

CHEMICAL CHARACTERISTICS AND ORIGIN OF ORDOVICIAN K-BENTONITES ALONG THE CINCINNATI ARCH

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Abstract—K-bentonites of the Middle Ordovician High Bridge Group along the Cincinnati arch are characterized by interstratified illite/smectite (I/S) clays with rectorite-type ordering. Approximately 20% of the layers are expandable. They are structurally similar to I/S formed at temperatures exceeding 100°C during burial diagenesis, however stratigraphic evidence and a color alteration index of <1.5 for conodonts in associated carbonates reveals they have never been deeply buried or subjected to temperatures greater than 80°C.

Whole-rock samples of K-bentonites contain ~8% K₂O and ~4% MgO, whereas the <0.1- μ m size fraction contains 6–7% K₂O and 5% MgO. By comparison with a hypothetical parent ash, these values represent a net gain of K and Mg and a net loss of Si, Fe, Ca, and Na during post-depositional alteration. K-fixation is accounted for by a layer charge imbalance arising primarily out of octahedral substitution of Mg⁺² for Al⁺³, indicating that the interstratification evolved from a montmorillonite precursor. The chemical characteristics of I/S layers in K-bentonites developed early during the alteration of volcanic ash to montmorillonite. Relatively high contents of K and Mg probably reflect both seawater and parent material composition at the time of formation. The composition and ordered stacking in K-bentonites was determined by the composition of the original smectite rather than by the pressure-temperature conditions of burial diagenesis.

Key Words—Bentonite, Chemical composition, Illite/smectite, Interstratification, K-bentonite, Rectorite.

INTRODUCTION

K-bentonite beds of Middle Ordovician age have been reported from localities throughout eastern North America as well as from parts of Scandinavia and western Europe (Kay, 1935; Weaver, 1953; Byström, 1956; Bergstrom and Nilsson, 1974; Brun and Chagnon, 1979). Their clay mineralogy is typically dominated by a regularly interstratified illite/smectite (I/S) in which the swelling component accounts for 20–40% of the total structure. Accessory clays are commonly either kaolinite or chlorite.

Recent studies of clay mineral alteration during burial diagenesis concluded that ordered I/S phases develop in response to increasing temperature and whole-rock chemical disequilibrium (Perry and Hower, 1970; Weaver and Beck, 1971; Hower *et al.*, 1976; Boles and Franks, 1979). This development is seen as one in a series of transformations between a smectite starting material and pure illite, although the presence of 100% non-expanding illite as verification of the completed reaction is not always detectable. I/S in thick sedimentary sequences develops a rectorite-type (or allevar-dite-type) interstratification from 100° to 175°C and can be represented by the reaction: Smectite + K⁺ + Al³⁺ → Illite + Si⁴⁺ (Hower *et al.*, 1976). The required Al and K apparently originate from the destruction of

detrital K-feldspars and, to a lesser extent, micas. The Al substitutes for tetrahedral Si in smectite and thereby generates an overall increase in layer charge, which is compensated for by K-fixation (Hower *et al.*, 1976).

The application of this model to the interpretation of clay mineral assemblages in both young and old sediments is made more attractive by the agreement between field evidence (Dunoyer de Segonzac, 1959; Srodoń, 1978; Eslinger *et al.*, 1979) and experimental studies (Velde, 1973; Eberl and Hower, 1976, 1977; Eberl, 1978) which supply answers for some of the important thermodynamic and kinetic questions involved. If mixed-layer phases are thermodynamically stable, their stability fields can be illustrated by activity-temperature diagrams. However, if the mixed-layer phases are metastable their paragenesis can be regarded as more a function of time and temperature (Eberl, 1978).

I/S clays in K-bentonites clearly resemble the ordered I/S stage of burial diagenesis. However, these clays are known to occur in geologic terrains which give no evidence of ever having been subjected to the burial conditions thought necessary to form them. For example, the Middle Ordovician platform carbonates of the Cincinnati arch in the eastern mid-continent of North America are shallow water, cratonic sediments deposited on the relatively stable margin of the Appalachian basin. Several major unconformities occur in the section as a result of the periodic removal of enormous quantities of surficial cover during and after the Paleozoic, thus preventing the accumulation of a thick

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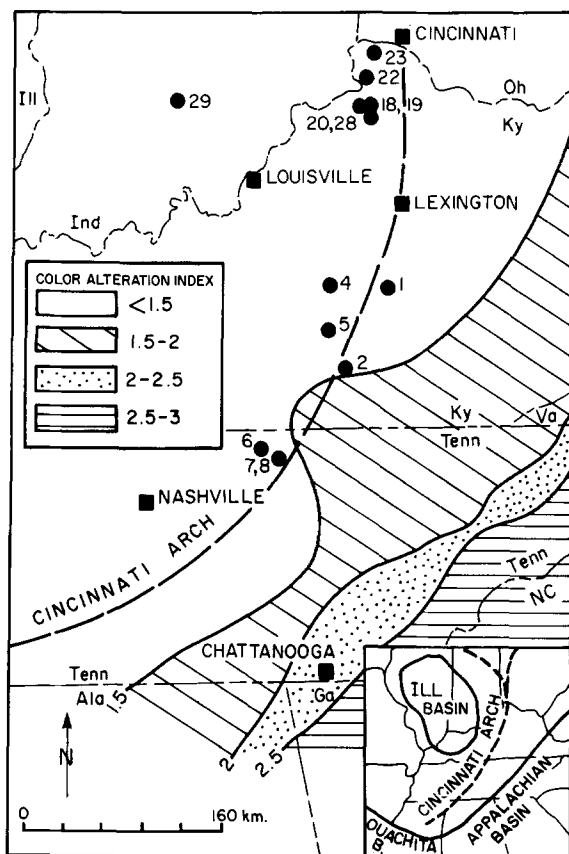


Figure 1. Sample location map showing positions of cores sampled (circles) and major cities (squares). Regional structural features are shown on the inset map. Isograds representing variation in the color alteration index (CAI) of conodonts in Middle Ordovician limestones are taken from Harris (1979). Temperature ranges for equivalent CAI categories are: 1 = <50–80°C; 1.5 = 50–90°C; 2 = 60–140°C; 3 = 110–200°C.

sedimentary sequence. Further, the color-alteration indices of conodonts in Ordovician carbonate rocks along the arch indicate maximum burial temperatures have not exceeded 80°C.

The non-clay minerals in K-bentonites include abundant and well-preserved biotite and K-feldspar (Günel, 1979). These minerals do not appear to have served as the primary source of K for formation of the I/S phase since they do not disappear systematically with the development of mixed layering. Thus, it is possible that if the I/S evolved from a smectite parent by means of increased layer charge and K-fixation, (1) the whole rock chemistry of the original ash must have been supplemented by an external source of potassium sufficient to form I/S with approximately 70% illite, and (2) the tetrahedral substitution of Al^{3+} for Si^{4+} considered necessary to create the layer charge must have occurred at temperatures below the ~100°C threshold value inferred for diagenetic formation of ordered I/S (Hower *et al.*, 1976).

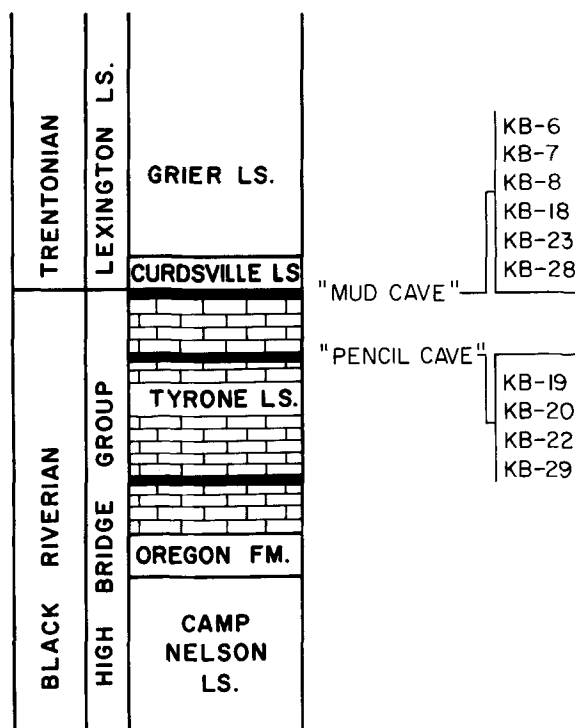


Figure 2. Stratigraphic column of a portion of the Middle Ordovician High Bridge Group in central Kentucky showing K-bentonite horizons (not to scale).

The purpose of the present investigation was to reconcile the chemical and mineralogical composition of some K-bentonites with regional geologic, mineralogical, and paleontologic evidence regarding their burial history. To this end, a group of samples was chosen from cores in the Middle Ordovician Tyrone Limestone and equivalents along the crest of the Cincinnati arch from southern Indiana across central Kentucky to north-central Tennessee (Figure 1).

STRATIGRAPHY

The Tyrone Limestone in central Kentucky is part of the High Bridge Group (Figure 2) and is a mixture of supratidal, intertidal, and subtidal carbonate deposits (Cressman and Noger, 1976). Dolomite in the High Bridge Group occurs commonly in the supratidal facies as finely crystalline laminae alternating with micrite and as burrow-fillings in the subtidal facies. Cressman and Noger (1976) concluded that the laminar form resulted from dolomitization in tidal flats that were subjected to extended subaerial exposure by an evaporative pumping mechanism. Comparison with modern and ancient carbonate sediments indicates a high-Mg, but not evaporitic environment during High Bridge time. Dever (1974) described High Bridge carbonates with as much as 15% $MgCO_3$ in a northern Kentucky core.

Three prominent K-bentonites occur within the Tyrone Limestone of central Kentucky (Figure 2). The

“Mud Cave” bentonite of local drillers is found at or near the contact between the Tyrone Limestone and the overlying Curdsville Limestone Member of the Lexington Limestone. In parts of the region it has been removed along the pre-Lexington disconformity (Cressman, 1973) and hence has limited usefulness in long-range correlation. The equivalent bed in the Carvers Limestone of central Tennessee is thought to be the T-4 bed (Wilson, 1949). The “Pencil Cave” bentonite of local usage occurs 4 to 6 m below the top of the Tyrone Limestone and varies in thickness from a few centimeters to 1.5 m. Some reworking of the original ash by waves and bottom currents undoubtedly occurred, however the influx of terrestrial clastics was so minimal as to preclude contamination of the K-bentonite by anything other than carbonate mud. The “Pencil Cave” is the most persistent K-bentonite marker in the area. Its probable equivalent in central Tennessee is the T-3 bed (Wilson, 1949). A third, widespread K-bentonite occurs about 24 m below the top of the Tyrone Limestone and is generally less than 3 cm thick.

ANALYTICAL METHODS

Sample preparation

Samples weighing about 10 g were crushed to pea-size fragments and boiled for 5 min in a 2% solution of Na_2CO_3 (Jackson, 1975). This treatment effectively removed all amorphous alumina and silica and replaced easily exchanged cations with sodium. Most samples dispersed in 1 to 2 min, and all dispersed completely after 5 min. Thereafter, several cycles of washing with distilled water and centrifugation followed by resuspension with a high-speed stirrer eliminated all tendency toward flocculation. The suspensions were then separated by centrifugation into $<2\text{-}\mu\text{m}$ and $<0.1\text{-}\mu\text{m}$ fractions.

X-ray powder diffraction

Oriented mounts of the $<2\text{-}\mu\text{m}$ and the $<0.1\text{-}\mu\text{m}$ fractions were prepared on glass petrographic “well” slides² by the smear method. The slides have an etched depression $24 \times 40 \times 0.03$ mm and lend themselves easily to the rapid preparation of clay mounts having identical thicknesses. After drying at room temperature, the slides were placed in an ethylene glycol saturated atmosphere at 60°C for 4 hr to insure maximum solvation. Samples were scanned from 4° to $55^\circ 2\theta$ at rates of both $2^\circ 2\theta/\text{min}$ and $0.22^\circ 2\theta/\text{min}$ using filtered $\text{CuK}\alpha$ radiation and a General Electric XRD-6 diffractometer operated at 40 kV and 16 mA. The proportional amounts of smectite and illite were determined from the $0.2^\circ 2\theta/\text{min}$ tracings of the $<0.1\text{-}\mu\text{m}$ samples using the curves of Reynolds and Hower (1970).

² Sold by Buehler Ltd. under cat. #40-8001.

Table 1. Chemical analyses of the $<2\text{-}\mu\text{m}$ fraction of K-bentonites.

	KB-6B	KB-7B	KB-7D	KB-8A	KB-8C	KB-18A	KB-18B	KB-19D	KB-20A	KB-22A	KB-23C	KB-28A	KB-28D	KB-28G	KB-28H	KB-29
SiO_2	56.50	57.30	57.10	58.50	53.50	52.30	52.30	52.40	55.10	51.80	53.70	53.70	51.90	56.60	55.60	50.90
Al_2O_3	19.11	19.25	19.64	18.24	19.94	19.58	21.15	20.69	20.19	20.64	21.26	20.95	20.74	20.55	21.35	24.47
Fe_2O_3^1	2.00	1.86	2.00	1.78	1.60	1.49	1.13	1.43	1.65	1.22	1.29	1.26	1.26	1.19	1.07	0.62
MgO	4.35	4.54	4.62	3.74	4.63	4.53	4.34	5.05	4.82	4.58	5.35	4.37	4.49	4.28	4.62	3.65
K_2O	6.93	6.82	7.11	6.20	6.86	7.75	7.00	7.15	7.06	6.75	6.66	6.74	6.50	6.43	6.59	7.26
TiO_2	0.18	0.20	0.16	0.30	0.21	0.28	0.09	0.24	0.29	0.17	0.09	0.15	0.15	0.11	0.18	0.29
CaO	0.10	0.80	0.60	0.60	0.20	0.40	0.10	0.10	0.00	0.50	0.10	0.00	0.50	0.60	0.40	0.50
Na_2O	1.16	1.32	1.28	1.32	1.29	0.92	1.18	1.06	0.72	1.18	1.11	1.44	1.49	1.08	1.27	1.07
MnO	0.06	0.02	0.02	0.01	0.03	0.03	0.01	0.00	0.01	0.07	0.02	0.01	0.01	0.04	0.02	0.02
LOI^2	10.98	11.19	11.01	11.01	10.72	10.60	10.61	11.03	11.08	10.55	11.00	10.76	10.57	11.04	11.06	10.78
Total	101.37	103.30	103.77	101.70	98.98	97.86	98.00	101.86	102.28	97.41	101.57	99.38	97.64	101.92	102.16	99.56

¹ Total Fe expressed as Fe_2O_3 .

² Loss on ignition (see text).

Table 2. Chemical analyses of the >0.1- μm fraction of K-bentonites.

	KB-28A	KB-28B	KB-28C	KB-28D	KB-28E	KB-28F	KB-28G	KB-28H	KB-20B	KB-6C	KB-7C	KB-22A	KB-29
SiO ₂	57.1	57.1	57.1	57.1	57.7	57.1	57.9	55.5	54.6	56.4	56.1	54.6	52.8
Al ₂ O ₃	20.4	20.7	20.4	20.7	20.4	20.7	20.1	22.3	20.8	22.1	21.9	22.7	25.8
Fe ₂ O ₃ ¹	3.1	1.0	1.3	2.0	1.1	2.0	1.1	0.9	1.5	1.7	1.9	0.9	0.5
MgO	4.9	4.8	4.9	5.4	5.1	4.8	4.9	4.7	5.6	5.0	5.5	5.1	4.0
K ₂ O	6.9	7.2	7.1	6.9	7.1	7.0	6.9	6.8	7.1	7.3	7.6	7.2	7.4
TiO ₂	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.14	0.10	0.10	0.13	0.14
CaO	0.08	0.5	0.3	1.0	0.3	0.3	0.2	0.3	0.4	0.4	0.3	0.4	0.4
Na ₂ O	0.7	1.2	1.7	0.9	1.4	1.4	1.5	1.6	1.7	1.7	1.6	1.9	1.7
MnO	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.02	0.01	0.02	0.02	0.02
LOI ²	6.89	6.78	6.80	6.89	6.82	6.84	6.79	6.75	6.74	6.93	6.96	6.82	6.80
Total	100.89	99.25	99.60	100.87	99.92	100.11	99.39	98.85	98.64	101.53	101.85	99.82	99.50

¹ Total Fe expressed as Fe₂O₃.

² Loss on ignition (see text).

Chemical analyses

Major elements were determined for eight bulk, sixteen <2- μm , and thirteen <0.1- μm samples using atomic absorption (AA) and wavelength-dispersive X-ray fluorescence (XRF) spectrophotometry. AA samples were prepared according to the method of Medlin *et al.* (1969) and analyzed on a Perkin-Elmer model 403 flame spectrophotometer. Total oxides for the <0.1- μm samples were determined by this method as well as SiO₂, MgO, CaO, Na₂O, and MnO for the bulk and the <2- μm samples. Total iron as Fe₂O₃, Al₂O₃, K₂O, and TiO₂ in the bulk and the <2- μm fractions were determined by XRF using fused borate glass pellets prepared according to the method of Elsheimer and Fabbi (1977).

The <2- μm samples were ignited at 1000°C for 1 hr prior to fusion and casting for XRF analysis, thus the weight percent reported for loss on ignition (LOI) in Table 1 includes both H₂O+ and H₂O-. The <0.1- μm samples were heated at 120°C to remove H₂O- prior

to digestion for AA analysis. The weight percent reported for LOI in Table 2 refers to H₂O+ only. All data plots in this discussion include both groups of samples unless otherwise stated.

Mean structural formulae were calculated on the basis of the theoretical total half-cell ionic charge of -22 (Foster, 1960) corresponding to a O₁₀(OH)₂ formula unit. The difficulties inherent in determining meaningful structural formulae for I/S lie in the necessity of relying on assumptions about partitioning of structural cations and charges between swelling and non-swelling layers, as was discussed by Weaver and Pollard (1973) and Hower and Mowatt (1966). Computing idealized formulae, however, permits comparison on an equal basis with data from other studies. This is particularly useful and perhaps the only way that one can evaluate I/S compositions against the swelling and non-swelling end members which represent the starting materials and their metamorphic products.

It was assumed that the Na₂CO₃ treatment removed

Table 3. Half-cell structural formulae of <0.1- μm K-bentonites.

	KB-28A	KB-28C	KB-28E	KB-28G	KB-28H	KB-6C	KB-22A	KB-29	KB-7C	KB-20B	MEAN	
IV	Si	3.80	3.84	3.84	3.88	3.75	3.74	3.69	3.57	3.71	3.74	3.76
	Al	0.20	0.16	0.15	0.12	0.25	0.26	0.31	0.43	0.29	0.26	0.24
	Charge	-0.20	-0.16	-0.15	-0.12	-0.25	-0.26	-0.31	-0.43	-0.29	-0.26	-0.24
VI	Al	1.40	1.46	1.45	1.46	1.53	1.46	1.50	1.63	1.42	1.141	1.47
	Fe ¹	0.16	0.07	0.06	0.06	0.05	0.09	0.05	0.03	0.09	0.08	0.07
	Mg	0.49	0.49	0.51	0.49	0.47	0.49	0.51	0.40	0.54	0.57	0.50
	Ti	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Charge	-0.38	-0.45	-0.47	-0.47	-0.34	-0.35	-0.31	-0.21	-0.36	-0.36	-0.37	
Total layer charge	-0.58	-0.61	-0.61	-0.59	-0.59	-0.62	-0.62	-0.64	-0.65	-0.62	-0.61	
K	0.58	0.61	0.61	0.59	0.59	0.62	0.62	0.64	0.64	0.62	0.61	
Interlayer charge	+0.58	+0.61	+0.61	+0.59	+0.59	+0.62	+0.62	+0.64	+0.64	+0.62	+0.61	

¹ Total Fe expressed as Fe₂O₃.

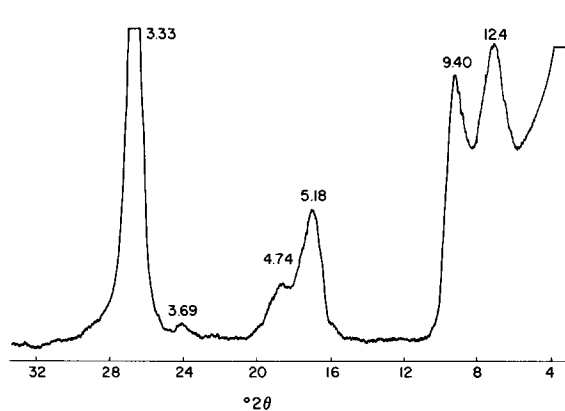


Figure 3. XRD tracing of the $<0.1\text{-}\mu\text{m}$ fraction of KB-7 after saturation with ethylene glycol. Peak positions indicate rectorite-type illite/smectite with 18% expandable layers.

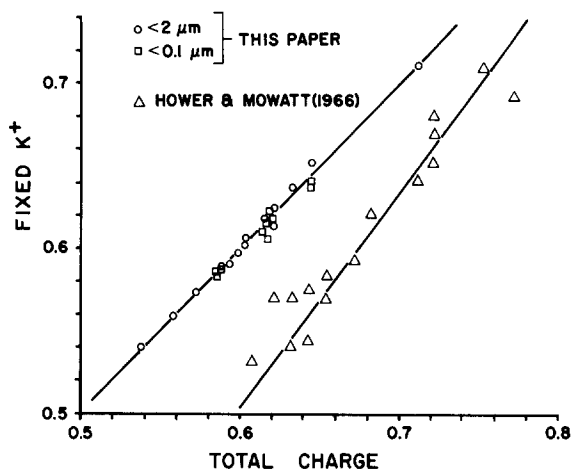


Figure 4. Relationship between fixed K and total charge in K-bentonites.

all exchangeable K and Mg so that the analyzed values represent only non-exchangeable K and Mg in interlayer and octahedral sites, respectively. Na and Ca values were ignored in recasting the data into structural formulae because: (1) the amounts are small and most likely do not represent structural site occupancy, and (2) calcium, particularly, is a likely contaminant because these beds occur in a massive carbonate section. Moreover, Na values may be misleading as a result of the Na_2CO_3 treatment. K is considered to be the only significant interlayer cation, a conclusion borne out by the close agreement between the calculated interlayer and the total layer charges.

XRF precision expressed as the coefficient of variation ranges between 0.01 and 0.03; AA precision varies from less than 0.01 to 0.08. The highest coefficient of variation, 0.08, is for Na, which is notoriously difficult to analyze by AA. All other AA coefficients lie below 0.05. Analytical data and structural formulae are reported in Tables 1–3.

RESULTS AND DISCUSSION

Clay mineralogy

XRD analyses of the $<0.1\text{-}\mu\text{m}$ fraction indicate a rectorite-type ordering of I/S in which the smectite component varies from 18% to 27%. I/S proportions were determined using the $(005)_{27\text{\AA}}/(003)_{17\text{\AA}}$ reflection that occurs between 15.6° and $17.7^\circ 2\theta$ for IM ordering and the twin reflections between 43° and $48^\circ 2\theta$ (Reynolds and Hower, 1970). Figure 3 is a diffraction tracing of sample KB-7 showing typical mixed-layer characteristics.

Chlorite was detected in only one sample of the $<2\text{-}\mu\text{m}$ fraction but not in the corresponding $<0.1\text{-}\mu\text{m}$ fraction. The chlorite may have formed by the alteration of biotite rather than by neof ormation of an Fe-Mg-rich clay.

Chemical analyses

Oxide analyses for the $<2\text{-}\mu\text{m}$ fraction are reported in Table 1 and for the $<0.1\text{-}\mu\text{m}$ fraction in Table 2. Differences between the two groups are generally slight and may reflect the presence of non-clay minerals in the coarser fraction.

Half-cell structural formulae for the $<0.1\text{-}\mu\text{m}$ specimens are listed in Table 3. K is considered to be the only fixed interlayer cation. As might be expected, K increases linearly with total charge (Figure 4) which varies between 0.54 and 0.71 and has a mean value of 0.61. The K curve coincides with the theoretical curve of Hower and Mowatt (1966) calculated for K_n in illites and illite/montmorillonite if all the interlayer charge were satisfied by fixed K. Their data for the same range of lattice charges are also plotted in Figure 4 for comparison. The difference in distribution curves is accounted for by exchangeable ions in mixed-layer illite/montmorillonite (Hower and Mowatt, 1966) which balance the excess charge not satisfied by K. K-bentonites behave as though the total lattice charge is satisfied entirely by K. Accordingly, the illitic component has K as the only interlayer ion, and the amount present is sufficient to balance the total charge deficiency of the I/S structure. Calculated total layer and interlayer charges (Table 3) agree extremely well with one another when only K is included and less well when the small amounts of Na and Ca are included. Presumably, further collapse of the smectite component by K-fixation would require additional tetrahedral and/or octahedral substitution to provide the necessary charge imbalance.

Data from other workers indicate that I/S structures tend to have a total charge greater than that satisfied by fixed cations (Hower and Mowatt, 1966; Schultz, 1978). The excess charge increment varies directly with the proportion of the two components and indicates a ca-

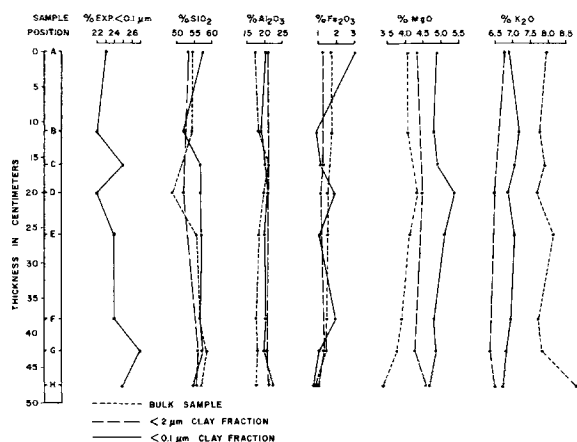


Figure 5. Vertical variation of the percentage of expandable layers in the $<0.1\text{-}\mu\text{m}$ fraction, and the percentage of some major element oxides within a 50 cm-thick K-bentonite (KB-28). The distribution of subsamples A-H is shown on the left.

pability in some I/S clays to evolve toward the illite end member of the series given the proper physico-chemical environment. Schultz (1978) estimated that 35% of the smectite component of I/S clays in the Pierre Shale are beidellitic. Although I/S forms under a variety of conditions in various geological environments, its development during burial diagenesis seems to require a smectite precursor that is beidellitic in its charge distribution and chemistry. The K-bentonites of the present study have retained their montmorillonitic character, and K-fixation appears to have been controlled largely by a charge density resulting from substitution of octahedral Mg for Al.

Detailed analyses of bulk, $<2\text{-}\mu\text{m}$, and $<0.1\text{-}\mu\text{m}$ fractions of a 50-cm thick bentonite (KB-28) are summarized in Figure 5. K_2O values of the $<0.1\text{-}\mu\text{m}$ fraction are slightly but consistently higher than those of the $<2\text{-}\mu\text{m}$ fraction and lower than the bulk analysis values. The bulk samples are rich in K-feldspar and biotite (Günel, 1979) which probably account for the large K_2O values in Figure 5. The difference between the K content of the $<2\text{-}\mu\text{m}$ fraction (mean = 6.9% K_2O) and the $<0.1\text{-}\mu\text{m}$ fraction (mean = 7.1% K_2O) may not be due to contributions from accessory minerals. Because there is no corresponding difference in Mg or Al, the difference appears to be real, and reflects a higher proportion of illite layers in the finer fraction.

Velde and Brusewitz (1978) suggested that K became mobilized during the alteration of Ordovician volcanic ash to K-bentonite in Sweden, and that K diffused toward the margins of thick beds. In contrast, the present data reveal no significant vertical variation of five major elements. The abundances of all elements are essentially constant through the thickness of the bed and between size fractions, except for K and Mg. Mg increases in abundance with decreasing particle size from

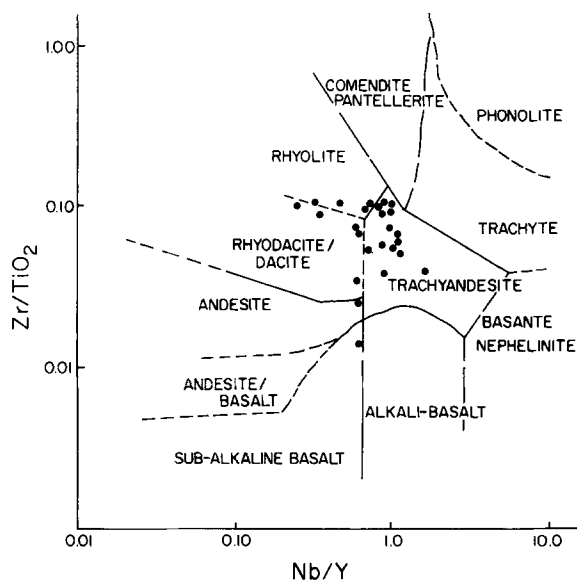


Figure 6. $\text{Zr}/\text{TiO}_2\text{-Nb}/\text{Y}$ diagram showing the distribution of volcanic rocks as interpreted by Floyd and Winchester (1978). Circles are K-bentonite samples plotted to show their probable original composition.

the bulk samples to the $<0.1\text{-}\mu\text{m}$ fraction, whereas K increases in abundance from the $<2\text{-}\mu\text{m}$ fraction to the $<0.1\text{-}\mu\text{m}$ fraction. Both size fractions, however, contain less K than the bulk samples.

Several problems arise in trying to fit these observations into a thermally driven, burial diagenesis model. First, the high MgO values in the fine fraction are inconsistent with the conclusion of Hower *et al.* (1976) that chlorite is formed from Mg and Fe released during the construction of ordered I/S, because the sparse chlorite detected is in the $<2\text{-}\mu\text{m}$ fraction but not the $<0.1\text{-}\mu\text{m}$ fraction. Petrographic evidence (Günel, 1979) suggests the chlorite is a product of minor biotite alteration. Chlorite in K-bentonites (Weaver, 1953; Bystrom, 1956; Snäll, 1977) has been reported from localities where the likelihood of deep burial is much greater than it was along the Cincinnati arch where the High Bridge Group is exposed. Second, the high K_2O values in the $<0.1\text{-}\mu\text{m}$ fraction are not logically explained by redistribution of K in a closed system during devitrification. Petrographic examination (Günel, 1979) revealed well-preserved biotite and K-feldspar in many samples. Since it is assumed most K is associated with these minerals, it seems unlikely that mass transfer of K from primary crystalline phases to a neo-clay phase occurred.

The possibility that the dissolution of very fine-grained K-feldspar may have contributed to the K content of the clays cannot, however, be completely excluded. No petrographic evidence was found to resolve this question. The obvious difficulty is in not knowing

Table 4. Calculation of gains and losses during post-depositional alteration of K-bentonite (after Günl, 1979).

Oxide	1 ²	2	3	4	5
SiO ₂	52.56	54.28	49.71	-2.85	-5
Al ₂ O ₃	18.39	20.08	18.39	0	0
Fe ₂ O ₃ ¹	8.19	1.92	1.76	-6.43	-78
MgO	2.12	3.78	3.47	+1.35	+63
CaO	5.64	0.74	0.68	-4.96	-87
Na ₂ O	5.76	1.02	0.93	-4.82	-83
K ₂ O	3.91	8.22	7.53	+3.61	+92
TiO ₂	1.73	0.37	0.34	-1.39	-80
MnO	0.14	0.03	0.02	-0.12	-86

¹ Total iron expressed as Fe₂O₃.

² 1 = Average reference trachyandesite (weight percent) (see text). 2 = Average of K-bentonite samples (weight percent). 3 = Recalculated weight of K-bentonite sample after alteration (weight percent). 4 = Difference between values in columns 1 and 3. 5 = Difference expressed in percent of the original amount (%).

the original composition of the ash. An attempt was made to determine original composition by plotting the Zr/Ti and Nb/Y ratios of 25 whole-rock K-bentonite samples against one another after the method of Floyd and Winchester (1978). The results, shown in Figure 6, indicate that a majority were trachyandesitic in composition. Some data points are in the rhyolite and rhyodacite/dacite compositional fields. K-bentonite compositions were then compared with representative analyses of trachyandesites taken from Carmichael *et al.* (1974, tables 8-8, 10-2, 10-3) in order to estimate the gains and losses of major elements during devitrification. Al was assumed to have been immobile during alteration; hence, a direct comparison between K-bentonite and trachyandesite compositions was made first by equating Al values and then by recalculating K-bentonite analyses on a proportional basis. The results are tabulated in Table 4. Assuming the computation to be at least of the correct order of magnitude, the most notable changes involve increases in K and Mg. If average analyses of rhyolites and dacites are used, the increases are even greater. Thus, K-bentonites do not seem to have behaved as a closed system with respect to K and Mg.

The origin of the excess K and Mg is unknown, but it is noteworthy that the excess is consistent with reports of widespread Mg-rich carbonates and K-Mg-rich shales in early Paleozoic sediments (Chilingar, 1956; Vinogradov and Ronov, 1956; Swett, 1968; Ronov and Migdisov, 1971; van Moort, 1972; Buyce and Friedman, 1975). The High Bridge Group of central Kentucky contains abundant, finely laminated micritic limestone and dolomite which represent tidal-flat sedimentation in a high-magnesium environment (Cressman and Noger, 1976). Alteration of volcanics is one of several mechanisms suggested by various authors to explain K and Mg enrichment in Cambro-Ordovician

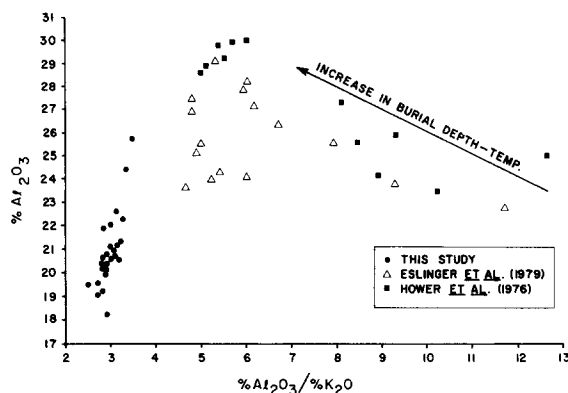


Figure 7. Relationship between Al₂O₃/K₂O and Al₂O₃ for K-bentonites and I/S produced during burial diagenesis. An increase in K relative to Al reflects increasing tetrahedral substitution of Al for Si with depth and temperature.

sediments. Perry *et al.* (1976), for example, provided evidence that the submarine weathering of calc-alkaline volcanics to smectite involved first the release of Ca and Mg to the pore waters which caused an increase in alkalinity. Mg was then extracted from the water as smectite formed. They concluded that the increase in the Mg/Al ratio of the sediment column studied and the corresponding depletion of Mg in the pore waters indicated that smectite formation had extracted the Mg originally present in seawater and the Mg originally present in the volcanics. The net effect was a Mg depletion and a Ca enrichment in the pore waters.

Hypersalinity has also been cited as a concentration mechanism for K and Mg. Normal seawater contains about 330 ppm K. When the salinity becomes high enough through evaporation to precipitate gypsum, the K content of seawater is 3.2 moles/20,100 moles H₂O (Braitsch, 1971, table 8). This is probably insufficient to provide the K required to collapse 80% of the smectite layers without having an enormous amount of water flush through the sediment column. Ronov and Migdisov (1971), among others, suggested that the K/H ratio in sediment pore fluids has decreased since early Cambrian time based on their observations of high K₂O in lower Paleozoic shales. If their suggestion is correct, the K content of K-bentonites might be more reasonably explained.

Tetrahedral substitution of Al⁺³ for Si⁺⁴ in smectite during burial diagenesis creates a high layer charge which, in turn, is compensated by K dehydration and fixation (Hower *et al.*, 1976; Eslinger *et al.*, 1979). Illite formed in this way should have a high total Al content but a relatively low Al₂O₃/K₂O ratio, compared to the smectite starting material. Figure 7 compares two well-documented cases of I/S formation with K-bentonite samples. The progressive decrease in the Al₂O₃/K₂O ratio with increasing depth and temperature can be clearly seen from data in the two published studies. K-ben-

tonites have much lower ratios although the ordered I/S stacking is very similar to the high temperature end products reported in the two studies. The average $\text{Al}_2\text{O}_3/\text{K}_2\text{O}$ ratio of illites is about 3.7, which is larger than that of most muscovites (Weaver and Beck, 1971, p. 46). For K-bentonites the ratio is 3.0, close to that of phengites and well-crystallized illites, which have ratios near 2.6 and K_2O values near 10%. Thus, K-bentonites have more fixed K than can be accounted for by tetrahedral substitution of Al. Considering the relative accessibility of migrating cations to octahedral and tetrahedral sheets, octahedral substitution of Mg^{+2} for Al^{+3} is probably a less likely phenomenon than tetrahedral substitution of Al^{+3} for Si^{+4} under low temperature conditions (Weaver and Beck, 1971). Octahedral substitution of Mg for Al is the principal cause of the high layer charge in K-bentonites and is a function of parent material and pore fluid composition rather than thermal history.

Boles and Franks (1979) concluded that aluminous smectites react to form illite more rapidly than magnesium-rich smectites during burial diagenesis based on experimental studies of dioctahedral and trioctahedral clay reaction rates. However, Eberl (1978) showed that K-montmorillonite develops ordering at a higher expandability and reacts faster than K-beidellite due to a tendency toward ordering in the parent montmorillonite. The results of this study show K-bentonites possess a Cheto-type montmorillonite structure (Grim and Kulbicki, 1961) in which octahedral substitution of Mg for Al is almost twice as much as is that described for Wyoming-type montmorillonite. It seems likely this composition was established early rather than late in the burial history of the K-bentonites.

BURIAL AND THERMAL HISTORY

Stratigraphic evidence

Middle Ordovician rocks along the crest of the Cincinnati arch have probably never been subjected to deep burial conditions. Repeated uplift and erosion of the southeastern Appalachian interior plateau during the Paleozoic has prevented the accumulation of a composite section thick enough to provide the temperatures required by the burial diagenesis model for the formation of I/S structures (Hyde, 1953; Woodward, 1961; Wolcott *et al.*, 1972; Borella and Osborne, 1978).

There is no evidence the Cincinnati arch was in existence in pre-Trenton time, however, it appears to have been a positive feature periodically from Trenton time through the Late Mississippian (Woodward, 1961). Scotford (1965) suggested that the maximum possible depth of burial of Upper Ordovician shales on the Cincinnati arch would have been approximately 5000 ft if the entire post-Ordovician Paleozoic section had formed without interruption. Thus, several major episodes of regional uplift and erosion, resulting in the removal of perhaps several thousands of feet of sedi-

ment overlying Middle Ordovician rocks of the Cincinnati arch, have prevented any appreciable deep burial of K-bentonites.

Mineralogic and paleontologic evidence

Scotford (1965) concluded that Late Ordovician shales and mudstones of the Cincinnati arch show no evidence of significant post-depositional compaction beyond lithification. He regarded the 2M polytype prevalent in the illite as evidence for a detrital origin, based on K-Ar dating by other workers, and not as evidence for low-grade metamorphism.

In Figure 1 K-bentonite sample locations in this study are superimposed on isograds delineating the color alteration index for conodonts in Ordovician carbonate rocks as proposed by Harris (1979, figure 3). The index is a guide to thermal alteration of the rocks. Isograds are drawn on the first occurrence of index values so that isograd 2, for example, passes through sample localities having conodonts with index values of 1.5 to 2. Clearly K-bentonites occurring along the crest of the Cincinnati arch lie to the west of the 1.5 isograd and well within a zone that has experienced maximum burial temperatures no greater than 80°C. This temperature is less than the minimal temperature (~100°C) needed to form ordered I/S from random I/S in the manner proposed by Hower *et al.* (1976). If the thermal drive model were applicable here, randomly interstratified I/S and perhaps some relict smectite should be present, as well as sparse kaolinite. Instead, the I/S is well ordered and exists without accessory clay minerals. Moreover, K-feldspar and biotite are well preserved in the whole rock mineral suite and give no evidence of having served as a major source of potassium during diagenesis.

It is instructive to compare K-bentonites along the Cincinnati arch with those reported from Middle Ordovician terrains that give some evidence of having undergone deep subsidence and burial. Weaver (1953), Byström (1956), and Snäll (1977) described K-bentonites which, when interpreted according to the method of Reynolds and Hower (1970), are rectorite-type ordered I/S structures in which illite and smectite components have approximately the same proportion as the sample studied for this report. It is reasonable to apply the thermal drive model to these samples. Also, the I/S structures occur in thick stratigraphic sections which have histories of deep burial and would therefore be expected to have developed ordered interlayering through burial diagenesis. However, Snäll (1977, p. 64–65) noted that the I/S ratio does not increase consistently with depth of burial and attributed between-bed variation to differences in the chemical composition of the original ash. Such differences must exert a fundamental influence on the composition of clay minerals developed as ash devitrification products during diagenesis. K-bentonites had a montmorillonitic rather

than a beidellitic precursor, and K-fixation occurred in response to octahedral substitution of Mg for Al rather than tetrahedral substitution of Al for Si. Consequently, the I/S is structurally similar but chemically dissimilar to those produced during burial diagenesis. The application of clay mineralogical criteria in paleothermometry analysis must be approached with some caution if little is known of the geological history of the sediments.

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REFERENCES

- Bergstrom, S. M. and Nilsson, R. (1974) Age and correlation of the Middle Ordovician bentonites on Bernholm: *Medd. Dan. Geol. Foren.* **23**, 27–48.
- Boles, J. R. and Franks, S. G. (1979) Clay diagenesis in Wilcox sandstones of southwest Texas: implications of smectite diagenesis on sandstone cementation: *J. Sediment. Petrology* **49**, 55–70.
- Borella, P. E. and Osborne, R. H. (1978) Late Middle and early Late Ordovician history of the Cincinnati arch province, central Kentucky to central Tennessee: *Geol. Soc. Amer. Bull.* **89**, 1559–1573.
- Braitsch, O. (1971) *Salt Deposits, Their Origin and Composition*: Springer-Verlag, New York, 297 pp.
- Brun, J. and Chagnon, A. (1979) Rock stratigraphy and clay mineralogy of volcanic ash beds from the Black River and Trenton Groups (Middle Ordovician) of southern Quebec: *Can. J. Earth Sci.* **16**, 1499–1507.
- Buyce, M. R. and Friedman, G. M. (1975) Significance of authigenic K-feldspar in Cambrian-Ordovician carbonate rocks of the proto-Atlantic shelf in North America: *J. Sediment. Petrology* **45**, 808–821.
- Byström, A. M. (1956) Mineralogy of the Ordovician bentonite beds at Kinnekulle, Sweden: *Sver. Geol. Unders. Arsb.* **48**, 62 pp.
- Carmichael, I. S. E., Turner, F. J., and Verhoogen, J. (1974) *Igneous Petrology*: McGraw-Hill, New York, 739 pp.
- Chilingar, G. V. (1956) Relationship between Ca/Mg ratio and geologic age: *Amer. Assoc. Petrol. Geol. Bull.* **40**, 2256–2266.
- Cressman, E. R. (1973) Lithostratigraphy and depositional environments of the Lexington Limestone (Ordovician) of central Kentucky: *U.S. Geol. Surv. Prof. Pap.* **768**, 61 pp.
- Cressman, E. R. and Noger, M. C. (1976) Tidal-flat carbonate environments in the High Bridge Group (Middle Ordovician) of central Kentucky: *Kentucky Geol. Surv. Rept. Invest.* **18**, 15 pp.
- Dever, G. R., Jr. (1974) High-carbonate rock in the High Bridge Group (Middle Ordovician), Boone County, Kentucky: *Kentucky Geol. Surv., Series X, Inf. Circ.* **22**, 35 pp.
- Dunoyer de Segonzac, G. (1969) Les minéraux argileux dans la diagenèse passage au métamorphisme: *Mem. Serv. Carte Geol. Alsace Lorraine* **29**, 320 pp.
- Eberl, D. D. (1978) Reaction series for dioctahedral smectites: *Clays & Clay Minerals* **26**, 327–340.
- Eberl, D. D. and Hower, J. (1976) Kinetics of illite formation: *Geol. Soc. Amer. Bull.* **87**, 1326–1330.
- Eberl, D. D. and Hower, J. (1977) The hydrothermal transformation of sodium and potassium smectite into mixed-layer clay: *Clays & Clay Minerals* **25**, 215–227.
- Elsheimer, H. N. and Fabbri, B. P. (1977) Application of an automatic fusion technique to minor and trace element XRF analysis of silicate rocks: 26th Ann. Conf. Applications of X-ray Analysis, Univ. Denver, 31–33, (abstract).
- Eslinger, E., Highsmith, P., Albers, D., and deMayo, B. (1979) Role of iron reduction in the conversion of smectite to illite in bentonites in the disturbed belt, Montana: *Clays & Clay Minerals* **27**, 327–338.
- Floyd, P. A. and Winchester, J. A. (1978) Identification and discrimination of altered and metamorphosed volcanic rocks using immobile elements: *Chem. Geol.* **21**, 291–306.
- Foster, M. D. (1960) Interpretation of the composition of trioctahedral micas: *U.S. Geol. Surv. Prof. Pap.* **354-B**, 48 pp.
- Grim, R. E. and Kulbicki, G. (1961) Montmorillonite. High-temperature reactions and classification: *Amer. Mineral.* **46**, 1329–1369.
- Günal, A. (1979) Clay mineralogy, petrography, chemical composition and stratigraphic correlation of some Middle Ordovician K-bentonites in the eastern mid-continent: Ph.D. Thesis, University of Cincinnati, 237 pp.
- Harris, A. G. (1979) Conodont color alteration, an organomineral metamorphic index, and its application to Appalachian basin geology: *Soc. Econ. Paleontol. Mineral. Spec. Publ.* **26**, 3–16.
- Hower, J. and Mowatt, T. C. (1966) The mineralogy of illite and mixed-layer illite/montmorillonites: *Amer. Mineral.* **51**, 825–854.
- Hower, J., Eslinger, E. V., Hower, M. E., and Perry, E. A. (1976) Mechanism of burial metamorphism of argillaceous sediment: I. Mineralogical and chemical evidence: *Geol. Soc. Amer. Bull.* **87**, 727–737.
- Hyde, J. E. (1953) The Mississippian formations of central and southern Ohio: *Ohio Geol. Surv. Bull.* **51**, 355 pp.
- Jackson, M. L. (1975) *Soil Chemical Analysis—Advanced Course*: 2nd ed., 10th printing, Publ. by author, Madison, Wisconsin, 895 pp.
- Kay, G. M. (1935) Distribution of Ordovician altered volcanic materials and related clays: *Geol. Soc. Amer. Bull.* **46**, 225–244.
- Medlin, J. H., Suhr, N. H., and Bodkin, J. B. (1969) Atomic absorption analysis of silicates employing LiBO₂ fusion: *At. Absorption Newslett.* **8**, 25–29.
- van Moort, J. C. (1972) The K₂O, CaO, MgO and CO₂ contents of shales and related rocks and their implications for sedimentary evolution since the Proterozoic: *24th Int. Geol. Cong.* **10**, 427–439.
- Perry, E. A., Jr. and Hower, J. (1970) Burial diagenesis in Gulf Coast pelitic sediments: *Clays & Clay Minerals* **18**, 165–177.
- Perry, E. A., Jr., Giekes, J. M., and Lawrence, J. F. (1976) Mg, Ca and O¹⁸/O¹⁶ exchange in the sediment-pore water system, Hole 149, DSDP: *Geochim. Cosmochim. Acta* **40**, 413–423.
- Reynolds, R. C. and Hower, J. (1970) The nature of interlayering in mixed-layer illite-montmorillonites: *Clays & Clay Minerals* **18**, 25–36.
- Ronov, A. B. and Migdisov, A. A. (1971) Geochemical history of the crystalline basement and the sedimentary cover

- of the Russian and North American platforms: *Sedimentology* **16**, 137–185.
- Schultz, L. G. (1978) Mixed-layer clay in the Pierre Shale and equivalent rocks, northern Great Plains region: *U.S. Geol. Surv. Prof. Pap.* **1064-A**, 28 pp.
- Scotford, D. M. (1965) Petrology of the Cincinnati Series shales and environmental implications: *Geol. Soc. Amer. Bull.* **76**, 193–222.
- Snäll, S. (1977) Silurian and Ordovician bentonites of Gotland (Sweden): *Stockholm Contrib. Geol.* **31**, 80 pp.
- Środoń, J. (1978) Correlation between coal and clay diagenesis in the Carboniferous of the Upper Silesian coal basin: *Prog. Abstracts, Int. Clay Conf.*, Oxford, 1978, p. 307.
- Swett, K. (1968) Authigenic feldspars and cherts resulting from dolomitization of illitic limestones: a hypothesis: *J. Sediment. Petrology* **38**, 128–135.
- Velde, B. (1973) Phase equilibria for dioctahedral expandable phases in sediments and sedimentary rocks: in *Proc. Int. Clay Conf., Madrid, 1972*, J. M. Serratos, ed., Div. Ciencias C.S.I.C., Madrid, 283–300.
- Velde, B. and Brusewitz, A. M. (1978) Evidence for metasomatic diagenesis and non-metasomatic metamorphism of Ordovician meta-bentonites in Sweden: *Prog. Abstracts, Int. Clay Conf.*, Oxford, 1978, p. 306.
- Vinogradov, A. P. and Ronov, A. B. (1956) Evolution of the chemical composition of clays of the Russian platform: *Geokhimiya*, **2**, 3–18 (in Russian). English translation in *Geochemistry*, **1960**, 123–139.
- Weaver, C. E. (1953) Mineralogy and petrology of some Ordovician K-bentonites and related limestones: *Geol. Soc. Amer. Bull.* **64**, 921–943.
- Weaver, C. E. and Beck, K. C. (1971) Clay water diagenesis during burial: How mud becomes gneiss: *Geol. Soc. Amer. Spec. Pap.* **134**, 96 pp.
- Weaver, C. E. and Pollard, L. D. (1973) *The Chemistry of Clay Minerals*: Elsevier, New York, 213 pp.
- Wilson, C. W., Jr. (1949) Pre-Chattanooga stratigraphy in central Tennessee: *Tennessee Dept. Conserv. Div. Geol. Bull.* **56**, 407 pp.
- Wolcott, D. E., Cressman, E. G., and Connor, J. J. (1972) Trend-surface analysis of the thickness of the High Bridge Group (Middle Ordovician) of central Kentucky and its bearing on the nature of the post-Knox unconformity: *U.S. Geol. Surv. Prof. Pap.* **800-B**, 25–33.
- Woodward, H. P. (1961) Preliminary subsurface study of southeastern Appalachian Interior Plateau: *Amer. Assoc. Petrol. Geol. Bull.* **45**, 1634–1655.

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Резюме—К-бентониты из Группы Средней Ордовикской Высокий Мосе вдоль Синсинатской дуги характеризуются наличием переслаивающихся иллито-сметитовых (И/С) глин, упорядоченных по типу ректорита. Приблизительно 20% слоёв способно расширяться. По структуре они схожи с И/С, формированными при температурах, превышающих 100°C во время глубинного диagenеза. Однако стратиграфические данные и показатель изменения цвета <1,5 для конодонтов в ассоциированных карбонатах показывают, что они никогда глубоко не залежали или не подверглись воздействию температур выше 80°C.

Цельные образцы скальной породы К-бентонитов содержат ~8% K₂O и 4% MgO в то время, как фракция размером <0,1 μm содержит 6–7% K₂O и 5% MgO. По сравнению с гипотетическим пепелом эти величины говорят о приобретении К и Mg и о потере Si, Fe, Ca, и Na в результате послеосадочных изменений. Фиксация К рассчитывалась по увеличению дисбаланса заряда слоя, в основном, путем октаэдрического замещения ионов Al³⁺ ионами Mg²⁺, указывая на то, что промежуточные напластования развивались от монтмориллонитового предшественника. Химические характеристики И/С слоёв в К-бентонитах формировались ранее во время преобразования вулканического пепела в монтмориллонит. Относительно высокое содержание К и Mg, возможно, является отражением как морской воды, так и состава исходного материала во время образования. Состав и упорядоченная укладка в К-бентонитах определялась скорее составом первоначального смектита, чем условиями температуры и давления при диagenезе. [E.C.]

Resümee—K-Bentonite der mittel-ordovizischen High Bridge Gruppe entlang des Cincinnati-Bogens sind durch Illit/Smektit-Wechsellagerungen (I/S) mit einer Ordnung vom Reaktorit-Typ charakterisiert. Ungefähr 20% der Lagen sind expandierbar. Sie sind strukturmäßig den I/S-Wechsellagerungen ähnlich, die bei Temperaturen über 100°C während der Versenkungs-Diagenese gebildet wurden. Die Stratigraphie und ein Farb-Umwandlungs-Index von <1,5 für Konodonten in benachbarten Karbonaten zeigen jedoch, daß sie niemals tief versenkt oder einer Temperatur über 80°C ausgesetzt wurden.

Gesamtgesteinsproben der K-Bentonite enthalten ~8% K₂O und ~4% MgO, während die Kornfraktion <0,1 μm, 6–7% K₂O und 5% MgO enthält. Durch den Vergleich mit einer hypothetischen Ausgangsasche bedeuten diese Werte einen Nettogewinn von K und Mg und einen Nettoverlust von Si, Fe, Ca, und Na während der Umwandlung nach der Ablagerung. Die K-Fixierung erklärt sich aus einem Ladungsungleichgewicht der Lagen, das vor allem durch die oktaedrische Substitution von Mg für Al hervorgerufen wird. Dies deutet darauf hin, daß die Wechsellagerung aus einem Montmorillonit-Vorläufer entstanden ist. Die chemischen Charakteristika der I/S-Lagen in den K-Bentoniten entwickelten sich zu Beginn der Umwandlung der vulkanischen Asche zu Montmorillonit. Relativ hohe Gehalte an K und Mg spiegeln wahrscheinlich sowohl die Zusammensetzung des Meerwassers als auch die der Ausgangssubstanz zur Zeit der Bildung wieder. Die Zusammensetzung und die regelmäßige Anordnung in den K-Bentoniten wurde eher durch die Zusammensetzung des ursprünglichen Smektit bestimmt als durch die Druck-Temperatur-Bedingungen einer Versenkungs-Diagenese. [U.W.]

Résumé—Des bentonites-K du groupe Ordovicien Moyen High Bridge le long de l'arche de Cincinnati sont caractérisées par des argiles interstratifiées illite/smectite (I/S) avec un rangement du type rectorite. Approximativement 20% des couches sont expansibles. Structuralement, elles sont semblables aux I/S formées à des températures excédant 100°C pendant la diagénèse d'ensevelissement, l'évidence stratigraphique, cependant, et un indice d'altération de couleur <1,5 pour les conodontes dans des carbonates associés révèlent qu'elles n'ont jamais été profondément enterrées ou soumises à des températures plus élevées que 80°C.

Des échantillons de roche entière de bentonites-K contiennent ~8% K₂O et ~4% MgO, alors que la fraction de taille <0,1- μ m contient 6-7% K₂O et 5% MgO. En comparaison avec une cendre hypothétique apparentée, ces valeurs représentent un gain net de K et Mg et une perte nette de Si, Fe, Ca, et Na pendant l'altération produite après déposition. La fixation de K est expliquée par un déséquilibre de charge de couche produit par la substitution octaèdre de Mg⁺² à Al⁺³, indiquant que l'interstratification avait évolué d'un précurseur montmorillonite. Les caractéristiques chimiques des couches I/S dans les bentonites-K se sont développées tôt pendant l'altération de la cendre volcanique en montmorillonite. Des contenus relativement élevés en K et Mg reflètent probablement à la fois l'eau de mer et la composition de la matière parente au moment de la formation. La composition et l'ordre d'empilement dans les bentonites-K étaient déterminées par la composition de la smectite d'origine plutôt que par les conditions de pression et de température pendant la diagénèse d'enterrement. [D.J.]