

MINERALOGY OF ORDOVICIAN K-BENTONITES IN KENTUCKY

by

WARREN D. HUFF

University of Cincinnati, Cincinnati, Ohio

ABSTRACT

Preliminary results of investigations of Trenton–Black River (Ordovician) K-bentonites from well cores in northern Kentucky and from outcrops along the Kentucky River illustrate the variations in some physical and chemical properties. It is hoped that some features may eventually be useful in stratigraphic correlation, considering that the very nature of these altered ash beds makes them ideal time-lines.

That these beds are derived from volcanic ash is evidenced by significant amounts of biotite, magnetite, leucoxene, apatite, and zircon.

The following means of investigation have been employed: X-ray diffraction, DTA, cation exchange, heavy mineral studies, and insoluble residue studies of adjacent limestones. X-ray analyses of untreated and glycolated clay samples indicate a mixed-layer, dioctahedral, illite–montmorillonite type structure with an I–M ratio varying from 4:1 to 3:2. The proportion of expandable layers in many samples is higher than that reported for Ordovician K-bentonites elsewhere. No evidence of chlorite is detected.

DTA data show a primary hydroxyl peak near 725°C suggesting a basic montmorillonite-type of hydroxyl bonding. Treatment with 1M solutions of various cations produces a slight expansion of the expandable layers with Ca^{2+} , and contraction with Na^+ , K^+ , and NH_4^+ giving some indication of original environmental composition. The evidence supports suggestions by earlier authors that the clays are basically montmorillonites which have undergone partial contraction due to the adsorption of potassium in the interlayer positions.

While euhedral zircons are most likely non-detrital, recent work on zircons in igneous rocks suggests the same may also be true for some of the sub-rounded and fractured species.

Insoluble residues of limestones contain abundant chert and mixed-layer illite–montmorillonite clay directly adjacent to the ash beds, but farther away illite and chlorite dominate and are probably detrital in origin.

INTRODUCTION

Since the late 1800's attempts have been made in the mid-continent region to correlate Ordovician strata over large areas using as datum planes various bentonite beds occurring in age from early Chazyan to late Trentonian. The abundance of reported bentonites and their apparent sensitivity to physical–chemical changes together with the extremely short time span in which it is thought they were deposited over wide areas have made them a

source of continued interest among stratigraphers, sedimentologists, and mineralogists.

Kay (1931, 1935), Rosenkrans (1933), and Nelson (1922) have reported Ordovician bentonites in southern and western New York, southern Ontario, Vermont, Virginia, Pennsylvania, Alabama, Georgia, Missouri, Iowa, Wisconsin, Minnesota, Kentucky, and Tennessee. Others (Allen, 1932; Ross, 1955) have suggested that the same beds may be extensive in Ohio, Michigan, Oklahoma, Arkansas, Louisiana, and Florida. Hence, a detailed study of the structure and composition of these bentonites and of the enclosing Ordovician rocks should prove quite useful both from the point of view of defining and correlating stratigraphic horizons and of gaining more knowledge concerning the range and extent of physical and chemical changes subsequent to deposition. The present report is part of a larger program aimed at these ends, and deals primarily with the various properties of the ash beds and associated limestones as revealed by laboratory analysis.

Bradley (1945), and more recently Weaver (1953), have shown that these bentonites differ significantly from the Cretaceous and Tertiary montmorillonitic bentonites of the western United States in that they consist of randomly interstratified dioctahedral illite and montmorillonite layers with illite constituting 75–80 per cent of the total structure. Furthermore, they have shown that the collapse of some montmorillonite layers to an illite-type structure by the adsorption of potassium in the interlayer exchange position has accounted for the apparent “metamorphism” envisioned by earlier workers and hence the name K-bentonite has supplanted the term metabentonite in present-day literature. Weaver has also reported a small amount of chlorite in K-bentonites from Pennsylvania.

SAMPLES STUDIED

In the present study eighteen specimens were collected from six areas in central and northern Kentucky. Stratigraphically, the K-bentonites are located near the Trenton–Black River contact (Fig. 1) which locally is represented by a transition from the sub-lithographic, dove-gray, unfossiliferous Tyrone limestone below to the medium- to coarse-grained, gray, fossiliferous Curdsville limestone above. The contact is generally considered to be a gradational one since stringers of sub-lithographic limestone are encountered within the lower portion of the Curdsville.

The K-bentonites range from $\frac{1}{2}$ in. to 32 in. in thickness and average about 4 to 6 in. with discontinuous zones of chert and cherty limestone up to 8 in. thick above and below. Fresh samples are greenish-gray to bluish-gray and dark gray, quite hard, and break with a conchoidal fracture. In many of the outcrops along the Kentucky River considerable digging was required before fresh samples were encountered. Weathered K-bentonites range from shaly, easily broken fragments to a highly plastic clay varying from reddish-brown to grayish-tan in color. X-ray diffraction patterns of weathered specimens

MIDDLE ORDOVICIAN						
MOHAWKIAN						
BLACK RIVER			TRENTON			
CAMP NELSON	OREGON	TYRONE	CURDSVILLE	HERMITAGE	JESSAMINE	BENSON
						CYNTHIANA

FIGURE 1.—Stratigraphic range of samples.

show a larger layer spacing than those of fresh specimens due to the leaching of some potassium.

The K-bentonites were studied by X-ray diffraction, cation exchange, DTA and heavy mineral analyses, while insoluble residue studies and carbonate ratio tests were carried out on a few samples of adjacent limestone.

X-RAY DATA

Untreated and Glycolated Samples

X-ray diffraction studies of the less than 2 micron fractions of 14 samples oriented on glass slides reveal a fairly wide range of values for the most diagnostic reflections of the untreated samples and a narrower range for those treated with various cations. For example, in sample KR-9-3 (Fig. 2) the untreated pattern has three prominent reflections in the range 0–30 degrees, 2θ corresponding respectively from right to left to 12.2 Å, 5.05 Å, and 3.22 Å. Using the data of MacEwan *et al.* (1961) it can be calculated that each peak is intermediate between the known positions for a 10 Å illite and a 15.4 Å montmorillonite such that the proportion of each is about 60 per cent illite and 40 per cent montmorillonite. The most intense peak, then, must represent combined reflections from each of the first order basal peaks of the two end members. Similarly, MacEwan *et al.* have shown that subsequent peaks are combined reflections of the second order illite and third order montmorillonite peaks, and the third order illite and fifth order montmorillonite peaks respectively. On this basis the three individual reflections indicate a montmorillonite component ranging in abundance from 20 to 40 per cent. Chlorite was not found in any of the samples.

Cation Exchange

Cation exchange treatments were made on fourteen samples of K-bentonite of which the less than 2 micron fractions were placed separately in 1 M solutions of K^+ , Ca^{2+} , Na^+ , and NH_4^+ and suspended in a high frequency ultrasonic water bath at $60^\circ C$ for 5 hr and then washed and dried at room temperature. This method of treatment was found in several trial runs to give quite consistent results since flocculation of individual particles is greatly retarded. Sample KR-9-3 experienced a 1 Å contraction with K^+ and NH_4^+ , 0.8 Å with Na^+ , and an expansion of 0.1 Å with Ca^{2+} . Second and third maxima are similarly broadened or sharpened due to contraction or expansion of the 15 Å unit. Variations in the period for first maxima of fourteen treated samples is illustrated in Fig. 3. It can be seen that while there is a variation of about 1 Å in the peak positions of the untreated samples, the reactions to various cations are fairly uniform. Both K^+ and NH_4^+ are readily adsorbed by the clays with corresponding peak shifts ranging from 0.1 to 1.0 Å. Samples treated with Ca^{2+} and dried at room temperature show a large lattice expansion compared to some of the untreated and to most of the otherwise treated samples.

Ca^{2+} has a higher free bonding energy than either K^+ , Na^+ , or NH_4^+ . As a result, Ca^{2+} is compatible with two layers of water in the interlayer position and fosters an expansion of several angstroms, whereas K^+ , Na^+ , and NH_4^+ are compatible with either one layer of water or none and hence effect partial

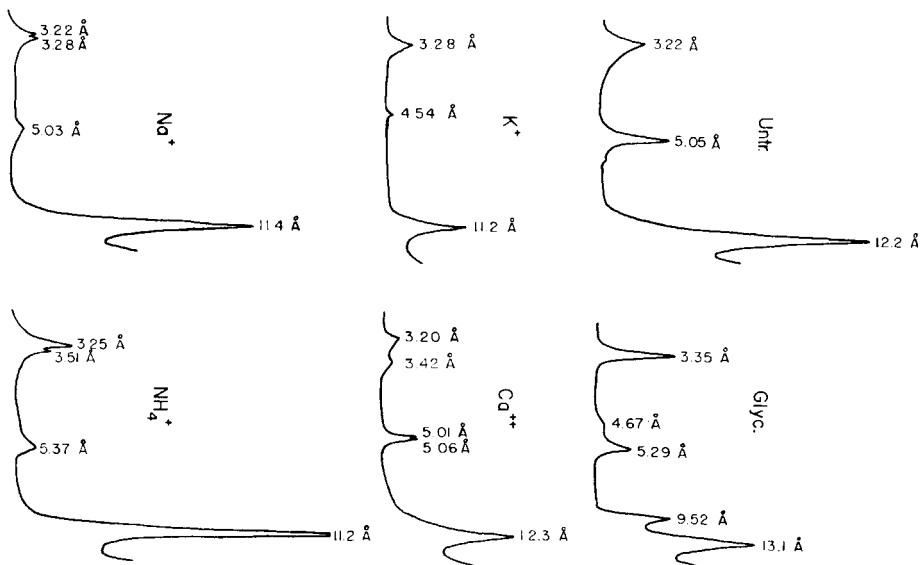


FIGURE 2.—Spectrometer tracings of sample KR-9-3 showing peak shifts following cation treatments.

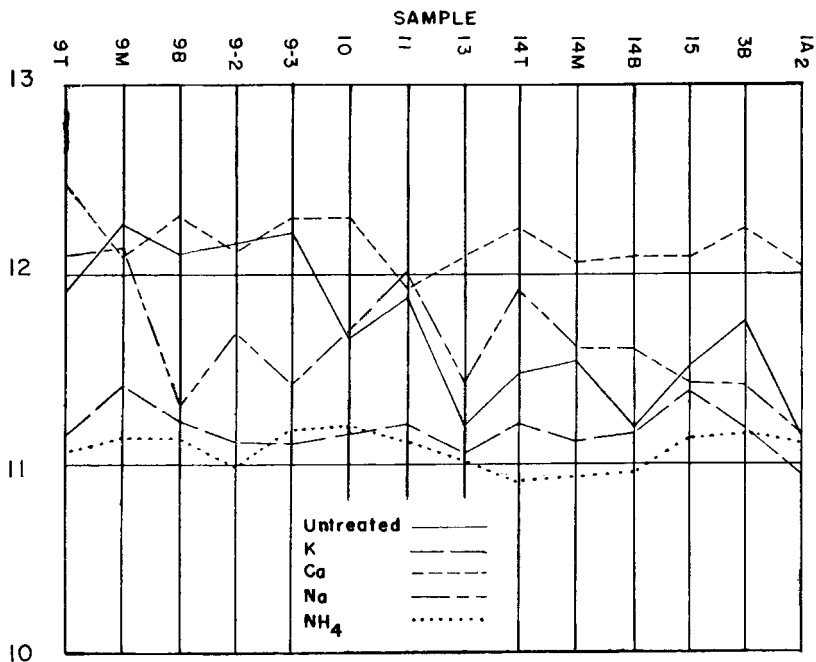


FIGURE 3.—Chart showing variation of 001/001 with cation treatment.

collapse of the structure. Those samples showing little reaction to Ca^{2+} were collected from the same stratigraphic horizon over a distance of several miles in the vicinity of Highbridge, Kentucky. Sample number 10 was taken from the API reference site in that area. A comparison with samples 13 through 1A₂ (Fig. 3) collected in northern Kentucky shows a much more pronounced reaction to Ca^{2+} . In general, the replacing power of a cation increases with increasing concentration of the cation in solution. Hence, there is the possibility that some degree of equilibrium was attained between what was in one case an environment rich in Ca^{2+} , and in the other, one more concentrated in Na^+ , or perhaps K^+ . Under these circumstances, treatment with Ca^{2+} in one situation and Na^+ and K^+ in the other produces little change in structures already rich in these cations.

However, Weaver (1958) has pointed out that montmorillonite derived from volcanic minerals differs from montmorillonite derived from the breakdown of micas in having more of the interlayer charge located in the octahedral layer, and further, that such montmorillonite can vary in the amount of adsorbed potassium depending upon the distribution of this charge between the tetrahedral and octahedral layers. Thus for montmorillonites with moderate exchange capacities a state of disequilibrium with respect to the

surrounding environment can exist for a period of time under conditions of low temperatures and pressures (Siever, 1962) which might be reflected in a significant range of 001/001 values for a large number of samples. Further base exchange and spectrographic data should provide useful information in this respect.

DIFFERENTIAL THERMAL ANALYSIS

Thermograms were made of the less than 2 micron fractions of six representative samples as shown in Fig. 4. A prominent endothermic reaction at about 150°C has been shown by Grim and Rowland (1942) to be the result of a loss of non-structural adsorbed water, while other endothermic peaks in the

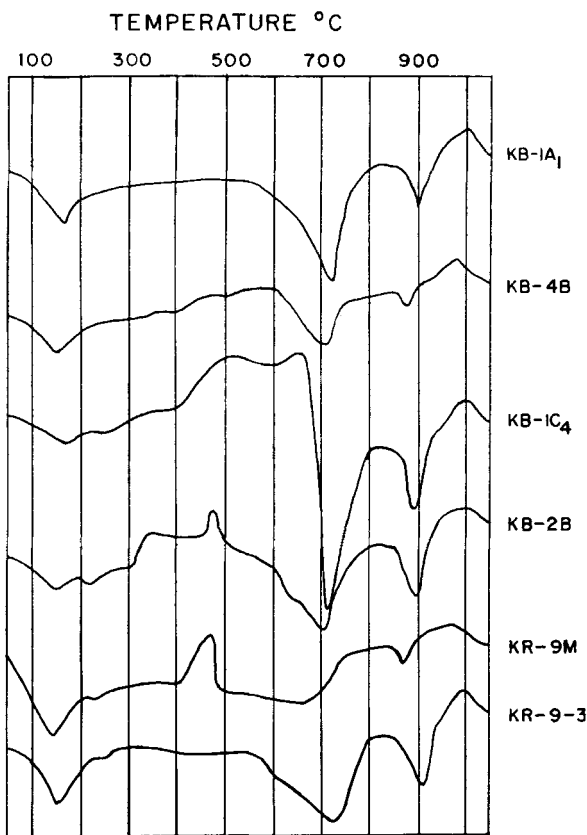


FIGURE 4.—Differential thermal curves for six untreated samples.

range from 600° to 950°C indicate loss of hydroxyl water and finally complete breakdown of the silicate lattice. Exothermic reactions around 1000°C are probably associated with the formation of a spinel-type structure (MacKenzie, 1957, p.153). Several samples show slight endothermic peaks between 200° and 250°C. Weaver (1953) has reported similar reactions in Ca-treated K-bentonites and in some untreated samples, and suggests that they represent the presence of the hydrated Ca ion. This may or may not be in the form of gypsum. Various exothermic peaks in the range from 450° to 500°C probably reflect minor amounts of secondary iron sulfide.

A search of the literature reveals several instances of seemingly anomalous mixed-layer illite-montmorillonite clays with primary endothermic peaks varying from 525° to 725°C. However, by grouping those patterns with similar peak positions, MacKenzie (1957, p.261) has shown that the mixed-layer patterns with hydroxyl endothermic peaks between 525° and 625°C probably represent an illite-type hydroxyl bonding in a structure partially altered toward montmorillonite. Similarly, those reactions between 650° and 725°C represent a basic montmorillonite-type hydroxyl bonding in a lattice partially altered toward illite. Although the position of the peaks does not appear to bear any relationship to the percentage of each component, the use of DTA data in conjunction with X-ray analyses may provide useful structural information on interlayered illite-montmorillonite minerals. From this standpoint the interpretation of these thermograms agrees quite closely with work by previous authors (Bradley, 1945; Weaver, 1953) who suggest that K-bentonites are essentially calcium montmorillonites that have been partially transformed to non-expandable 10 Å illites through adsorption of potassium in the interlayer position.* Such a relationship was interpreted by Kerr, Kulp and Hamilton (1949) as suggesting that a non-statistical distribution of replaceable ions in a highly substituted montmorillonite lattice might produce a high temperature reaction, whereas in a slightly substituted lattice a lower temperature reaction could result.

HEAVY MINERAL ANALYSIS

Heavy mineral studies of the K-bentonites reveal a fairly consistent suite composed of biotite, magnetite, leucoxene, and apatite with lesser amounts of zircon. Trace amounts of hematite, chlorite, and fluorite were also recognized. Together, both anhedral and euhedral flakes of biotite constitute as much as 85 per cent of the total heavy mineral suite in some samples, whereas they are almost absent in others. Individual flakes range up to 0.9 mm in diameter and can be easily seen with the naked eye. Several samples of biotite are now undergoing K-Ar age determinations to better standardize the Ordovician section in the mid-continent region.

Colorless apatite crystals, 0.05 to 0.3 mm in length, account for as much as

* The analogous transformation of sodium montmorillonites is also to be expected.

30 per cent of the heavy minerals in some K-bentonites and show a variety of forms including commonly long, prismatic crystals terminated either singly or doubly by pyramidal or pinacoidal surfaces. Small inclusions of bubbles and zircon crystals are oriented parallel to the *c*-axis in some samples. Leucoxene crystals range up to 50 per cent of the total heavies occasionally, but in general it is a minor constituent.

Colorless zircon crystals vary from 0.03 to 0.4 mm in length and are found in most samples as a minor constituent. Zircons exhibit habits similar to those described by Larsen and Poldervaart (1961) which include euhedral, doubly terminated, prismatic crystals with simple and complex forms; singly terminated, subhedral crystals; and anhedral crystals with irregular forms. Although the appearance of apparently rounded or broken crystals within a K-bentonite might indicate a detrital origin, it should be pointed out that alternative interpretations are possible. Larsen and Poldervaart (1957) have shown that the irregular forms on zircon crystals taken from granodiorites and tonalites of the Bald Rock Batholith, near Bidwell Bar, California, are not a product of mechanical abrasion or impact, but rather are products of incomplete crystallization.

Magnetite is present in many samples as intergrowths with biotite and leucoxene and as individual euhedral crystals. Small anhedral grains of hematite and chlorite are occasionally found but never constitute a major portion of the heavy minerals. Fluorite with its characteristic octahedral cleavage is present in trace amounts only.

Biotite, magnetite, leucoxene, apatite, and zircon are commonly associated with intermediate to acid volcanics and their abundance here only attests to the pyroclastic origin of these beds. Hematite and fluorite are undoubtedly authigenic, while chlorite is found abundantly in the insoluble residues of adjacent limestones and so is probably detrital. No characteristic physical properties of the heavy minerals were found to be consistently useful for stratigraphic correlation.

INSOLUBLE RESIDUES

Insoluble residue studies of limestone adjacent to several K-bentonites were made by first dissolving samples of the limestone in weak HCl. From the two representative sequences shown in Fig. 5 it can be seen that there is a very definite and rapid decrease of insoluble content away from the K-bentonites. Samples taken every 2 ft up to a distance of 6 ft on either side show that almost all insoluble material adjacent to the K-bentonites is composed of chert, more so below than above, with only minor amounts of clay. The accumulation of chert as a devitrification product of ash falls has been discussed by previous workers (Fox and Grant, 1944; Ross and Hendricks, 1945; Siever, 1962).

Although by far the majority of insoluble material from 2 to 6 ft away is clay, X-ray diffraction data of several bulk limestone residues reveal weak

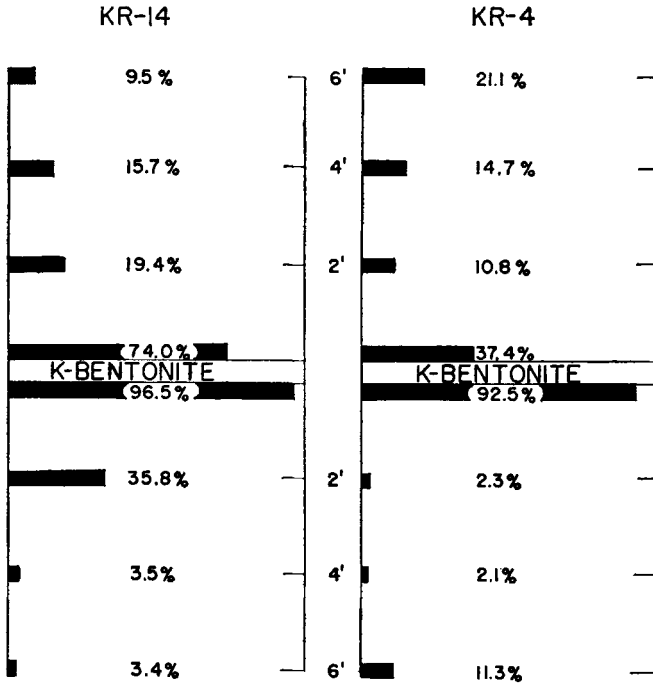


FIGURE 5.—Chart showing vertical variation in insoluble residue content adjacent to two K-bentonites.

orthoclase patterns. Carbonate peaks belong primarily to calcite though minor dolomite reflections occasionally show up.

In addition to a regular 10 Å sequence, both 14 and 7 Å reflections, characteristic of chlorite, are found in the clay portion of limestone residues. Glycolation showed expansion effects only on those clays directly adjacent to the K-bentonites, while heating at 550°C for 2 hr did not appreciably shift the 14 Å peak, a characteristic reaction for chlorite (Warshaw and Roy, 1961). In sample KR-4 (Fig. 5), the insoluble content increases at the bottom of the section as another K-bentonite is approached, while the higher readings at the top of the section probably reflect differences inherent in the lithologic change from the Tyrone to the Curdsville limestone.

CONCLUSIONS

It can be concluded that Ordovician K-bentonites in Kentucky contain from 20 to 40 per cent montmorillonite randomly interstratified with illite. Cation adsorption data show the probable effect of different chemical environments and, perhaps to some extent, variation in interlayer charge

distribution. DTA information supports the suggestion that the clays have a basic montmorillonite structure which has partially altered toward illite. Mineralogical constituents and insoluble residues of associated limestones reflect the volcanic origin of the beds, and their relationship to detrital and autochthonous material.

REFERENCES

- Allen, V. T. (1932) Ordovician altered volcanic material in Iowa, Wisconsin, and Missouri: *J. Geol.*, v.37, pp.239-247.
- Bradley, W. F. (1945) Diagnostic criteria for clay minerals: *Am. Min.*, v.30, pp.704-713.
- Fox, P. P., and Grant, L. F. (1944) Ordovician bentonites in Tennessee and adjacent states: *J. Geol.*, v.52, pp.332.
- Grim, R. E., and Rowland, R. H. (1942) Differential thermal analyses of clay minerals and other hydrous materials: *Amer. Min.*, v.27, pp.801-818.
- Kay, G. M. (1931) Stratigraphy of the Ordovician Hounsfield metabentonite: *J. Geol.*, v.39, pp.361-376.
- Kay, G. M. (1935) Distribution of Ordovician altered volcanic materials and related clays: *Geol. Soc. Amer. Bull.*, v.46, pp.225-244.
- Kerr, P. F., Kulp, J. L., and Hamilton, P. K. (1949) DTA of reference clay mineral specimens: Prelim. rept. No. 3, *Reference Clay Minerals, A.P.I. Research Project 49*, Amer. Petrol. Inst., New York.
- Larsen, L. H., and Poldervaart, A. (1957) Measurement and distribution of zircons in some granitic rocks of magmatic origin: *Min. Mag.*, v.31, pp.544-564.
- Larsen, L. H., and Poldervaart, A. (1961) Petrologic study of Bald Rock Batholith, near Bidwell Bar, California: *Geol. Soc. Amer. Bull.*, v.72, pp.69-92.
- MacEwan, D. M. C., Amil, A. R., and Brown, G. (1961) Ch. XI in Brown, G. (ed.) *The X-ray Identification and Crystal Structures of Clays and Clay Minerals*: Mineralogical Society, London, pp.393-445.
- MacKenzie, R. C. (1957) ed., *The Differential Thermal Investigation of Clays*: Mineralogical Society, London, 456 pp.
- Nelson, W. A. (1922) Volcanic ash beds in the Ordovician of Tennessee, Kentucky and Alabama: *Geol. Soc. Amer. Bull.*, v.33, pp.605-615.
- Rosenkrans, R. R. (1933) Correlation of Ordovician bentonites: M.S. Thesis, Pa. State College.
- Ross, C. S. (1955) Provenance of pyroclastic materials: *Geol. Soc. Amer. Bull.*, v.66, pp.427-434.
- Ross, C. S., and Hendricks, S. B. (1945) Minerals of the montmorillonite group: *U.S.G.S. Prof. Paper 205-B*, pp.23-79.
- Siever, R. (1962) Silica solubility, 0°-200°C, and the diagenesis of siliceous sediments: *Jour. of Geol.* v.70, pp.127-150.
- Warshaw, C. M., and Roy, R. (1961) Classification and a scheme for the identification of layer silicates: *Geol. Soc. Amer. Bull.*, v.72, pp.1455-1492.
- Weaver, C. E. (1953) Mineralogy and petrology of some Ordovician K-bentonites and related limestones: *Geol. Soc. Amer. Bull.*, v.64, pp.921-943.
- Weaver, C. E. (1958) The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material: *Amer. Min.*, v.43, pp.839-861.