

CLAY MINERALOGY OF PALEOZOIC K-BENTONITES OF THE EASTERN UNITED STATES (PART 1)

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ABSTRACT

Samples of altered volcanic materials, interbedded with dominantly carbonate sediments, were collected from Ordovician, Silurian, and Devonian strata in Michigan, Illinois, Kentucky, Pennsylvania, Virginia, and Alabama. These altered volcanics, originally called metabentonite and more recently K-bentonite, occur in thin seams commonly only a few inches thick and are generally believed to be altered Paleozoic volcanic ash falls because they contain typical igneous minerals in the heavy suite and retain textures and structures characteristic of ash deposits.

Petrographic, differential thermal, and X-ray analyses were made of these samples to determine the clay mineralogy. Mixed-layer illite-montmorillonite occurs in the majority of samples. Illite is present in all samples and chlorite occurs in a few samples. This is in general accord with findings of previous studies. The mixed-layer clay is believed to have been deposited as montmorillonite in a marine environment and subsequently altered largely to illite through fixation of K in the interlayer position.

K-bentonites from Michigan and Illinois contain a constituent which has a 7.6 Å *d*-spacing. It is suggested that this material may be of regional significance because its occurrence was confined to the Upper Mississippi Valley K-bentonites in samples of this study.

INTRODUCTION

PYROCLASTIC material in the form of altered volcanic ash has been reported and described from one or more stratigraphic units in every Paleozoic rock system, except the Cambrian, in the eastern part of the United States. This ash, variously called bentonite, metabentonite, or K-bentonite depending on the degree of alteration and chemical composition was described and analyzed from Mesozoic rocks of Wyoming early in this century; however, the first pertinent description of similar units of Paleozoic age was by Nelson (1921, 1922) who recognized its occurrence in Ordovician rocks of Kentucky, Tennessee, Alabama, and Virginia. The geographic range of the Ordovician bentonites has been extended subsequently westward to a line running from Missouri to Minnesota and north-

ward nearly to Lake Superior and into Ontario. Bentonitic units have been found also widely distributed, mostly in the subsurface, in Silurian, Devonian, Pennsylvanian, and Permian beds. G. M. Kay (1935) described the distribution of altered volcanic materials in the eastern United States.

Many geologists have used or attempted to use these bentonitic layers as time-markers in establishing stratigraphic sequences or as lithologic markers in regional correlation of various Paleozoic rock units. The multiplicity of ash layers, their thinness (normally only a few inches thick) and consequent ease of post-depositional erosion, and their somewhat lenticular distribution has resulted in only moderately successful application to stratigraphic problems. Studies by Rosenkrans (1934) and G. M. Kay (1944) are illustrative of the attempted use of bentonite seams for correlation.

Some studies have been made of gross physical properties and general mineralogy of the Ordovician metabentonites, for example by Ross (1928) and Fox and Grant (1944). Allen (1929, 1932) petrographically studied altered volcanic material from Ordovician rocks of the Upper Mississippi valley region and suggested (1929, p.242) that some of the larger fragments seen in thin-section had a texture similar to pumice, indicative of formation from volcanic glass with partial retention of the original vitreous structure.

X-ray diffraction pattern studies of bentonites or metabentonites appear to be relatively few. The A.P.I. reference book of clay minerals describes K-bentonite samples from High Bridge, Kentucky and Tazewell, Virginia, and samples from these localities have been re-examined in conjunction with our current study. Weaver (1956) described the mineralogy of Middle Devonian "Tioga" K-bentonite from Pennsylvania, and the published paper includes an X-ray diffraction diagram for this material. A recent abstract of Nelson (1959) describes the petrography and X-ray mineralogy of a newly-discovered bentonite zone from Pennsylvanian rocks of southwestern Virginia. Grim (1962, p.895) in a review of current problems in clay mineralogy has discussed briefly the potential importance of relatively minor amounts of volcanic ash in influencing the character of accumulating terrigenous sediments in Paleozoic shales over wide geographic areas and extensive stratigraphic intervals.

It can be stated only that (1) Paleozoic K-bentonites or metabentonites always have been considered but not definitely proved to be altered products derived from volcanic ash, (2) much effort has been directed to use of thin bentonitic seams as time or lithologic markers in stratigraphic correlation studies, and (3) only limited mineralogic study has been made of these materials. In view of Grim's discussion cited above, and estimates by Ross (1955) that Paleozoic bentonites are geographically present underlying an area of perhaps 400,000 square miles of the eastern United States, more attention to the mineralogy of bentonites seems appropriate. This paper, therefore, reports on our preliminary study of bentonites, ranging in age from Ordovician to Devonian, from selected localities.

MATERIALS STUDIED

Although the widespread distribution of K-bentonite in Paleozoic rocks of some southern, eastern and middle western states has become increasingly well known, little information has been published on the composition and mineralogy of the altered ash falls. Since Nelson (1921) recognized the pyroclastic nature of thin beds of volcanic material intercalated with Paleozoic sediments at High Bridge, Kentucky, the altered ash or K-bentonite has been reported from Paleozoic units in New York, Pennsylvania, Virginia, West Virginia, Alabama, Tennessee, Missouri, Illinois, Wisconsin, Minnesota, Michigan and Ontario. Ross (1928) proposed the term metabentonite for these altered volcanic ash deposits. Since, as Weaver (1953) points out, these materials are frequently not metamorphosed, they are not metabentonites. He suggests use of the term K-bentonite for these deposits.

The evidence for volcanic origin of these horizons has been cited by a number of workers, following Nelson's original interpretation. Allen (1922) offers as proof of volcanic origin that textures characteristic of volcanic

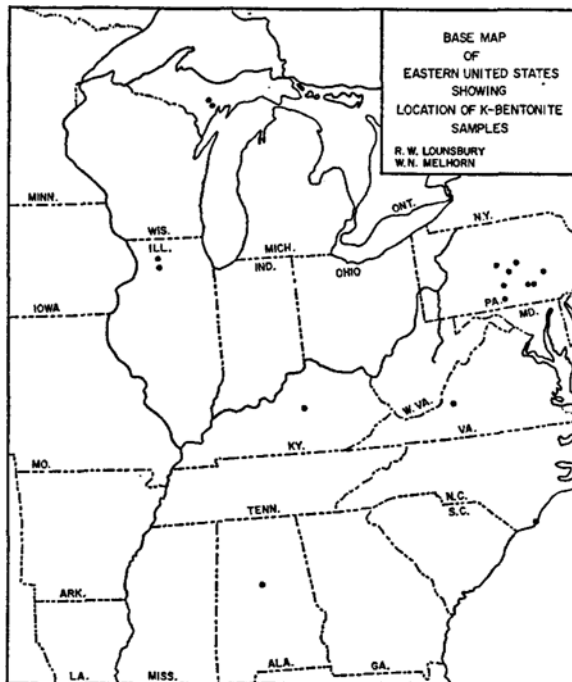


FIGURE 1.—Base map.

tuffs have been retained. Pumice fragments with elongate vesicles are present in deposits south of St. Louis. At Decorah, Iowa there are crescent-shaped shard structures preserved in the Ordovician ash bed, according to Allen. He notes the presence of sanidine, euhedral zircon and apatite in all samples, suggestive of volcanics. Weaver (1953) comments on the presence of volcanic glass, biotite, euhedral apatite and zircon in support of the igneous nature of Ordovician material from Pennsylvania. In describing the Devonian Tioga ash bed of Pennsylvania, Weaver (1956) points out the presence of biotite, euhedral zircon and apatite in the heavy mineral suite, which are commonly of volcanic origin.

The vast areal extent of Paleozoic K-bentonite derived from ancient volcanic ash made it possible to gather samples from widely separated areas for comparison. In the present study samples were obtained and examined from localities in Alabama, Virginia, Kentucky, Pennsylvania, Michigan and Illinois, from rocks ranging in age from Ordovician through Devonian. Other specimens from Tennessee, Wisconsin, Minnesota, Iowa, Missouri and New York will be studied in a continuing phase of the present work. Figure 1 shows the locations of the samples studied in this phase of the current work.

In the field these altered ash beds are usually a few inches and less than 1 ft thick. Interbedded with thick carbonate rocks, the K-bentonite layers generally cause a recess in the rock outcrop owing to their inferior resistance to weathering. In outcrop these fine-grained materials vary in color from white and gray to tawny yellow, and may have a waxy luster.

CLAY MINERALS OF THE K-BENTONITES

Allen (1932) reported that the clay mineral of the Missouri metabentonite is similar to montmorillonite but has less water and about 4.57 per cent K_2O . In examining this material, Kerr concluded that it was different from montmorillonite, and it was termed potash bentonite. Bradley (1945) suggested that K-bentonite is mixed-layer illite-montmorillonite. In studying 22 K-bentonite samples and insoluble residues of related limestones from Pennsylvania, Weaver (1953) reported random interstratified expanded and non-expanded 2:1 clays in a 1:4 ratio. He noted the presence of chlorite packets and suggested a direct relation between K content and the amount of non-expanded layers (illite) present. In a later study of the Devonian Tioga horizon in Pennsylvania and its K-bentonite (1956), he concluded that the clay content is similar to Ordovician K-bentonite and consists of interstratified illite-montmorillonite in 4:1-3:1 proportions.

In the current phase of this work, K-bentonites of Ordovician, Silurian, and Devonian age were studied by petrographic, differential thermal and X-ray analyses. In general the results of these analyses show that the

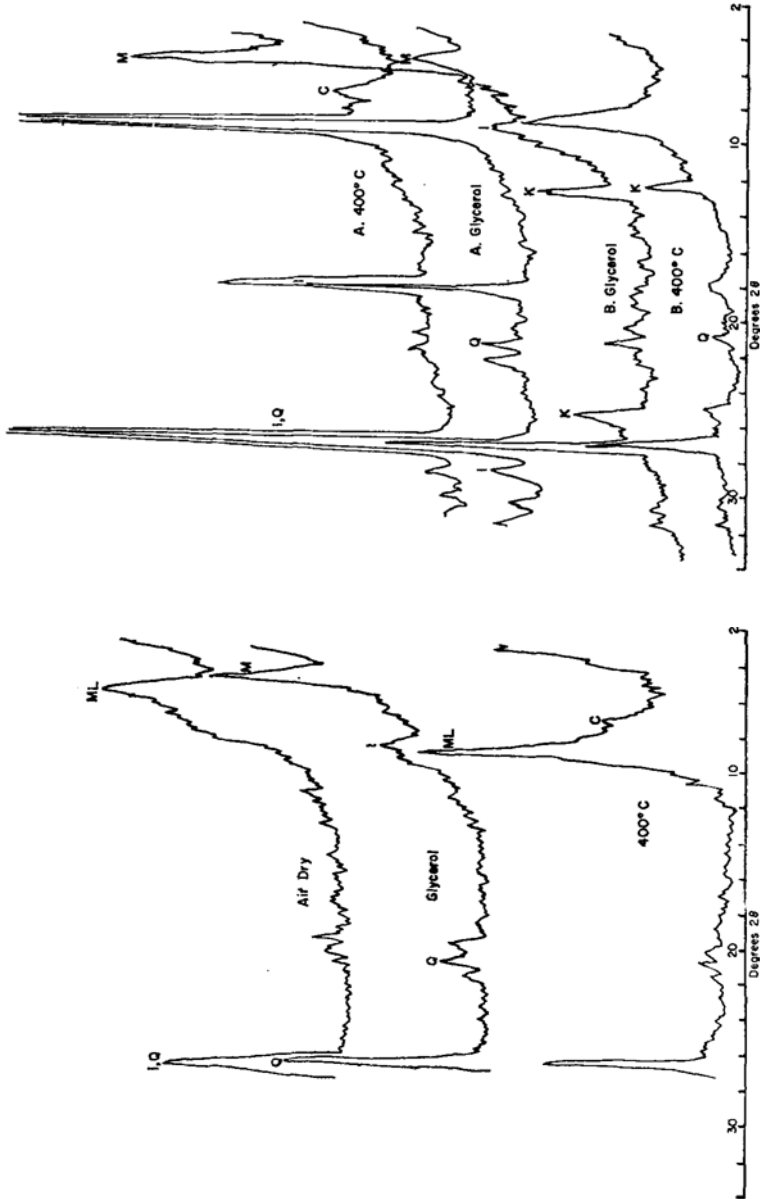


FIGURE 3.—Diffractometer traces of K-bentonite from: A, Evansville, Pa., Ordovician; B, Bixler, Pa., Devonian Tioga Horizon. I, Illite; C, Chlorite; M, Montmorillonite; Q, Quartz; K, Kaolinite.

FIGURE 2.—Diffractometer traces of K-bentonite from Birmingham, Alabama, Silurian Clinton Formation. I, Illite; M, Montmorillonite; ML, Mixed Layer Illite-Montmorillonite; Q, Quartz.

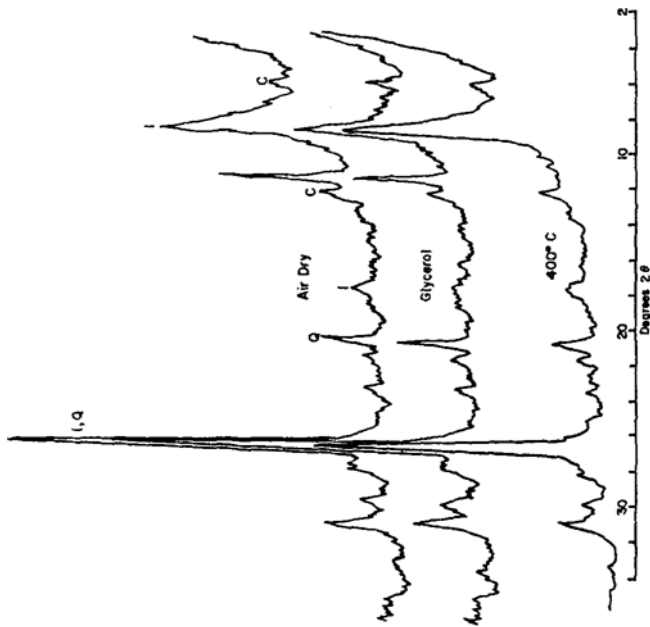


FIGURE 4.—Diffractometer traces of K-bentonite from Cornell, Escanaba River, Michigan, Ordovician Black River Group. I, Illite; C, Chlorite; Q, Quartz

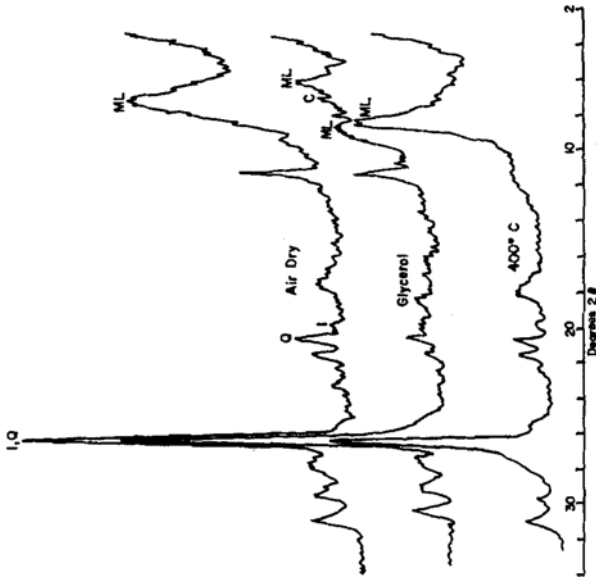


FIGURE 5.—Diffractometer traces of K-bentonite from Dixon, Illinois, Ordovician Galena Formation. C, Chlorite; ML, Mixed Layer Illite-Montmorillonite; Q, Quartz.

K-bentonites from selected localities indicate a clay mineralogy similar to those described by Weaver.

All samples contain illite, and chlorite is present in a few of the specimens. About half of the samples have mixed-layer illite–montmorillonite, and montmorillonite is readily identified in K-bentonites from some localities, Huff (1963) reports the same minerals in K-bentonites of Kentucky, but found no chlorite in these samples.

Figure 2 shows the diffractometer traces of K-bentonite from the Silurian Clinton formation at Birmingham, Alabama. The untreated sample has a broad peak from the mixed layer clay at 14.9 Å. On glyceration a montmorillonite peak at approximately 18 Å, and a poorly defined illite peak at 10 Å appear. The illite peak is reasonably distinct from montmorillonite scattering at only slightly larger angle. Heating to 400°C collapses the montmorillonite, and a single peak at approximately 10Å is produced for the mixed illite–montmorillonite layers. The samples illustrated by Fig. 3 from Evansville and Bixler, Pennsylvania, closely approximate the clay mineralogy of the Birmingham sample, and provide similar results when treated with glycerol and heated to 400°C. These samples were collected from an Ordovician formation and the Devonian Tioga unit respectively. The chief differences in the mineralogy of the K-bentonites are the presence of chlorite in the Evansville specimen and kaolinite in the one from Bixler.

K-bentonites from the Northern Peninsula of Michigan to Illinois have similar clays, although the mixed-layer material is not as evident in some specimens as others. Examples of their X-ray diffraction patterns are shown in Figs. 4 and 5. Most samples contain chlorite. The altered volcanic ash collected near White Pines State Park north of Dixon, Illinois, is characteristic of the clay mineralogy of this region. Untreated clay of this specimen shows a broad mixed-layer peak at 11.7–12.6 Å from which on glyceration, poorly defined illite and montmorillonite peaks are only doubtfully distinguished from the more important mixed-layer scattering. The expansive clay collapses on heating and a single peak appears at 10 Å.

A constituent which has a *d*-spacing of approximately 7.6 Å is present in all of the samples from Michigan to Illinois. It is suggested that this constituent may have regional significance, because it seems to be confined to the altered ash falls of the upper Mississippi valley. The identity of this constituent has not been definitely ascertained, but some lines of evidence described in the next section suggest that it may be gypsum or some other hydrate.

Samples from Kentucky and Virginia contain expansive material in the clays. In addition to illite, about half of the specimens from Pennsylvania contain chlorite. Some have small amounts of mixed-layer illite–montmorillonite, but in others the evidence for expansive material is lacking.

DISCUSSION

The evidence for the volcanic origin of the thin seams of K-bentonite in midwestern and eastern Paleozoic rocks appears to be substantiated by the euhedral volcanic minerals present and volcanic structures retained during alteration of the ash to clay minerals. Alteration of the volcanic minerals and later changes in the resulting clay minerals have apparently taken place in the depositional marine carbonate environment and in post-depositional alterations. The presence of brachiopod layers in the tops of ash zones and the enclosing dolomite and limestone beds attest to the marine depositional environment.

The occurrence of kaolinite in the Pennsylvania sample may have been produced by weathering during fairly recent geologic time.

The clay of the altered ash probably formed from volcanic glass. Some workers have postulated the formation of mixed-layer illite-montmorillonite in the depositional environment. Weaver (1953) suggests that the montmorillonite, originally resulting from glass alteration, adsorbed K ions from sea water to produce non-expanding illite (about 80 per cent of the mixed-clay layers), and this appears consistent with the observed proportions of illite and montmorillonite in the altered ash. Huff (1963) also concluded that the Kentucky K-bentonites contain clays that were basically montmorillonite which have undergone partial contraction due to the adsorption of potassium.

The material with a *d*-spacing of 7.6 Å found in the upper Mississippi valley K-bentonites is apparently characteristic of this region, and was not detected in samples from other localities in this study. Most of the samples in this study are outcrop specimens including those of the Michigan-Illinois area, and surficial weathering effects are not excluded in evaluating the identity of this material. The sharp 7.6 Å peak disappears on heating the samples to 400°C. The substance may be gypsum or some other hydrate, and further study is being made of it. The reason for the apparent northern midwest regional distribution of this material is not certain. It may be linked to post-depositional weathering conditions peculiar to this area.

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