peu après l'emplacement du flot de lave. Près du lieu de contact, les fluides hydrothermaux originant de la lave et de l'altération synchronique de fragments de basalt par des eaux aux pores fortement échauffées ont fourni une souree de magnésium. Aux endroits plus éloignes du lieu de contact, le magnesium a été principalement dérivé de la dissociation thermale de dolomite. Les concentrations de K_2O et la distribution de minéraux argileux dans les rouches argileuses rouges suggèrent que la chlorite-vermiculite a été formèe á partir d'illite ou de vermiculite pré-existante alors que le potassium était relâché et des couches brucitiques étaient incorporées dans des positions interfeuillet. [D. J.]