INTERSTRATIFIED CLAY MINERALS IN CONTACT AUREOLES, WEST ROCK, CONNECTICUT

Key Words---Chlorite, Contact metamorphism, Hydrothermal, Interstratification, Smectite.

A recent paper by April (1980) described a regularly interstratified chlorite/vermiculite (C/V) in altered red beds of the East Berlin and Shuttle Meadow Formations (Early Jurassic) of the Newark Supergroup near Hartford, Connecticut, and Holyoke, Massachusetts. The mineral probably formed in response to elevated temperatures and the availability of magnesium and iron in the muds during and shortly after emplacement of overlying basalt flows. Magnesium was derived from both hydrothermal fluids and the thermal dissociation of dolomite. The interstratified C/V probably formed from pre-existing illite or vermiculite as potassium was released from the clay and brucitic sheets were formed in the interlayer positions.

This note reports on an interstratified chlorite/smectite (C/S) in contact aureoles produced by tholeiitic, basaltic intrusives at West Rock in New Haven, Connecticut. The basaltic feeder dikes and sills there are correlated with the Holyoke volcanic event (de Boer, 1968a) and intrude red beds of the New Haven Formation (Late Triassic). The geology of the Connecticut Valley and the stratigraphy of the Newark Supergroup were discussed by April (1980). A regularly interstratified C/S was previously reported by Blatter *et al.* (1973) from dike-intruded shales and siltstones of Early Cretaceous age in Montana.

The silt and sand fraction of the red mudstones and sandstones at West Rock are composed mainly of quartz and plagioclase feldspar, but they also contain K-feldspar and are cemented by hematite. Mixed-layer illite/smectite (US), discrete illite and smectite, and chlorite compose the clay mineral assemblage in the unaltered red beds (April, 1978). Important differences between the New Haven Formation red beds sampled in this study and those in the East Berlin Formation are: (1) samples from the New Haven Formation do not contain dolomite--a potential *in situ* source of magnesium; (2) a predominant clay mineral in unaltered New Haven Formation red beds is mixed-layer I/S whereas illite and chlorite are the chief clay minerals in the East Berlin red beds; (3) the New Haven Formation sediments were buried to a depth of 1-2 km during emplacement of the basaltic intrusives (de Boer, 1968b); and (4) calculations based on Jaeger's (1957) work show that ele~ vated temperatures in contact aureoles surrounding intrusive bodies 1-2 m thick were sustained for a few weeks rather than a year as estimated for the red beds underlying the Hampden basalt flow.

EXPERIMENTAL

Dikes and sills associated with the West Rock intrusive event are exposed in an abandoned trap rock quarry located 1 km east of West Rock Park and 0.8 km northwest of Southern Connecticut State College in New Haven, Connecticut. Red mudstones of the New Haven Formation were collected at this locality in three sampling traverses. Traverse 1 was taken in the contact aureole surrounding an irregularly shaped basalt dike about 2 m thick. Traverses 2 and 3 were taken above two different basalt sills about 1 m and 2 m thick, respectively. Samples were washed with distilled/demineralized water, crushed into small chips, and wet-sieved to remove artificially created clay-size material. The rock fragments were repeatedly sonified, and the $\langle 2-\mu m\rangle$ fraction was separated in a centrifuge and oriented on ceramic plate mounts (Kinter and Diamond, 1956). X-ray powder diffraction (XRD) diagrams were obtained using a Diano XRD-8535 diffractometer using Ni-filtered CuK α radiation. Six XRD patterns were obtained from the $\langle 2-\mu m \rangle$ fraction of each sample: (1) air-dried, (2) ethylene glycol-solvated, (3) Mg-saturated, glycerol-solvated, (4) K-saturated, (5) heated to 350° C, and (6) heated to 550° C.

Chemical analyses of whole-rock samples were obtained utilizing a Diano XRF-8560 vacuum path X-ray spectrometer. Samples were prepared using a modified version of Norrish and Hutton's (1969) method which involves fusion of rock powder with lithium tetraborate to produce a silicate glass disc. Matrix corrections were applied to raw data using an iterative computer correction routine kindly furnished by John Hower, Department of Geology, University of Illinois, Urbana, Illinois.

RESULTS AND DISCUSSION

Examination of the red-bed hornfels in thin section reveals the presence of recrystallized quartz, feldspar, and coarsegrained mica. The fissility of the rock has been destroyed because the phyllosilicates are now oriented at high angles to original bedding. Sparsely disseminated grains of garnet appear to have grown in the hornfels, and a few relict detrital grains of epidote and recrystallized tourmaline were also noted. The conversion of hematite to magnetite in the contact aureole turned the red beds dark grayish purple.

Figure 1 shows a representative series of XRD diagrams of the $\langle 2-\mu m \rangle$ fraction of mudstones in traverse 1 taken across a contact aureole adjacent to a dike that is about 2 m thick. XRD patterns for traverse 2 (not shown) taken above a 1-mthick sill at a nearby location are similar. The air-dried samples clearly show the presence of at least two clay minerals: (1) a mixed-layer US having low angle diffraction maxima that vary between 10.5 and 11.7 Å, and (2) a regularly interstratified C/S having a superlattice peak at \sim 29 Å and a series of rational higher order reflections to $d(006)$ at \sim 4.7 Å. The precise nature of the I/S was difficult to establish because some C/S peaks interfered with those of the I/S clay in XRD patterns of both ethylene glycol-solvated and Mg-saturated, glycerol-solvated samples. It is postulated, however, that the 10.5 to 11.7 \AA peaks represent a mixed-layer I/S having about 10% expand-

Table 1. Lattice spacings of $C/S(00\ell)$ reflections after chemical and thermal treatments.

Treatment	001(A)	002(A)	003(A)	004 (Å)	
Air-dried	29.5	14.7	9.75	7.25	
Ethylene glycol	32	15.8		7.9	
Mg-sat., glycerol	31			7.9	
K-sat.	28.5	14.2	9.2	7.15	
K-sat., heated at 110° C	28.5	14.25	9.1	7.15	
K-sat., heated at 350°C	ND ¹	$14 - 12.6$	8.2		
K-sat., heated at 550°C	ND	12.2	8.0		
Mg-sat., heated at 350°C	28.5	14.2		7.1	
Mg-sat., heated at 550° C	ND	12.3	7.9		

¹ ND, no "superlattice" diffraction detected.

Figure 2. X-ray powder diffraction patterns of the oriented $\langle -1-\mu m \rangle$ fraction of a mudstone sample taken in traverse 1 at the intrusive contact. (Scans made at $0.8^{\circ}2\theta/\text{min}$, CuK α radiation.)

Figure 1. X-ray powder diffraction patterns of the oriented $\langle 2-\mu m$, air-dried fraction of red mudstone samples taken in traverse 1 across a contact aureole. The clay-mineral assemblage consists of interstratified chlorite/smectite + mixedlayer illite/smectite + chlorite. The unaltered red mudstone sample contains mixed-layer illite/smectite $+$ illite $+$ chlorite (CuK α radiation).

able layers (Reynolds and Hower, 1970). Furthermore, the d-spacing shift from 10.5 to 11.7 Å away from the intrusive contact may reflect either a change in the hydration state of smectite layers in the air-dried samples or a compositional trend of decreasing proportions of illite in the US.

The relative peak intensities of the chloritic and mixed-layer I/S clays (Figure 1) show that the abundance of interstratified C/S in a single bed decreases with increasing distance from the basalt-mudstone contact. The broadening of the superlattice shoulder from \sim 29 Å obtained from the sample at the contact to \sim 25 Å for the sample taken 1 m from the contact suggests

Distance from contact	$Fe2O32$	MnO	TiO,	CaO	K,O	P_2O_5	SiO ₂	$A1_2O_3$	MgO	Na, O	Total
Traverse 1 contact	9.34	0.02	0.77	1.49	2.83	0.14	64.77	18.82	2.06	0.58	100.82
10 cm	9.74	0.02	0.87	1.33	3.34	0.29	61.23	20.32	2.50	0.91	100.55
50 cm	9.09	0.02	0.84	1.27	3.60	0.18	62.45	19.83	1.83	0.91	100.02
l m	5.78	0.01	0.64	1.05	3.36	0.15	68.19	17.55	1.33	1.90	99.96
Traverse 2 contact	9.56	0.02	0.88	1.30	3.89	0.27	61.66	20.41	1.93	0.83	100.75
50 cm	8.90	0.01	0.83	1.12	3.59	0.26	60.10	20.37	1.43	3.38	99.99
1 m	6.80	0.01	0.76	1.14	4.01	0.18	66.69	20.90	0.74	1.75	102.98
1.5 m	3.82	0.01	0.43	0.96	3.08	0.10	72.18	15.99	0.57	1.42	98.56
Traverse 3 contact	3.74	0.02	0.36	1.01	2.87	0.08	75.27	12.92	0.68	2.10	99.05
25 cm	4.83	0.01	0.50	0.70	3.67	0.09	69.71	17.91	0.96	1.59	99.97
50 cm	4.42	0.01	0.46	0.81	3.55	0.11	69.64	15.75	0.79	2.16	97.70
New Haven red beds											
(unaltered, avg. of 4 samples)	5.25	0.01	0.88	0.22	4.46		71.55	14.97	0.44	1.90	99.68

Table 2. Whole-rock chemical analyses of samples taken in traverses across contact aureoles.¹

¹ Chemical analyses on an ignited basis.

² Total Fe as $Fe₂O₃$.

that a regularly interstratified I/S (i.e., rectorite) becomes an important mixed-layer phase at some distance from the contact. Red mudstones of the New Haven Formation collected well outside any contact aureoles contain a clay-mineral assemblage of mixed-layer I/S (having 10-15% expandable layers) \pm illite \pm smectite \pm chlorite. No superlattice peaks were observed in the XRD patterns of these samples.

Table 1 lists the $d(00\ell)$ spacings of C/S clay from the intrusive contact after different chemical and thermal treatments of the $<$ 1- μ m separate. As shown in Figure 2, the superlattice peak at 29.5 Å in the air-dried sample shifts to \sim 32 Å after ethylene glycol solvation. It appears to shift to -31 Å after Mg-saturation and glycerol solvation, however, a concomitant change in the position of the d(002) reflection was not observed. Heating to 550°C for 1 hr apparently results in the complete collapse of the swelling layers to 10 Å. Although the superlattice peak is no longer present, a distinct d(002) diffraction reflection at \sim 12 Å indicates the regular alternation of 14-Å chlorite and $10-\text{\AA}$ collapsed swelling-layers. The data suggest that the mineral is a regularly interstratified chlorite/smectite. Failure of the swelling-layers to collapse on K-saturation and mild heat treatment suggests the possibility of hydroxy-interlayer contaminants. MacEwan and Wilson (1980) suggested that interlayers of polymerized hydroxy-hydrates of A1 or Mg ions can prop open adjacent silicate sheets and prevent complete contraction of the smectite structure. This property of the smectite layers in the C/S implies a gradation between smectite and swelling chlorite or chlorite. As noted in the diffraction traces in Figure 2, a considerable amount of discrete chlorite is present in this sample.

Table 2 lists the whole-rock chemical analyses of samples in three different traverses. The data for traverse 1 correspond to the diffraction traces in Figure 1. Concentrations of Fe, Ca, and Mg in traverses 1 and 2 decrease away from the basaltmudstone contact over a distance of approximately 1 m. These trends suggest that hydrothermal fluids were generated in the contact aureoles during emplacement of the basaltic intrusions. Because the basaltic magma likely contained less than 2% H20 by weight (Carmichael *et al.,* 1974, p. 323), the amount of water released from the cooling basalt may have been essentially negligible. It is suggested, therefore, that the bulk of any hydrothermal fluids originated from pore water that was entrained in the sedimentary deposits.

The chemical data for traverse 3 show no obvious trends, and it is inferred that local hydrological factors in the contact aureole or the physical characteristics of the rock or both, militated against the establishment of a chemical gradient. Samples from traverse 3 are comparatively coarser grained than those in traverses 1 and 2. It is possible that the rock in this locality was either less clayey and therefore less reactive or more porous and permeable so that water escaped from it easily during metamorphism. Moreover, XRD patterns of these samples show a clay-mineral assemblage composed predominantly of US and only minor amounts of C/S and chlorite. Indistinct to nonexistent C/S superlattice peaks suggest the presence of a more poorly ordered form of C/S having higher proportions of randomly interstratified layers.

CONCLUSIONS

The chemical and mineralogical data suggest that the interstratified C/S in the contact aureoles associated with the West Rock intrusive event formed at the expense of mixed-layer I/ S. Thermal and chemical gradients in the New Haven Formation red beds resulting from the cooling of the basalt and the generation of hydrothermal fluids rich in Mg and Fe caused the clay mineral transformation. These results together with April's *(1980)* findings *suggest* that the occurrence of interstratified chlorite/swelling-layer clays in contact aureoles of both extrusive and intrusive origin in the Newark Supergroup of the Connecticut Valley are the rule rather than the exception. The precursor of the interstratified clay minerals is a degraded 2:1 phyllosilicate such as illite, vermiculite, smectite, or mixed-layer I/S.

Although the nature of the mixed-layer US could not be determined with certainty, rectorite may also be a component of the contact aureoles at West Rock. The hydrothermal conversion of smectite to rectorite at temperatures and run times $(300^{\circ} - 400^{\circ}C; 7 - 30 \text{ days})$ similar to those estimated here for the contact aureoles, was demonstrated experimentally by Eberl (1978).

ACKNOWLEDGMENTS

We thank Michele Hluchy for her assistance in carrying out the XRF analyses. David Pevear and an anonymous reviewer read the manuscript and provided many valuable comments. This research was supported by the National Science Foundation, Grant SPI-7926989.

1 Present address: Department of Geology, University of Illinois, Urbana, Illinois 61801.

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, Massachusetts, 206 pp. (unpublished).
- April, R. H. (1980) Regularly interstratified chlorite/vermiculite in contact metamorphosed red beds, Newark Group, Connecticut Valley: *Clays & Clay Minerals* 28, 1-11.
- 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.
- Carmichael, I. S. E., Turner, F. J., and Verhoogen, J. (1974) *Igneous Petrology:* McGraw-Hill, New York, 739 pp.
- de Boer, J. (1968a) Paleomagnetic differentiation and correlation of the Late Triassic rocks in the central Appalachians (with special reference to the Connecticut Valley): *Geol. Soc. Amer. Bull,* 79, 609-626.
- de Boer, J. (1968b) Late Triassic volcanism in the Connecticut Valley and related structure: 1968 Guidebook for Fieldtrips in Connecticut, P. M. Orville, ed., State Geol. Nat. Hist. Surv. Conn., Guidebook 2, 290 pp.
- Eberl, D. D. (1978) The reaction of montmorillonite to mixedlayer clay: the effect of interlayer alkali and alkaline earth cations: *Geoehim. Cosmochim. Acta* 42, 1-7.
- Jaeger, J. C. (1957) The temperature in the neighborhood of a cooling intrusive sheet: *Amer. J. Sci.* 255, 306-318.
- 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.
- MacEwan, D. M. C. and Wilson, M. J. (1980) Interlayer and intercalation complexes of clay minerals: in *Crystal Structures of Clay Minerals and Their X-ray Identification, G. W.* Brindley and G. Brown, eds., Mineralogical Society, London, 197-248.
- Norrish, K. and Hutton, J. T. (1969) An accurate X-ray spectrographic method for the analysis of a wide range of geological samples: *Geochim. Cosmochim. Acta* 33, 431-453.
- Reynolds, R. C. and Hower, J. (1970) The nature of interlayering in mixed-layer illite-montmorillonites: *Clays & Clay Minerals* 18, 25-36.

(Received 23 June 1981; accepted 16 August 1981)