A STUDY OF MIDDLE ORDOVICIAN K-BENTONITES IN KENTUCKY AND SOUTHERN OHIO

A dissertation submitted to
The Graduate School
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1963

by

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A.B. Harvard College 1959

UNIVERSITY OF CINCINNATI

August 13 19 63

I hereby recommend that the thesis prepared under my supervision by WARREN DAVID HUFF

entitled A STUDY OF MIDDLE ORDOVICIAN K-BENTONITES IN KENTUCKY AND SOUTHERN OHIO

be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

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Form 668—Grad. Sch.—1M—4-61

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ABSTRACT

K-bentonites are the altered remnants of Paleozoic volcanic ash deposits found throughout much of the eastern United States. The present study is concerned with deposits occuring in rocks of middle Ordovician age in southern Ohio and central and northern Kentucky. Here, two prominent horizons are noted which appear equivalent to more numerous zones in rocks of the same age further to the east. As volcanic ash falls represent essentially an instant in geologic time it is desirable to find out what correlation parameters are present in them that can increase their usefulness in long range stratigraphic work.

In addition little is known about the nature of the K-bentonites themselves, except that they are composed predominantly of a mixed-layer, dioctahedral, illite-montmorillonite clay with minor amounts of volcanic minerals. Further information relating to the source of these deposits is also desired for purposes of more clearly outlining the paleogeographic setting of this region during the middle Ordovician.

The present study shows the clay portion of the beds to be composed of a randomly interstratified mixed-layer clay resulting from the adsorption of potassium by a 2:1 montmorillonite-type lattice during the early stages of ash devitrification. The resultant collapse of 60-70% of the swellable layers produced a mixture of mica-like

structures and expandable montmorillonite layers which cannot be separated by mechanical methods. Anomalous base exchange data plus additional thermal and electron microscope data are best accounted for by assuming high octahedral substitution and low tetrahedral substitution in the basic lattice. Coupled with a recent re-definition of the controlling factors in the fundamental mica stage in a diagenetic continuum between montmorillonite and illite, but rather are confined to a narrow range of composition between but separate from them. Accordingly, it is proposed that any general structural-chemical classification of clay minerals should provide separate status for this particular type of clay.

Insoluble residue studies show a rapid decrease in volcanic constituents within limestones adjacent to K-bentonite zones. The accumulation of chert above and below the zones is attributed to the release of silica during post-depositional devitrification.

Concentrated biotite within the uppermost horizon studied serves as the only indigenous parameter so far available for directly correlating any of the K-bentonite zones. It is suggested that quantitative trace element work holds the most promise in this respect.

X-ray fluorescence analysis of titanium in the high biotite horizon shows an increasing trend in concentration toward the south and is correlated with previous interpretations of a southeasterly source for the original volcanic material.

INTRODUCTION

Altered volcanic ash or bentonite is commonly recognized throughout the western United States in rocks of Cretaceous and Tertiary age. The primary component in these deposits is montmorillonitic clay with attendant minor amounts of volcanic glass shards and numerous heavy minerals commonly associated with rocks of volcanic origin. Beds of similar appearance are reported in rocks of Ordovician, Silurian, Devonian, and Pennsylvanian age. Ross (1928) lists the criteria for recognition of these older beds as, "presence of glass relict structure, presence of minerals and crystal forms characteristic of volcanic rocks, absence of minerals that do not have a volcanic origin in the same specimen, waxy luster, slaking reaction to water, and certain optical and chemical properties."

Paleozoic volcanic ash beds east of the Mississippi River were first described by Ulrich in 1888 and then examined in more detail later by Nelson (1922), especially in Tennessee, Kentucky, and Alabama. Nelson estimated that the bentonite horizon at the top of the Carters limestone of Lowville age extended over a three hundred thousand square mile area representing deposition that was essentially instantaneous in geologic time, thus providing ideally a time-stratigraphic marker more accurate than any faunal zone. Nelson cited the northernmost extent of the bentonite

as Highbridge, Kentucky, but suggested that further work might reveal its presence in Ohio and Indiana.

Later investigation by Bonnie and Honess (1929), Rosenkrans (1933), and Kay (1931, 1935) substantiated the existence of several ash beds within the same general stratigraphic interval in southern and western New York, southern Ontario, Vermont, Pennsylvania, Virginia, and Georgia, while Allen (1932) and Sardeson (1924) described Lowville bentonite from Iowa, Missouri, Wisconsin, and Minnesota. Ross (1955) and Allen (1932) further suggested the same beds might be found in Michigan, Oklahoma, Arkansas, Louisiana, and Florida, in view of the widespread distribution of middle Ordovician limestone and the conditions necessary for preservation of finely divided volcanic ash.

Initial chemical, X-ray, and optical analyses made by Kerr (personal communication in Ross, 1928) and later by Ross and Hendricks (1945) established the presence of clay minerals of the montmorillonite group, namely montmorillonite, beidellite, and "probably a third unnamed clay mineral" rich in potash, with montmorillonite being the dominant constituent. Subsequent study by Bradley (1945) suggested the unexplained clay mineral mentioned by Ross was easily accounted for if the entire clay component of the bentonite was considered in terms of a randomly interstratified, dioctahedral "illite"-montmorillonite structure with non-expandable "illite" forming

the major portion. This differs significantly from those bentonites of Cretaceous and Tertiary age in the western United States which are entirely montmorillonitic in nature. A concluding suggestion was made by Bradley (1945) that some sort of diagenetic adsorption of non-exchangeable potassium in the interlayer position of the clay lattice would cause a collapse of the swellable layers in a non-uniform or random sequence resulting in an "illite"-type structure interlayered with expandable montmorillonite layers. This type of cation "fixation" would probably be a secondary feature in the devitrification process undergone by the volcanic ash since consideration of the ionic potentials of calcium and potassium would require the preferential adsorption of calcium in a carbonate environment. However, with a sufficient concentration of potassium a reverse replacement could occur.

Ross(1928) realized that several Ordovician bentonites in Virginia had indeed undergone slight metamorphism subsequent to deposition, and so proposed the term "metabentonite" to distinguish those beds where additional compaction and alteration along bedding planes had occured. Supposedly, the less competent bentonite zones had served as "lubrication" planes during periods of folding and low-grade metamorphism toward the end of the Paleozoic. Unfortunately, although "metabentonite" was intended to apply only to these unique circumstances (personal communication, 1962), it nevertheless has been widely

adapted in the literature as a name for any occurence of potassium-rich altered volcanic ash.

Recently Weaver (1953) has re-examined samples of Ordovician bentonite and associated limestones in Pennsylvania in the light of modern knowledge and techniques and has produced constructive suggestions regarding the structure and formative processes of Paleozoic bentonites. He points out that the collapse of expandable montmorillonite layers due to interlayer adsorption of potassium accounts for what many earlier workers had misconstrued as metamorphism and that consequently the term "metabentonite" should be abandoned in the literature in favor of "K-bentonite" or "potassium bentonite." Using recent experimental data Weaver calculates the ratio of "illite" to montmorillonite-type structural layers at approximately 4:1.

Purpose

The present study was undertaken to investigate the occurence of middle Ordovician K-bentonite in southwestern Ohio and northern and central Kentucky with the following objectives in mind:

1. To determine what chemical and physical properties of either the bentonite clays or their related minerals could be usefully employed as stratigraphic parameters for medium or long-range correlation.

2. To investigate the bentonitic clays for structural features that might add further to the present knowledge of clay mineral types.
3. To initiate further study relating to the problem of the origin of Ordovician ash beds in terms of source area and in terms of post-depositional physical and chemical changes.

ACKNOWLEDGEMENTS

The writer is indebted to Dr. Ronald G. Schmidt and to Dr. Frank L. Koucky of the Geology Department of the University of Cincinnati for their guidance and constructive advice during the preparation of this thesis.

Procter and Gamble Laboratories in Cincinnati kindly made available the facilities of their electron microscope and the U.S. Corps of Army Engineers in Mariemont, Ohio, through Mr. Dan Keller of the Geology Department, gave unlimited access to differential thermal analysis equipment.

Grateful acknowledgement is also made to Earth Science Laboratories in Cincinnati, to the Cincinnati Gas and Electric Company, and to the State Geological Surveys of Ohio and Indiana for providing core samples used in the study.

Stimulating discussions with Dr. C. S. Ross of the U. S. Geological Survey, Dr. W. F. Bradley of the University of Texas, and Dr. R. E. Grim and Dr. Michael Wahl of the University of Illinois were invaluable.

Finally, thanks are extended to Mr. Gerald Cinnamon for assistance in the field and to the entire faculty and graduate student body of the Department of Geology at the University of Cincinnati for many helpful suggestions and criticisms.

GEOLOGY OF K-BENTONITE IN THE AREA OF STUDY

The areal distribution of sample localities is shown in figure 1. With the exception of the collection sites south of Lexington, Kentucky, and those at Frankfort, Kentucky, all specimens were obtained from recently drilled cores. The sorption properties of montmorillonite render bentonites highly susceptible to ground and surface water contamination making fresh core samples preferable to those collected from outcrops. Exposures in recent road cuts, new quarries and the like, however, often prove adequate.

The K-bentonites vary from ½ inch to 32 inches in thickness but average about 6 to 8 inches. Although the lateral extent of upper Black River K-bentonites has not been delineated in the eastern interior, investigations of fresh drill cores from northern and central Indiana and discussions with gas and oil company employees suggest that the K-bentonite horizons in this stratigraphic range become much thinner in south-central Indiana and are absent west of Bloomington. Similarly they are absent north of Fort Wayne and are unknown in the Michigan Basin.

Lithologically, K-bentonite consists predominantly of very fine-grained clay matrix which in fresh samples is hard, blocky, and often breaks with a conchoidal fracture. Occasionally, a crude stratification is produced by bands of concentrated biotite and other heavy minerals. K-bentonite varies in color

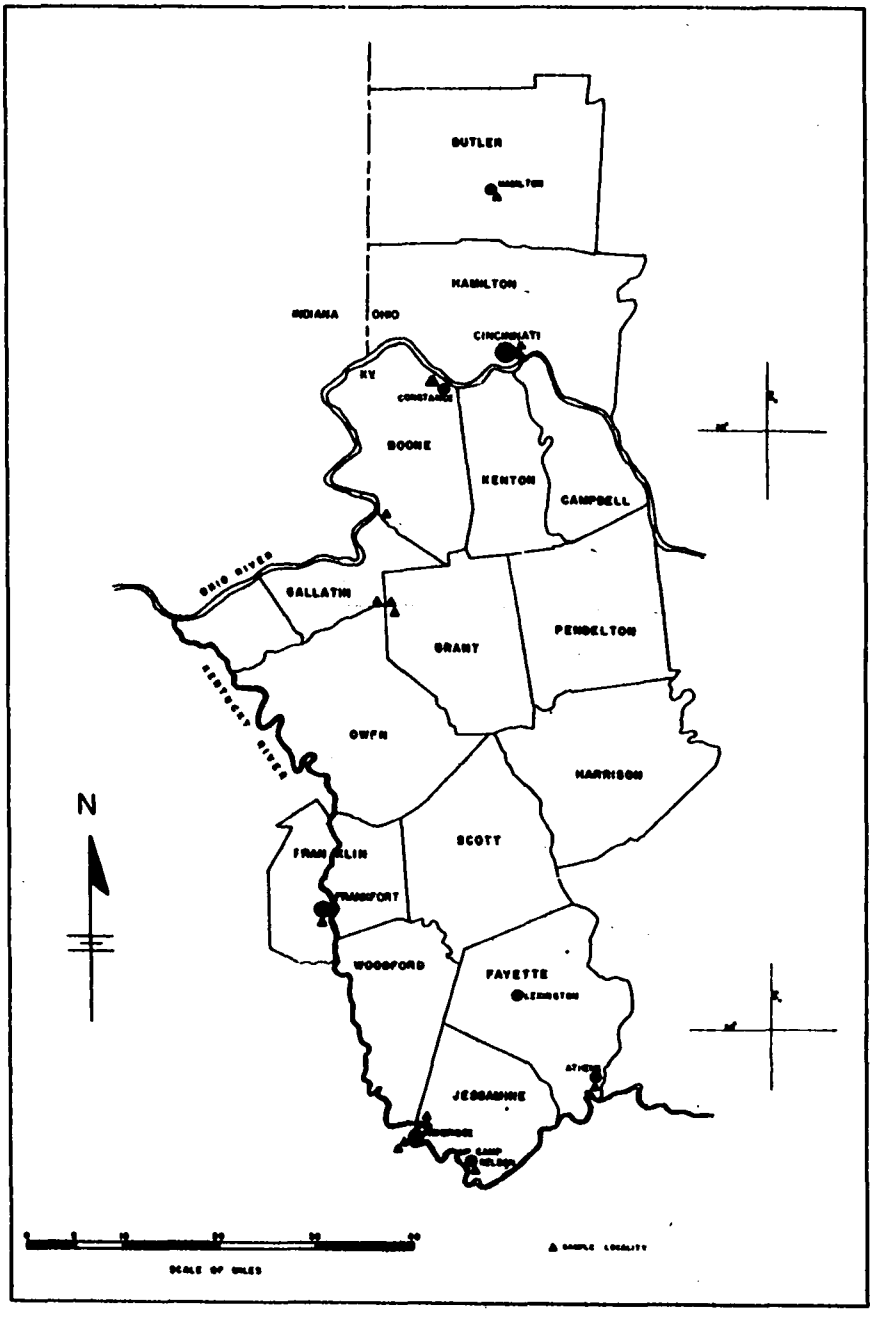

Figure 1. Map showing distribution of sample localities

from a dark grayish green through greenish gray to light gray and even a light tan in some instances. Horizontal color zonation does occur within one particular horizon of K-bentonite but forms no consistent pattern that is everywhere recognizable. An X-ray fluorescence spectrography study shows that the dark green clays have a higher iron content than the lighter colored ones.

Stratigraphy

Two prominent bentonitic horizons are recognized in outcrop and in the subsurface near the contact between middle Ordovician rocks of Trenton and Black River age throughout much of the eastern midcontinent. Figure 2 shows diagrammatically the lateral relationships of these rocks in the study area. The upper Black River Tyrone (upper Lowville) limestone in central Kentucky and southwestern Ohio is a massively bedded, dense, fine-grained, dove- or cream-colored, sub-lithographic, limestone with small nodes of coarsely crystalline "birdseye" calcite. Its total thickness is about 85 feet. On weathering the surface turns white, in which the darker nodes are conspicuous, giving rise to the name "birdseye" limestone. Figure 3 is a columnar section of middle Ordovician rocks in Kentucky, after MacFarlan (1943).

Rare recognizable fossils in the Tyrone, listed by MacFarlan (1943), include "Strophomena" incurvata, "Orthis" tricenaria, Rhinidictya nicholsoni, Phyllodictya frondosa,

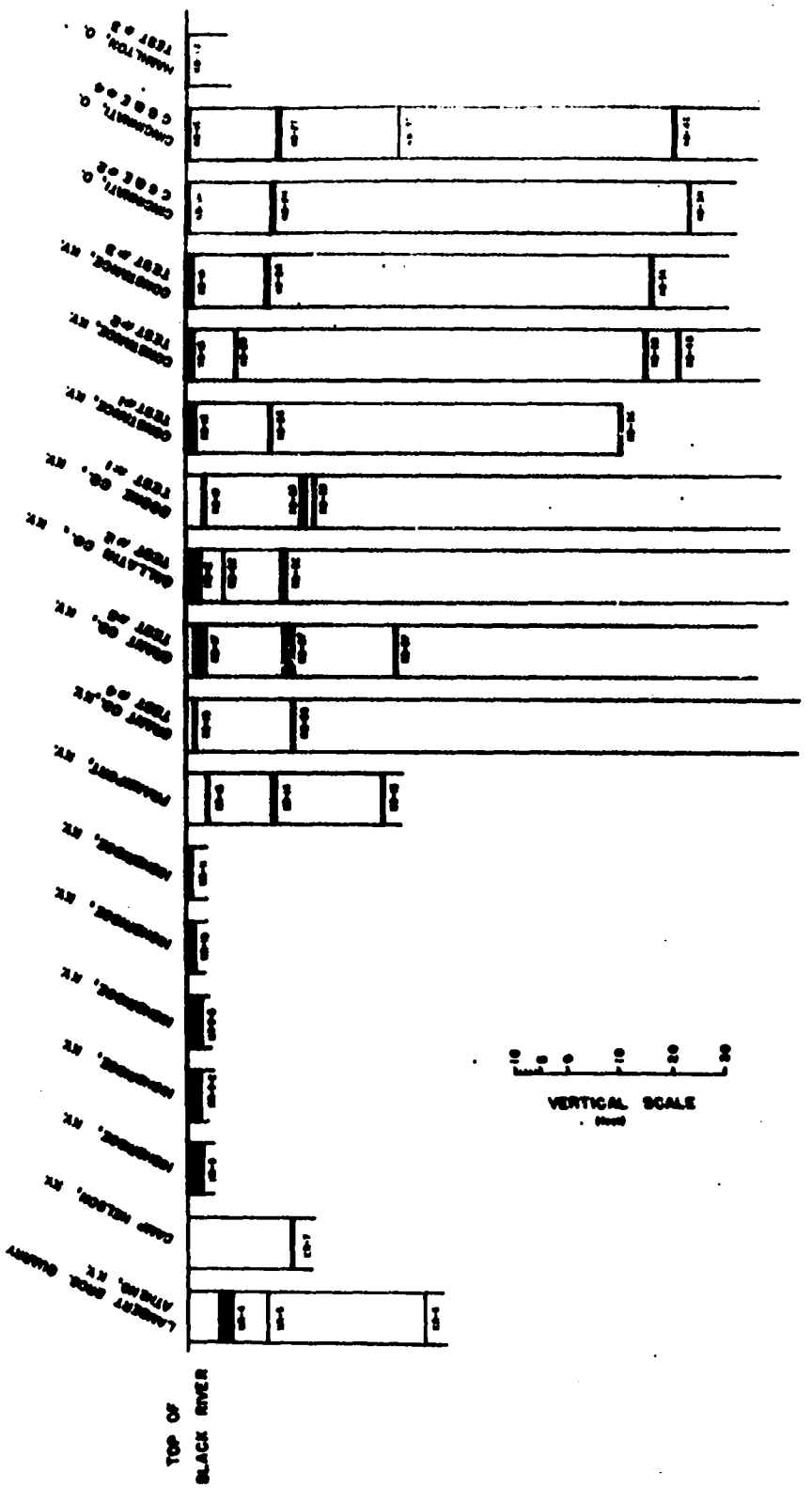

Figure 2. Correlation of K-bentonites in the study area.

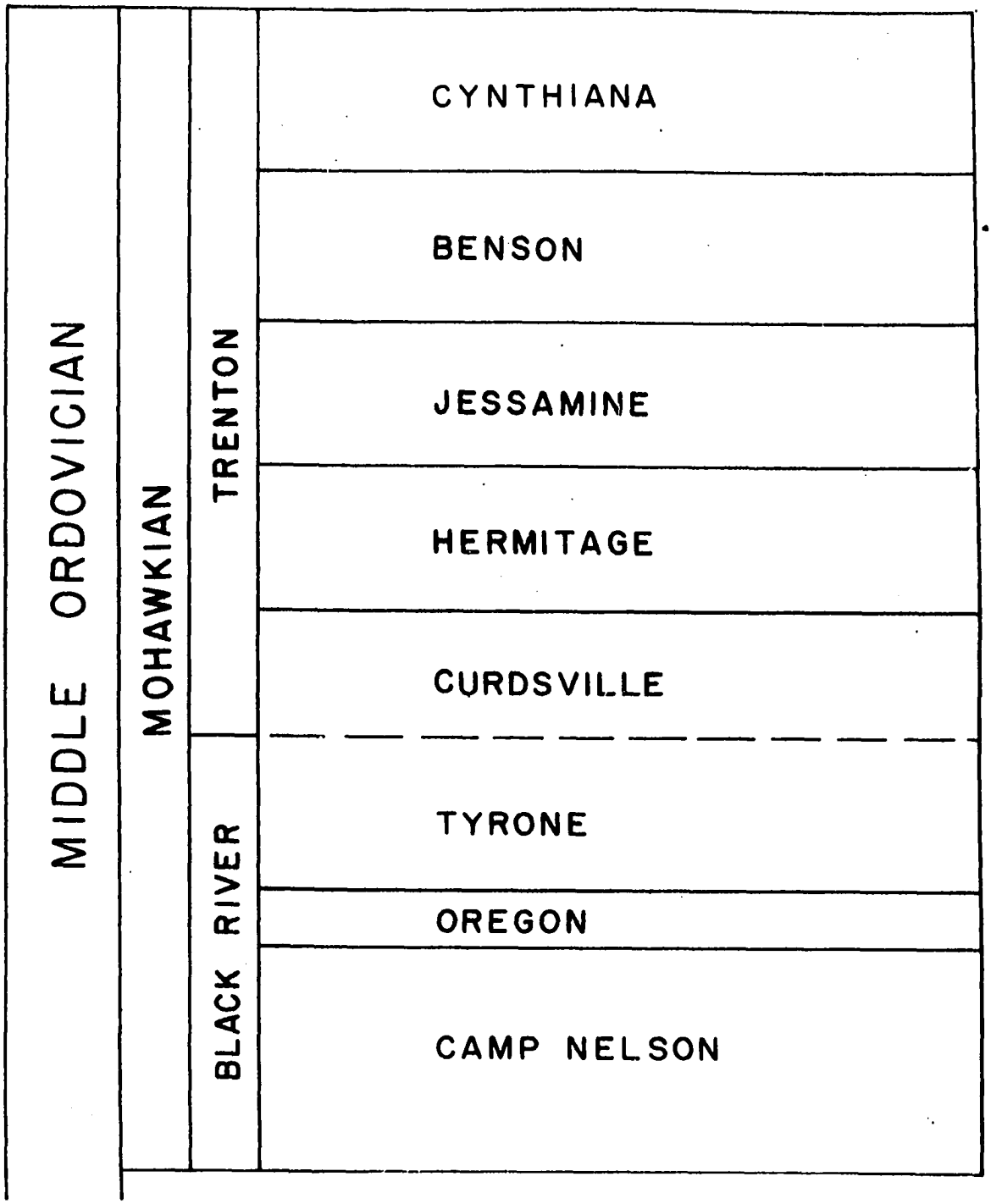

Figure 3. Middle Ordovician section in central Kentucky. (after MacFarlan, 1943)

Escharopora ramosa, Leperditia fabulites, Tetradium cellulosum, and the cephalopods Endoceras, Actinoceras, and Cameroceras.

Within the upper five feet of the Tyrone lies a fairly persistent K-bentonite horizon ("Mud Cave") varying from 32 inches thick in central Kentucky to about 6 inches in southwestern Ohio. This horizon is exposed in a railroad cut at the A.P.I. Project 49 reference locality (Kerr, et al, 1951) south of Highbridge, Kentucky, and in numerous other railroad cuts in that vicinity. Thickness data should be taken with some caution however, since local concentrations and attenuations, presumably a result of current action following deposition, are common. For instance the 21 inch K-bentonite (KR-4) at the top of the Tyrone at Lambert Bros. Quarry near Athens, Kentucky, (Fayette Co.) is absent entirely in an abandoned quarry at Camp Nelson, Kentucky, only to reappear again in its thickest outcrop at Highbridge (KR-10).

A second prominent K-bentonite found 15 to 20 feet below the top of the Tyrone is known as the "Pencil Cave" in central and western Kentucky and serves as a consistent marker horizon for drillers in that are. This bentonite was described by Ulrich (1888) and Nelson (1922) and is generally correlated on the basis of stratigraphic position with a similar zone at the top of the Carters limestone in Tennessee.

Above the Tyrone limestone in Kentucky lies the Curdsville limestone (figure 3) whose coarsely crystalline texture, medium to heavy bedding, and locally abundant chert

stand in marked contrast to the rocks below. Thickness is about 20 feet. Characteristic fauna include "Orthis" tricenaria, "Dinorthis" pectinella, Rhynchotrema subtrigonale, "Streptelasma" profundum, and "Sowerbyella" curdsvillensis. A similar sequence is recognized in the basal Hermitage (middle Ordovician) of central Tennessee (MacFarlan, 1943).

The relationship between the Curdsville and Tyrone, however, is not always obvious. MacFarlan (1943) reports a local basal "conglomerate" in the Curdsville incorporating Tyrone fragments while in other places, both outcrop and drill cores, the contact appears to be a gradational one.

Several K-bentonite horizons are known in lower Trenton rocks in Pennsylvania and New York (Weaver, 1953; Kay, 1935) but are virtually unknown in Kentucky and Ohio. Young (1940) has reported one horizon about 25 feet above the top of the Tyrone in the upper Curdsville, but this was not sampled in the present study.

A tendency to recognize only one K-bentonite zone at any particular stratigraphic horizon has led to extremes in long-range correlation (Kay, 1931). However, as interest in the stratigraphic value of K-bentonite was aroused and more field studies were made, it became increasingly evident that such horizons were more numerous than had originally been observed. Recent studies show 16 K-bentonites in the middle Ordovician of central Pennsylvania (Weaver, 1953), and similar multiple zones within the same stratigraphic interval in

Tennessee (Caldwell, 1936), New York, and Ontario (Kay, 1935).

The occurence of upper Black River K-bentonites in the subsurface of the Cincinnati region provides an interesting opportunity to study the various properties of two distinct horizons whose stratigraphic separation over a distance of 100 miles or more appears sufficiently consistent to provide reasonable confidence in selecting isolated samples from the same layer. This same stratigraphic section in Pennsylvania and New York is characterized by numerous K-bentonite zones whose correlation even over short distances presents many problems. The same seems to be true for the Tennessee section. It would be hoped then, that information gained from these studies could be applied to the more complex situations to the east and possibly enhance their value as stratigraphic markers.

Correlation by K-bentonite in Ordovician rocks has in the past been based primarily on "megascopic" features (Whitcomb, 1932) such as number of bentonites found in a single formation, distance between beds or distance of beds above or below some surface, thickness of individual beds of bentonite, relationship to known faunal zones, and presence of adjacent rock strata a-typical of the section. However, these are found to be inadequate criteria for accurate identification of individual beds, and so an attempt must be made to search for new and more definitive parameters.

EXPERIMENTAL DATA

Structural Features As Revealed By X-ray Analysis

X-ray diffraction and fluorescence spectrography serve as invaluable tools in analyzing and interpreting variations in the atomic geometries that characterize various minerals having a common structural and chemical foundation. The principles of X-ray diffraction and its application to crystal structure analysis are well outlined in the literature (Sproull, 1946; Buerger, 1958) and will not be given more than a cursory treatment here.

In ordinary diffraction work, mineral specimens are ground into a fine powder and mixed with an adhesive, usually a quick-drying household cement, and placed on a glass slide. The accuracy of diffraction maxima here depends primarily upon the degree to which random orientation of individual particles of sample in the path of the X-ray beam is achieved. If these particles are not so oriented, then preferential intensity of reflections will occur for those particles having a sub-parallel alignment and intensities of maxima will not be strictly related to the true structural properties of the sample.

Clay minerals present just such a problem. The pronounced basal cleavage of the layer-lattice silicates results in a plate-like form for even the smallest clay particles, and attempts to prepare even a moderately randomally oriented

specimen entail great difficulty (Grim, 1953). Consequently, use is made of the alignment tendencies of clays by preparing oriented aggregates (Bradley, 1945). This method substantially enhances the intensities of the basal (00ℓ) reflections at the expense of the non-basal peaks. As might be imagined, there are both advantages and disadvantages inherent in this procedure. However, it does provide a workable, useful, and most importantly, a reproducible method for clay mineral analysis. One will find that the classifications of micas and clay minerals are based upon information provided by the various sequences of basal reflections obtained from them.

Classification of Clay Minerals

Clay minerals are hydrous layer-lattice silicates belonging to the general subgroup of phyllosilicates. In most works on sedimentary petrography the term "clay" is used to define particles less than 1/256 mm in diameter or approximately less than four microns. However, when it is considered that the micas and clays are inseparably linked by common structures and chemistry, it can be seen that no such division on the basis of particle size alone is adequate. Mica flakes may occur in very large plates or as "clay size" particles intermixed with hydromicas and montmorillonite. One need only study the weathering history of muscovite or biotite to realize this is so.

Historically, classifications of clays have been based

upon structure, particle size, composition and physical properties such as water sorption, morphology, and compressional strength. Common practice among mineralogists today is to maintain a balance between structural and compositional aspects of clays with initial subdivision being based on the major structural differences, and only secondarily upon compositional variations.

One of the most significant contributions to the understanding of the structure of layer silicates was produced by Pauling (1930) in his analysis and derivation of the mica structure. Subsequent details which serve to further separate the numerous groups are reviewed and discussed by Grim (1953), Brown (1961), Brindley (1955), Weaver (1953), and Warshaw and Roy (1961).

The fundamental structural units of the layer-lattice silicates consist of a sheet of SiO_4 tetrahedra (fig. 4) interlayered in various proportions with sheets of brucite, $Mg(OH)_2$, or gibbsite, $Al(OH)_3$. Figure 4 illustrates the c-axis geometry of these units. The Si-O atoms are linked in tetrahedral coordination and the Mg^{+2} and Al atoms are in octahedral coordination. Al^{+3} atoms usually occupy a dioctahedral arrangement, that is, two out of the three possible cation sites in a structural repeat unit are filled, whereas Mg^{+2} commonly fills all three and hence is said to be in trioctahedral coordination.

The kaolin group is characterized by a 1:1 combination of Si-O and Al-OH layers. Si-O tetrahedra are arranged such

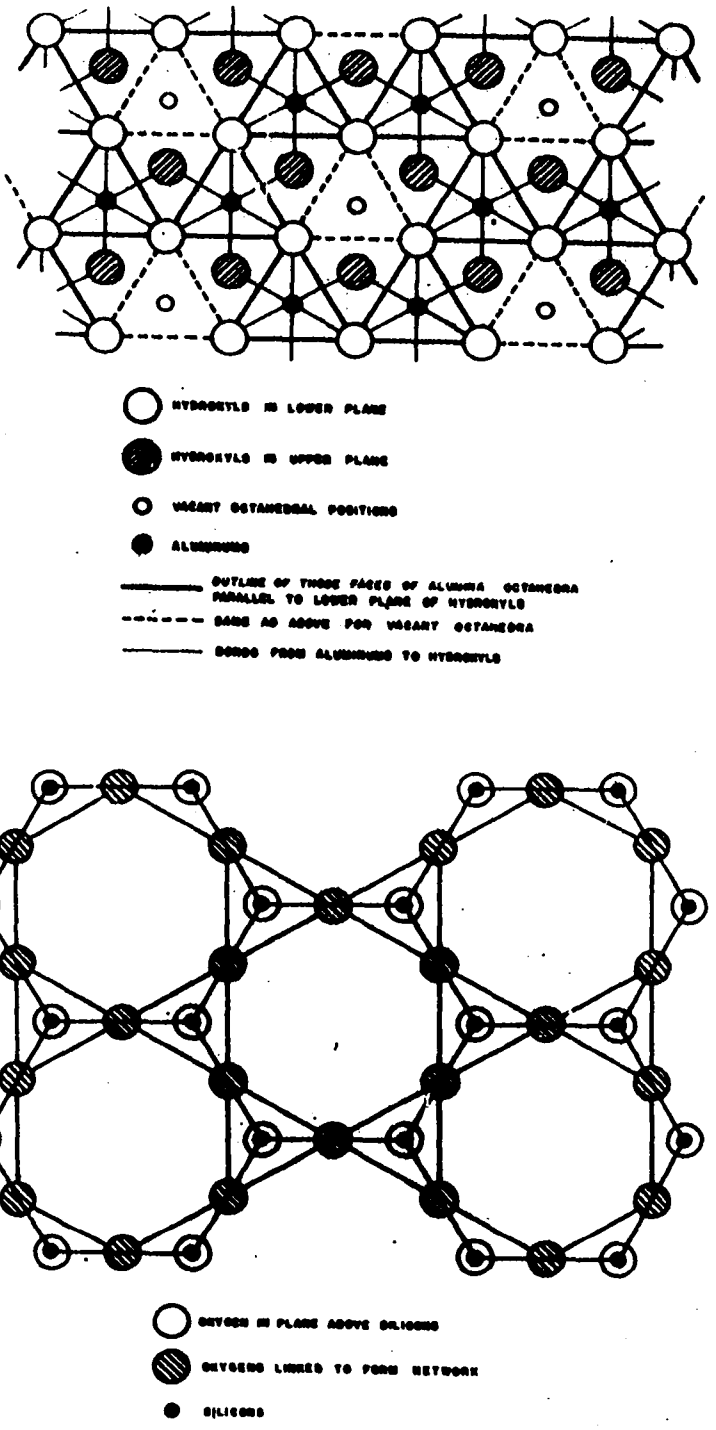

Figure 4. a-b plane configuration of the 2:1 tetrahedral (below) and octahedral (above) layers.

(Warshaw and Roy, 1961)

that all apices point "downward" and apical oxygens proxy for octahedral hydroxyls.

The muscovite-"illite"-montmorillonite group on the other hand consists basically of an octahedral Al-OH layer sandwiched in between the Si-O sheets with apical oxygens again substituting for octahedral hydroxyls (fig. 5). This 2:1 arrangement is further subdivided according to the types of interlattice substitutions (commonly Al^{+3} for Si^{+4} in the tetrahedral layer and Mg^{+2}, Fe^{+2}, Zn^{+2}, Ni^{+2}, and Li^{+} for Al^{+3} in the octahedral layer) which occur as a function of the environment in which the structures formed. As a result of unequal valence substitutions, such as Mg^{+2} for Al^{+3}, a negative residual charge remains in both octahedral and tetrahedral layers. This deficiency is to varying degrees satisfied by the adsorption of so-called exchangeable cations combined with water in the interlayer position (fig. 5) where only weak electrostatic bonds hold the sheets together.

Chlorites differ from montmorillonites in having a 2:1 sandwich of Si-O and Mg-O sheets with an additional Mg-O layer occupying the interlayer exchange position in place of exchangeable cations. Hence chlorite does not have the ability to vary the amount of interlayer water and produce an expandable lattice as does montmorillonite, but rather forms a "brittle" mica. In addition, substitutions in the octahedral layers are slightly different from those in montmorillonite. Chlorites are designated 4-layer or 3:1 layer silicates in most schemes of classification (table 1).

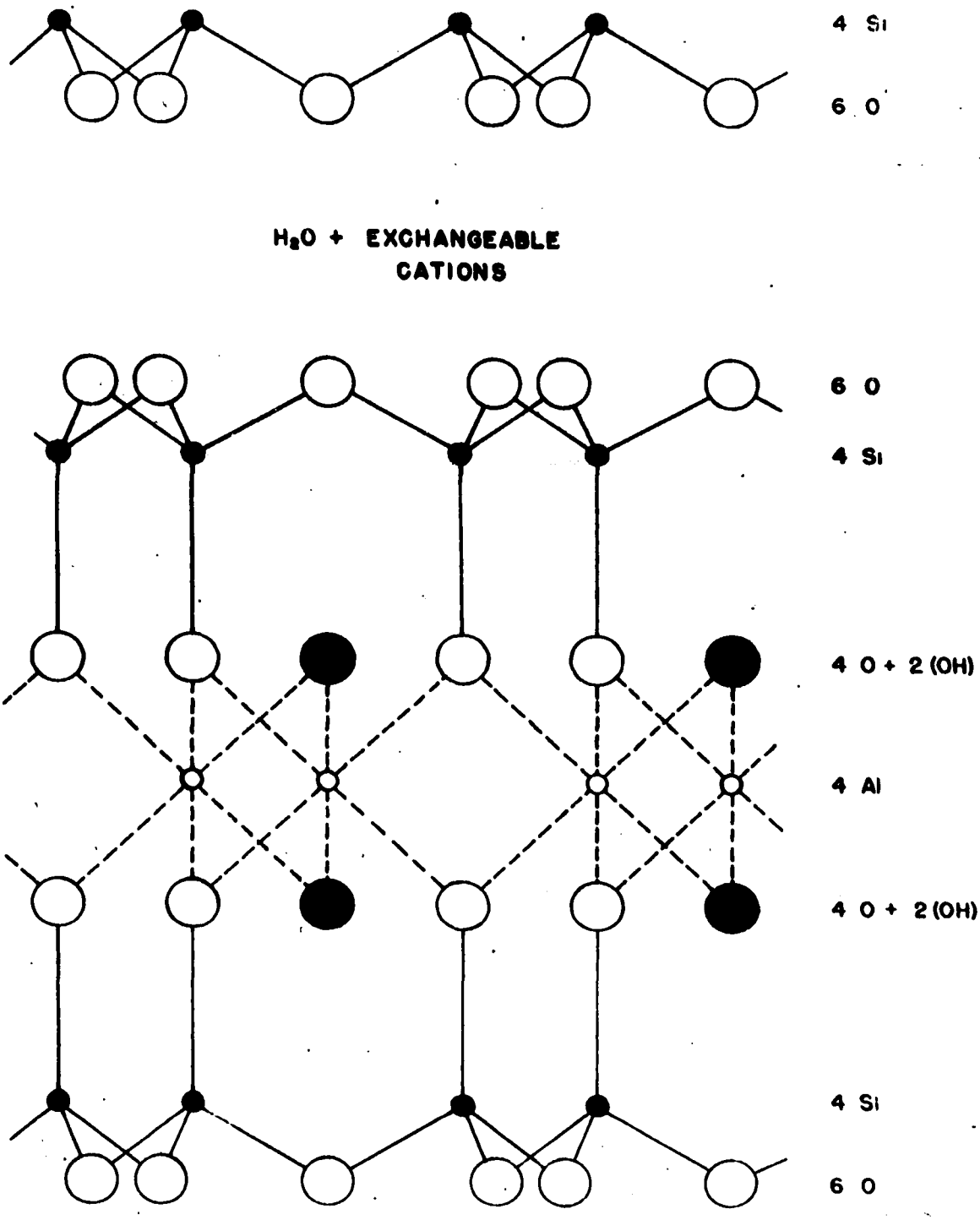

Figure 5. 2:1 structure viewed parallel to a-b plane.
(after Kerr, et al., 1951)

TABLE 1. PRINCIPAL GROUPS OF LAYER SILICATES

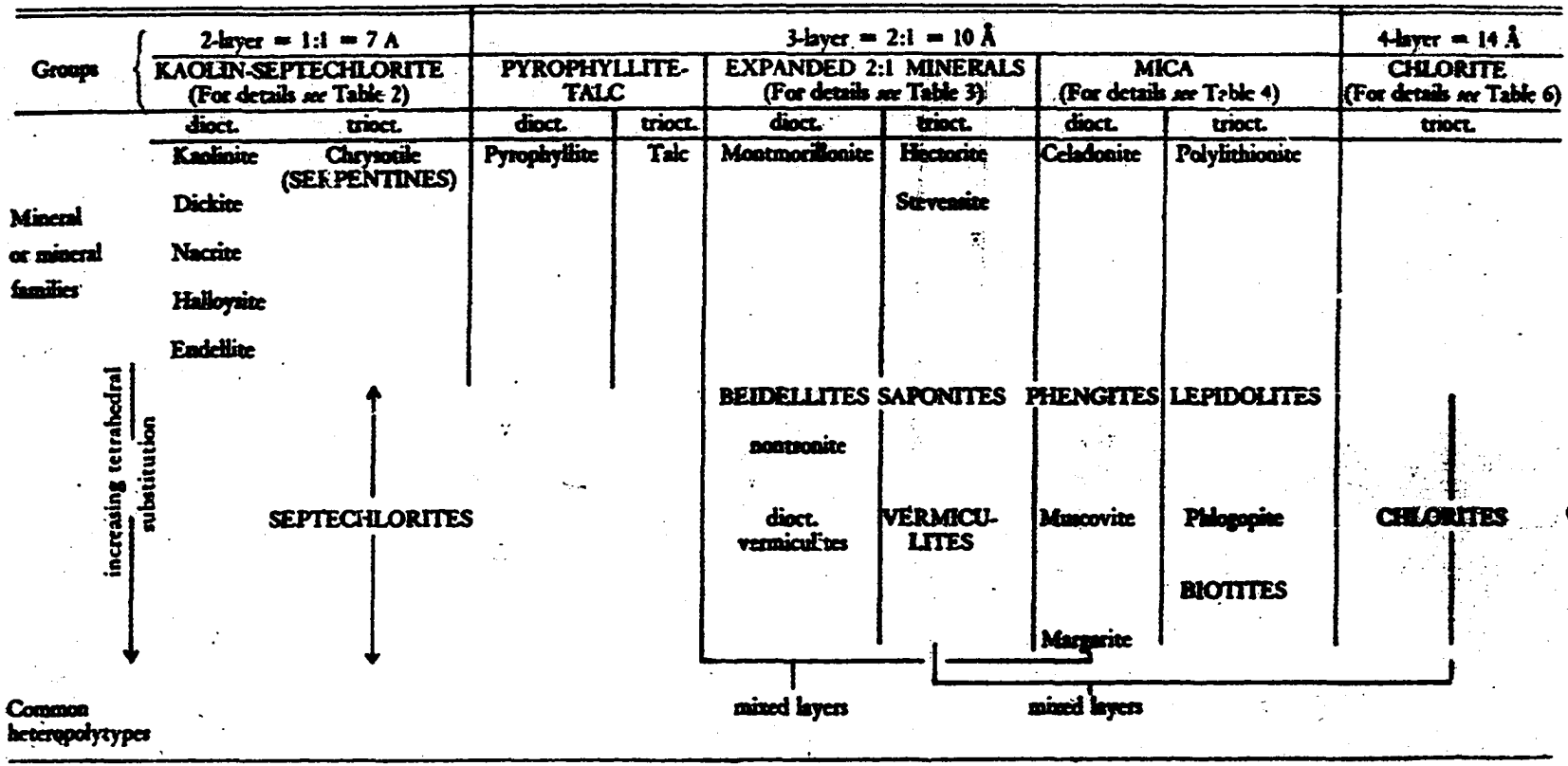

Table 1. (Warshaw and Roy, 1961)
(Instructions in parentheses refer to original publication)

Criteria For Recognition of K-bentonite by X-Ray Diffraction

Monomineralic clays produce a series of basal reflections in a definite integral sequence that is characteristic for each clay mineral type. As an example, "illite" has a prominent (001) peak at 10Å, (002) at 10/2 or 5Å, (003) at 10/3 or 3.3Å, (004) at 10/4 or 2.5Å, (005) at 10/5 or 2Å, and so on. These reflections are a function of the interplanar distance d and do not ordinarily vary for each particular clay type. Kaolinite (table 2) has a diagnostic sequence starting from 7Å and chlorite a series beginning at 14Å. Since the (002) reflection for chlorite falls at 14/2 or 7Å, the same as (001) for kaolinite, certain interpretative problems arise which are best solved by instituting a series of chemical and heat treatments whose reactions depend upon basic compositional and structural differences between the two clays (Warshaw and Roy, 1961).

In addition to the standard clay mineral groups, there exist certain mixed-layer structures which possess characteristics common to two or three separate clay species. Hendricks and Teller (1942) and Bradley (1945) describe the possible combinations that might exist. Generally all 2:1 clays may be thought of as essentially the same kind of structural sheet with different interlayer spacings being determined by the cations present in the exchange position, e.g., K^{+} = "illite", $(Mg,Al)(OH)_2$ = chlorite, Ca^{+2}, Na^{+}, Mg^{+2}, and H_2O = montmorillonite and vermiculite. In the case of the

non-mixed-layer clays, all exchange sites will be occupied by the same type of cation. However, if some layers contain K^+ ("illite") and others contain Ca^{+2} and H_2O (montmorillonite), a mixed layer structure is formed. Many mixed-layer clays exist and have been reported in the literature (Weaver, 1956). Common ones include illite-montmorillonite, illite-chlorite, chlorite-montmorillonite, chlorite-vermiculite, and illite-chlorite-montmorillonite.

Table 2. Diffractometer Spacings for Kaolinite, Illite, and Chlorite.

Kaolinite		Illite		Chlorite	
dÅ	I_{rel}	dÅ	I_{rel}	dÅ	I_{rel}
7.14	100	10.0	100	14.1-14.7	70-40
4.44	22	4.98	38	7.07-7.14	90
4.34	28	4.47	33	4.72	70
4.16	32	3.66	28	4.59	10
4.12	29	3.51	33	3.54	10-90
3.83	16	3.30	47	2.84	25-50
3.72	15	3.19	37		
3.57	73				
3.37	16				
(Kerr, et al, 1951)		(Kerr, et al, 1951)		(Brown, 1961)	

Basal reflections from mixed-layer clays produce anomalous patterns which for some time constituted a major enigma among clay mineralogists. However, the work of Hendricks and Teller (1942) and Bradley (1945) showed that mixed-layer structures were easily interpreted in terms of

their "end member" components and that many new mineral names which had been used to described these structures were not warranted.

Two kinds of mixed-layer structures occur in sedimentary rocks, those composed of regularly interstratified clays which produce basal reflections in an integral sequence and those composed of randomly interstratified layers producing a non-integral series. In both cases the (00ℓ) values are averages resulting from the combined reflections of the two end members. Since both layers produce scattering, the resultant maxima have positions intermediate between those normally characteristic of the different types and at a point that is proportional to the percentage composition of each. Actually, the position of the basal reflections is slightly more complicated by structure and polarization factors of the minerals as discussed by Bradley (1945), Hendricks and Teller(1942), and MacEwan, Amil and Brown (1961) in their development of the theoretical basis for the interpretation of interstratified clay minerals.

For both muscovite and "illite" a moderately high degree of Al^{+3} for Si^{+4} substitution in the tetrahedral layer produces a strong residual charge on the interlayer surface. Potassium satisfies a major portion of this charge by filling the interlayer sites and thus prevents any expansion through the addition of water. Dioctahedral montmorillonites for the most part have a much weaker surface charge density generated by replacements taking place principally within the octahedral layer.

Foster (1953) and Weaver (1958) point out a very important and fundamental difference between true montmorillonites and those dioctahedral 2:1 expandable clays derived from muscovite by the removal of interlayer potassium during weathering. Essentially, it is a difference between a greater tetrahedral substitution in micas and greater octahedral substitution in montmorillonites. True montmorillonites in this case refer to those 2:1 expandable clays derived from the breakdown of volcanic material or by other means and not simply degraded micas which have lost a portion of the binding interlayer cation population. Thus the seat of residual negative charge lies within the octahedral layer in the first case and within the adjacent tetrahedral layers in the second. This fosters a higher surface charge density for micas than for true montmorillonites and in part controls the degree to which interlayer cation adsorption takes place.

Oriented K-bentonite clay samples were run on a General Electric X-RD-5 diffractometer with nickel-filtered CuKα (λ = 1.54050 Å) radiation. The copper X-ray tube was operated at 40 kv and 16 ma with a function of X1 and a 2 second time constant for the flow proportional counter. Chart speed was 2° per minute with linear scale recording. The beam slit was set at 3°, the soller slit on medium resolution, and the detector slit at 0.05°MR. Low angle reflections were either rerun at a 0.2° per minute slow scan or were measured by averaging a series of scaler counts over the peak.

The (001) reflections of 47 untreated samples of K-bentonite vary between 10.9Å and 12.2Å with the majority falling near 11.1Å (table 3). Similarly, (002) and (003) peaks fall in a non-integral series near 5.05Å and 3.29 Å respectively. In all cases the first order reflections are the most intense, sometimes to the practical exclusion of succeeding peaks. The position of the (060) reflection at 1.50Å indicates a dioctahedral arrangement of octahedral cations (Weaver, 1953). Variations in degree of crystallinity are revealed through slight broadenings and sharpenings of the (001) peak, but in general, diffraction peak shapes suggest an abundance of well-formed structures.

The suggestion was made by R. E. Grim (personal communication, 1962) that possibly the mixed layering observed by previous investigators in Ordovician K-bentonites might be in fact a mechanical mixture of monomineralic packets, as are found in some soils, rather than a structural interlayering.

If this were the case, several things should be observed. First of all, although basal diffraction maxima of untreated samples might not reflect the true nature of the mixture, it should be theoretically possible to separate the constituents by physical means and to identify them by X-ray methods. Secondly, it is well known that saturation of montmorillonite with ethylene glycol, a polar organic liquid, produces maximum expansion of the layers without

Table 3. Table of (001) values for Cation Treated K-bentonites

Sample No.	Untr.	K^+	Na^+	NH_4^+	Ca^{+2}
KB-1AT	11.1	10.6	11.2	10.8	12.1
KB-1A2	11.2	10.9	11.2	11.1	12.1
KB-1BT	11.2	11.0	11.2	10.9	11.6
KB-1BM	11.0	10.5	11.2	10.9	11.3
KB-1BB	11.0	10.6	11.2	10.8	12.1
KB-1CT	11.0	10.9	10.9	10.8	12.1
KB-1CB	10.9	10.8	11.0	10.9	12.0
KB-1D	11.0	10.9	11.1	11.0	12.0
KB-1ET	11.1	11.0	11.1	10.9	12.0
KB-1EM	11.2	10.8	11.1	10.8	11.7
KB-1EB	11.0	10.6	10.9	10.8	11.9
KB-1F	11.0	10.6	11.0	10.9	11.9
KB-1G	11.0	10.9	11.2	10.9	12.0
KB-1H	11.0	10.9	11.0	10.9	11.9
KB-1I	11.0	10.9	11.2	10.9	11.9
KB-2B	11.0	10.8	11.0	10.8	12.0
KB-2D	11.0	10.8	10.9	10.9	11.8
KB-2ET	11.1	10.8	10.9	10.9	11.8
KB-2EM	11.0	10.8	10.9	10.8	11.5
KB-2EB	11.0	10.6	11.0	10.7	11.8
KB-2F	10.9	10.8	11.1	10.8	11.9
KB-2GT	11.0	10.7	11.1	10.9	11.8
KB-2GM	11.1	10.9	11.0	10.9	11.9
KB-2GB	11.1	10.7	11.1	10.8	11.8
KB-2H	11.0	10.6	11.2	10.8	11.9
KB-2I	11.1	10.8	11.2	10.9	11.9
KB-3B	11.0	10.6	11.0	10.8	11.4
KB-3G	11.1	10.9	11.1	10.9	12.0
KB-3E	11.2	10.8	10.9	10.8	11.6
KB-3FT	11.1	10.7	11.3	10.8	11.7
KB-3FB	10.9	10.7	11.0	10.8	12.0
KB-3G	11.1	10.9	11.1	10.9	12.0
KB-3H	11.1	10.8	11.2	10.9	11.9
KB-4I	11.0	10.8	11.1	10.9	11.7
KR-9T	11.9	11.2	12.1	11.1	12.5
KR-9M	12.2	11.4	12.1	11.2	12.1
KR-9B	12.1	11.2	11.3	11.1	12.3
KR-9-2	12.2	11.1	11.7	11.0	12.1
KR-9-3	12.2	11.1	11.5	11.2	12.3
KR-10	11.7	11.2	11.7	11.2	12.3
KR-11	11.9	11.2	12.0	11.1	12.0
KR-13	11.2	11.1	11.4	11.1	12.1
KR-14T	11.5	11.2	11.9	10.9	12.3
KR-14M	11.5	11.1	11.6	10.9	12.1
KR-14B	11.2	11.2	11.6	11.0	12.1
KR-15	11.6	11.4	11.5	11.2	12.1

adverse chemical effects. So the glycolation of K-bentonite should expand the montmorillonitic packets to the point where (001) reflections for the swellable and non-swellable portions are separated and become recognizable. Thirdly, electron micrographs might be expected to show two distinct types of morphology since "illite" normally has a more clearly defined outline than montmorillonite (Kerr, et al., 1951).

Ultracentrifuge separations of suspended clay particles less than four microns in size were made to study what variations might exist in the range of particle sizes. A Sorvall superspeed continuous flow centrifuge employing the unique Szent-Gyorkyi and Blum continuous flow system, which permits separatory speeds as high as 17,000 rpm was used. Under a constant head, gravity flow feed introduced suspended clay, which had previously undergone ½ hour disaggregation by ultrasonic vibration, into the centrifuge rotor inlet, and selective 200 ml samples were extracted of the effluent material at various rpm intervals. No attempt was made to standardize the density of the original suspension since only relative comparisons were desired. Similarly, the average effective spherical density represented at each sampling speed was not determined since elaborate analysis, unnecessary in this case, would be required.

Diffraction patterns of the first order basal

reflections of samples extracted at arbitrary periods shows no tendency toward subdivision into two distinct maxima (fig. 6). Nor is there any substantial shift in peak position to suggest a change in the relative proportions of the different structural layers. Although particle sizes represented by these patterns were not accurately measured it can be safely assumed that at speeds around 12,000 rpm those particles which do remain after centrifugation are in the range of 1/8 to 1/2 micron. As will be seen from electron micrographs this appears to include most of the finest particles present.

It is interesting to note that concomitant with decrease in particle size there is an increase in the intensity and sharpness of the (001) reflections. Although several factors are responsible for peak intensity, the comparative relationships here would seem to suggest the smaller particles possess a higher degree of organization than the larger ones.

Figure 7 illustrates smoothed spectrometer tracings of several K-bentonite samples of less than 2 micron size that have been subjected to saturation with ethylene glycol. Since various amounts of water can be accommodated in swellable 2:1 clays depending upon the surface charge density and type of exchange cation present, water is not a reliable swelling agent to use for tests of maximum expansion. Ethylene glycol, however, will replace whatever water is present and expand the lattice to a distance, for

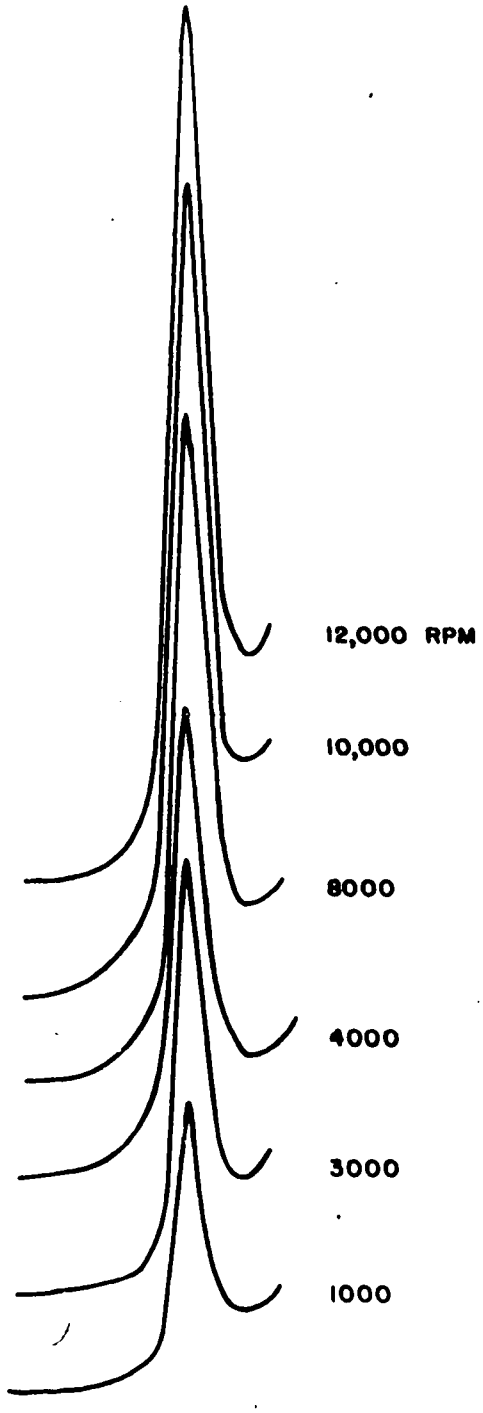

Figure 6. (001) peaks of sample KB-3F separated by centrifugation at various speeds.

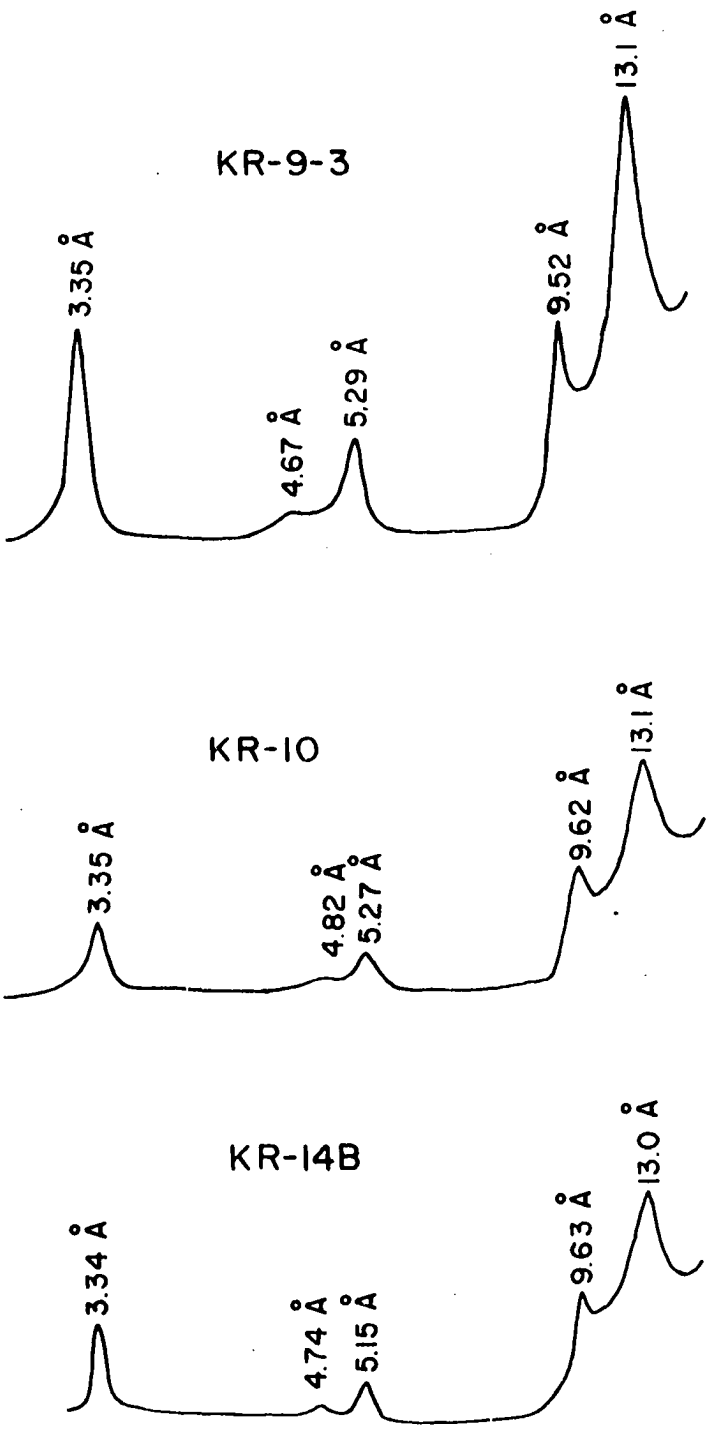

Figure 7. Three K-bentonite samples treated with ethylene glycol.

calcium montmorillonites, of approximately 17.7 angstroms (Bardshad, 1950). Hendricks and Teller (1942) and MacEwan, Amil and Brown (1961) have computed theoretical curves for random mixtures of 10/12.4Å, 10/14.0Å, 10/15.4Å, 10/17.7Å, and 7.14/10Å layers at intervals of 10 per cent. The two figures in each notation above refer to the (001) peaks contributing to the single reflection which is observed. The formula as expressed by Hendricks and Teller calculates ϕ, the mixing function, which represents the effect of the mixing of layers on the diffraction intensities.

Upon glycolation the (001) peaks divide with maxima appearing at 9.5Å and 13.0Å. These peaks again reflect the intermediate position of the mixed-layer lattice between the 10Å non-expandable unit and one expanded to 17.5Å with ethylene glycol. However, the position of the 9.5Å reflection does not coincide with a (001)/(001) combination. Weaver (1953) has suggested that a combination of (001) for the 10Å unit and (002) for the 17.5Å unit might better explain this peak rather than attributing it to the (003) reflection of a 28.5Å spacing (10 18.5Å) as suggested by earlier workers. This interpretation is substantiated by examining the data of MacEwan, Amil and Brown (1961). Their quantitative data for 10/15.4Å and 10/17.5Å combined reflections give essentially the same percentage values for (002)/(003) peaks but slightly different for (001)/(001) peaks. Bradley (personal communication, 1962) suggests that on the basis of his own work that (001)/(001) S-shaped

curves should not be given as much reliability as the more linear (002)/(003) curves. Hence percentage calculations are made on the basis of the (002)/(003) position where possible. From this standpoint the non-expandable to expandable layer ratio of K-bentonites in this area range between 3:1 and 3:2. No evidence is detected which would suggest a consistent vertical or horizontal change for these values. Upon heating to 550°C for two hours, the expandable layers collapse to a 10Å spacing as the interlayer water is driven off and the sequence of reflections becomes regular, indicating a uniformity of interlayer separation.

Misinterpretation of the glycolated samples could quite easily lead to the conclusion that upon glycolation the (001) reflections of the mechancially mixed components were distinctly separated since the (002)/(003) maximum falls very near the (001) reflection for the 10Å unit. Careful measuring is needed to distinguish the two.

Discussion of electron microscope results will be covered in more detail later, but it might be mentioned here that comparison with published photographs of purified montmorillonite and "illite" specimens reveals morphological characteristics that are for the most part consistent for both large (1-2μ) and small (0.25μ) particles, and which bear a greater resemblence to "illite" than to montmorillonite. Such is to be expected on the basis of X-ray data.

Thus the evidence points to an intimate interlayering of units having characteristics of both "illite" and montmorillonite-type clays and not a mechanical mixture of discrete parcels.

CATION EXCHANGE AND NATURE OF THE INTERLAYER CATIONS

The expansion properties of clays are related to a number of factors both indigenous and inherited as a result of the geochemical environment in which the clays form. Barshad (1950) has given as important determinants (1) the size of the interlayer cation, (2) the charge of the interlayer cation, (3) the total excess negative charge per unit cell, and (4) the nature of the interlayered substance. Although he minimizes the effect of particle size, recent work by Jonas and Roberson (1960) and Jonas (1962) suggests this factor may play an important role.

It is well known that a sphere with a diameter of 1.35Å will just fit into the open hexagonal holes of the tetrahedral Si-O sheet. Thus, when considering expansion properties, ionic size must determine largely the number of water molecules that can be included within the interlayer area. This factor is mitigated partially by ionic valence such that divalent cations have generally a higher hydration capacity than monovalent ones. Barshad's data demonstrate that montmorillonite saturated with K^+, Na^+, NH_4^+, and Ca^{+2} and air-dried give first order reflections respectively at 12.0Å, 11.9Å, 12.1Å, and 15.1Å. When saturated with water, these maxima shift to 13.2Å, 24-18Å, 13.2Å, and 18-19Å. Na-montmorillonites were found to form gels upon wetting, consequently expansion varied with the concentration of the gel. So with the exception of Na-montmorillonite,

K- and NH_4-montmorillonites appear to foster only one molecular layer of water, whereas divalent Ca^{+2} can accomodate two layers.

The ionic radii of K^+, Na^+, NH_4^+, and Ca^{+2} are 1.33Å, 0.95Å, 1.42Å, and 0.99Å respectively. Barshad (1950) has shown that ions having the dimensions in the range of 1.35Å (namely K^+ and NH_4^+) tend to be associated with contracted layers whereas those smaller than 1.35Å (Na^+, Ca^{+2}) will foster one to two molecular layers of water depending upon whether they are monovalent or divalent.

Table 3 shows the results of saturation of K-bentonite samples in 1N solutions of KOH, NaOH, NH_4Cl, and CaCl for five hours at 65°C, after which they were washed and dried at room temperature. The samples were kept suspended in an ultrasonic vibration bath in order to maintain as much particle separation as possible. Minimizing the amount of flocculation in this way was found to appreciably affect the accessibility of ions to the indiviual clay particles.

Untreated, air-dried samples show first order basal reflections that vary between 10.9Å and 12.2Å. Most peaks are well defined but showed a tendency to broaden under even slight changes in relative humidity. Accurate control of humidity conditions was not maintained, but the conditions of sample preparation were constant so that reasonable confidence can be placed in comparative interpretations of peak intensities and sharpness. Of greater importance here,

however, was the amount of sample used. Minimal amounts of sample often produced less distinct patterns, and often duplicates were required for confirmation of measurement.

Upon saturation of these samples with K^+, a slight shift towards the 10Å position can be noted (figs. 8, 9, 10). This shift is indicative of a partial contraction of the expandable layers with a resultant decrease in the value of the d spacing. (001) values for these maxima vary between 10.5Å and 11.4Å. Treatment with NH_4^+ produces a similar less complete collapse of the expandable layers with first order maxima ranging between 10.8Å and 11.2Å. Na^+ is seen to induce only mild collapse on some specimens and a peak expansion on others with peak values between 10.9Å and 11.9Å. Ca^{+2} on the other hand has the most profound effect in expanding layers between 0.5Å and 1.0Å. Ca-treated peak values range from 11.3Å to 12.5Å.

The interlayer cation in the expandable layers appears to be calcium, for comparison with theoretical studies by MacEwan, Brown and Amil (1961) reveals that the curves which most closely and consistently agree with each other are those for 10/17.7Å mixed-layers whose expandable portions have been glycolated and 10/15.5Å mixed-layers whose interlayer position is occupied by calcium and two molecular layers of associated water. The data for Na-montmorillonite do not correspond with the glycolation data.

Jonas and Roberson (1960) in discussing the importance

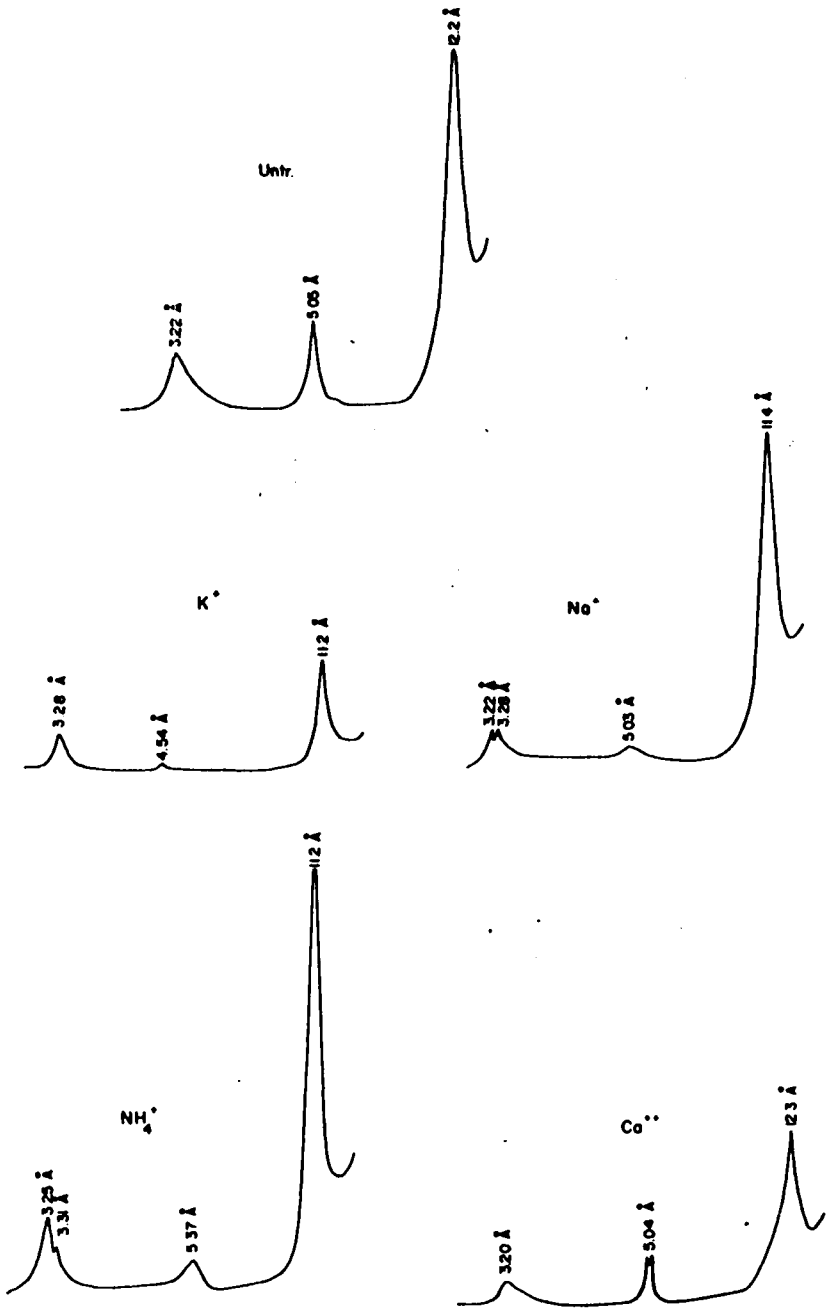

Figure 8. Smoothed diffractometer tracings for sample KR-9-3.

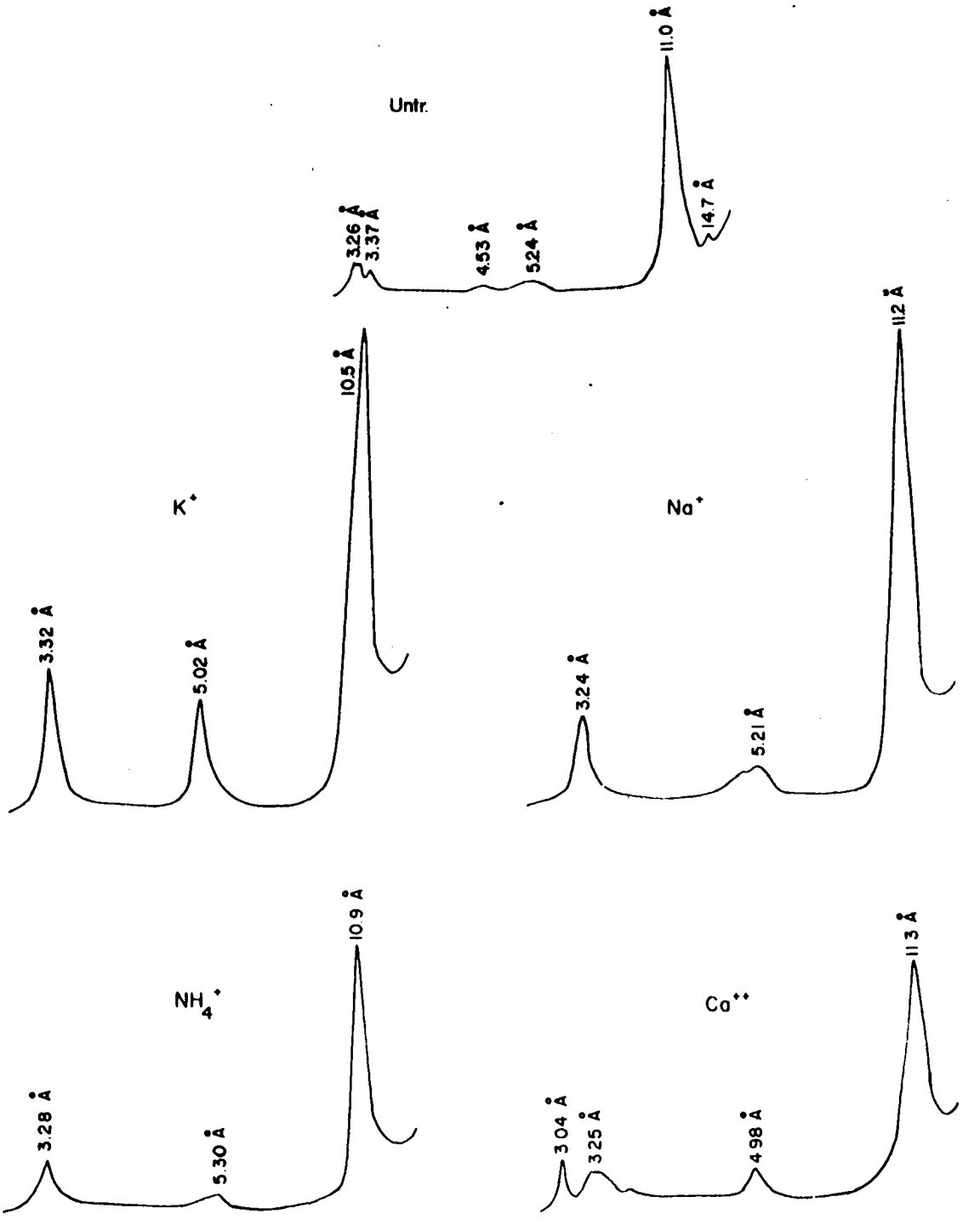

Figure 9. Smoothed diffractometer tracings for sample KB-2B.

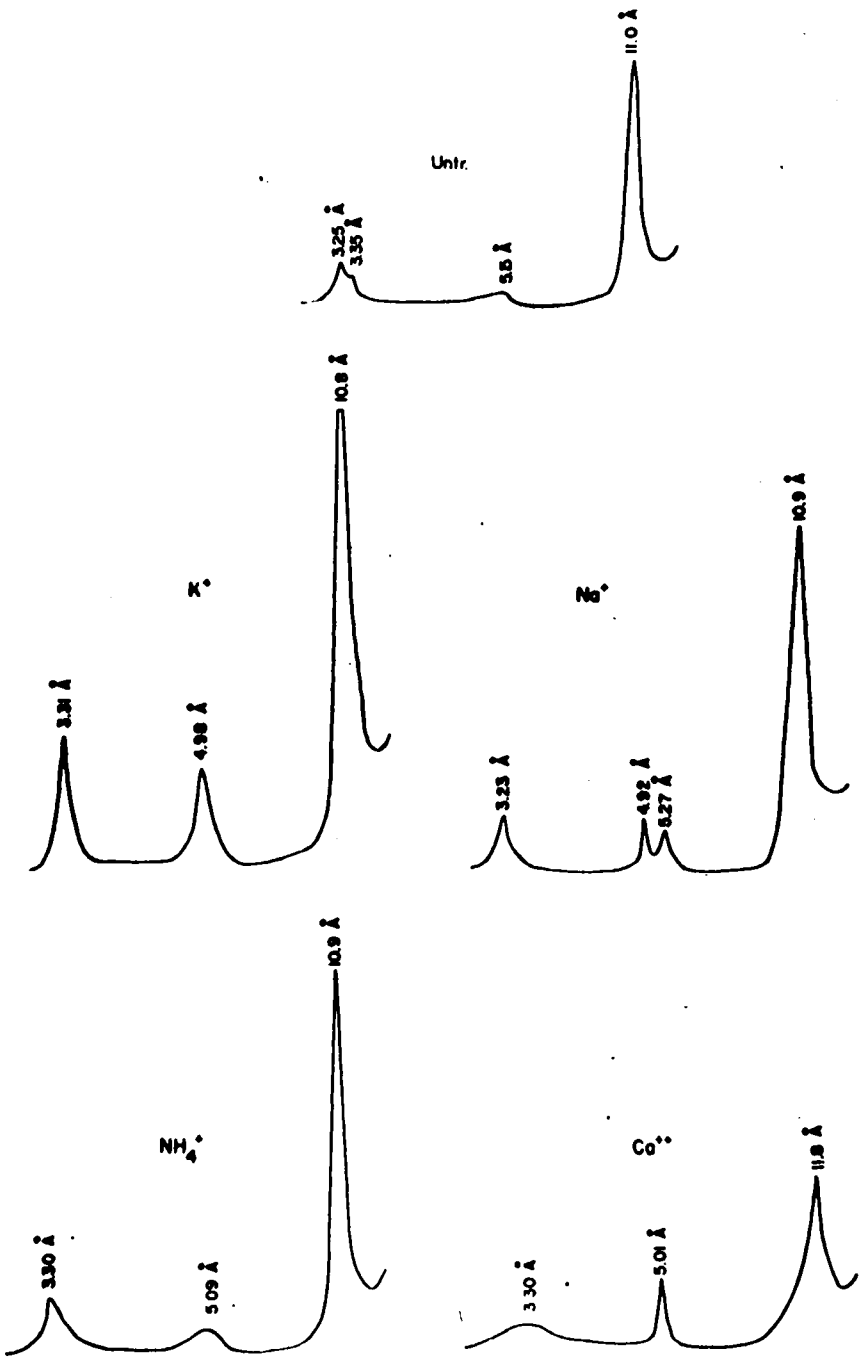

Figure 10. Smoothed diffractometer tracings for sample KB-1E top.

of particle size on the expansion properties of clays suggest that "there is no reason to believe that the degree of isomorphous substitution is not a continuous variable in the clay minerals, ranging from a minimum in the clay equivalent of the talc-pyrophyllite minerals to the maximum in the clay muscovite-biotite minerals. If expansion is truly related to the charge on the silicate layer and the charge is controlled by isomorphism, then expansion properties should be viewed as a continuous variable." The suggestion here, then, is that the idea of "illite" and montmorillonite as two distinct mineral species with only basic structural resemblences is an oversimplified generalization of the isomorphous relationships among the 2:1 clay minerals. However, the data assembled on K-bentonites plus some recent structural work (Radslovich, 1963) are not fully consistent with this view. One would expect to find, for instance, that the high sensitivity of clay minerals to a particular geochemical environment should reflect slight variations in concentration of certain ions, both in terms of the amount of substitution within the octahedral layer and tetrahedral layer and in terms of the interlayer cations present in exchangeable sites. This property has been well demonstrated in studies by Milne and Early (1958), Keller (1956), Weaver (1956, 1958) and others conducted on clay minerals from recent sediments. For montmorillonit-"illite" mixed-layer clays studied in the Gulf of Mexico it has been shown (Weaver, 1958) that

the "alteration" of montmorillonite to illite is merely a rejuvenation of degraded "illite"-muscovite which has undergone removal of interlayer K^+ and addition of water during weathering and transportation. In this kind of a mixed-layer structure there is indeed a gradation from one end-member to another, the ratio depending upon the time exposed to sea water and the environmental concentration of potassium. This is due primarily to the fact that degraded micas are characterized by high Al^{+3} for Si^{+4} substitution in the tetrahedral layer and hence possess a high surface charge density.

However, Ordovician K-bentonites represent silicate lattices formed as a result of the devitrification of volcanic ash of a probable latite or trachyte composition (Ross, 1928) and hence should reflect directly the geochemical conditions under which they originated. The reaction of samples studied here indicates a near-complete adjustment to lattice strains produced by octahedral substitution and seems to suggest the existence of a fairly stable silicate form.

The concept of potassium "fixation" should be examined for a moment in order to better understand the full significance of those K^+ ions which are exchangeable and those which are not. Agronomists are basically concerned with the cation and the relative ease with which it can be extracted from its interlayer site, hence with its fixation. On the other hand, mineralogists are interested in the effects of the cation on the clay lattice itself and the implications

regarding the lattice composition which can be inferred from the cation data. In a sense they are concerned more with contraction than extraction. It is possible that contraction data could be more useful than fixation information in making structural interpretations since it is not implicit that contraction means fixation nor, conversely, that fixation implies contraction. As an example, we can consider samples shown in figure 11 which illustrates (001) reflections from fourteen samples of K-bentonite ranging over a period of about one angstrom for untreated samples, but yet showing uniform reaction to cation treatments. This would indicate a variation in contraction rather than fixation of the 15Å units, since the uniform swelling reaction to Ca^{+2} means the same interlayer dimensions can be attained under uniform conditions regardless of the initial dimension of the clay lattice. Figure 11 is somewhat anomalous in comparison with the remainder of the cation data since the untreated maxima of samples KR-9T through KR-11 are situated near the 12Å line. The possibility cannot be excluded that the abnormal spacing results from slight degradation of the K-bentonites in outcrop with subsequent removal of potassium, but it is also quite possible that these samples owe a higher Ca/K ratio to either local environmental anomalies during formation or to subsequent diagenetic changes. It can be seen (table 5) that the cation exchange capacities reflecting total surface charge density are not markedly low in comparison to samples

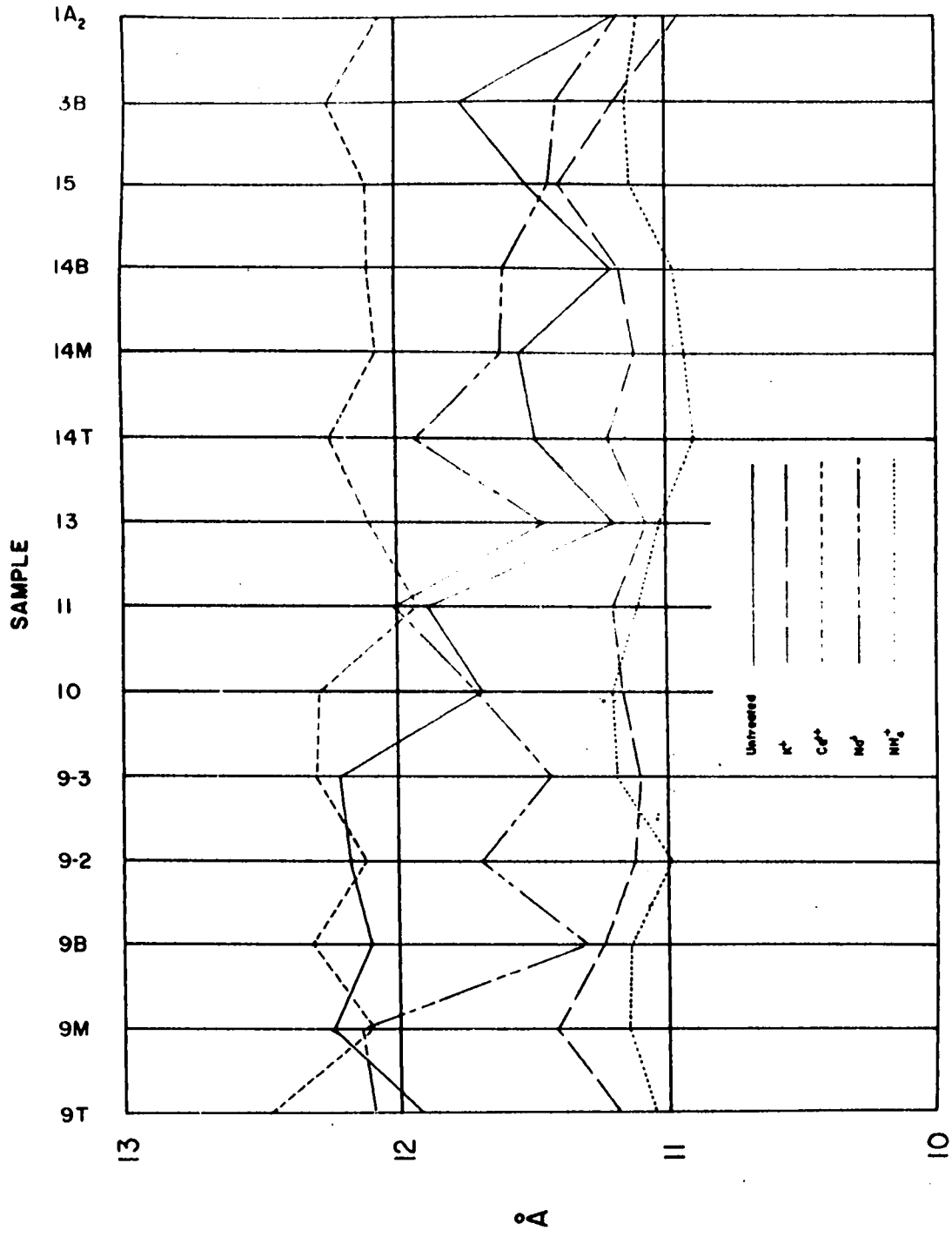

Figure 11. (001) values for fourteen treated K-bentonites.

KR-13 through KB-1A$_2$, nor are the reactions to K^+ and NH_4^+ exceptionally low. Hence the degree of contraction here does not necessarily reflect the amount of potassium fixation. No studies were made of the influence of particle size on the degree of expansion of the clay lattices, so the influence of this factor cannot be considered. Additional work in this direction might prove interesting in the light of studies by Jonas and Roberson (1960).

Treatments on sample KR-9T offer additional information on the fixation of some of the interlayer potassium. First order reflections of the untreated sample occur at 11.9Å. Suspension in a 1N solution of KOH for five hours at 60°C allowed the maximum amount of potassium that could be adsorbed to place itself in the exchange sites of the tetrahedral layers. The sample was then washed three times in distilled water, decanted, and air-dried at room temperature. Contraction resulted in a first order spacing of 11.2Å, a collapse of approximately 0.7Å. However, saturation of the K-rich sample with ethylene glycol expanded the 15.5Å units to the point where the total mixed-layer reflection occured at 11.6Å. Using the data of MacEwan, Amil and Brown (1961) the calculated percentage of non-swellable units for the untreated sample with glycol was 76%, while for the K-treated sample with glycol it was 80%, giving a 4% increase in non-expandable layers after treatment with potassium. This is an insignificant amount when it is considered that the initial lattice

was probably composed totally of swellable layers which shortly underwent contraction on the order of 70% to 75% by the adsorption of potassium.

So it might be assumed that although some additional adsorption of interlayer cations such as K^+, Na^+, and NH_4^+ is possible in the lattice of Ordovician K-bentonite essentially all the vacancies for fixed potassium have been filled. In the light of the above statement by Jonas and Roberson (1960), then, it seems that a more correct approach to the aspects of continuous isomorphism between the various 2:1 clay members requires consideration not only of the degree of tetrahedral-octahedral substitution and its effect on the expansive qualities of the clay, but also the nature of the sites into which these ions fit and the ratio between the exchangeable and non-exchangeable cations in these sites.

A consequent line of investigation from the foregoing would be to reverse the normal direction of procedure and study the geometry of the exchangeable cation sites to see what effect they may have on octahedral substitution.

First, however, it is important to consider what is meant by cation exchange capacity and how it can be measured. Total exchange capacity (TEC) is simply a standardized method of measuring the ability of a clay mineral to exchange those cations which are loosely held on and within the lattice by weak coulombic forces. Various methods have been outlined in the literature (Grim, 1953; Ormsby and Sand, 1953;

Lewis, 1951) and each has certain advantages depending upon the accuracy desired and the equipment available. The method described herein follows basically the ammonium method described by Lewis (1951) with a few refinements added by the Department of Geology of the University of Illinois (personal communication with Dr. Michael Wahl). The reproducibility is high and the amount of sample needed is quite small. The procedure is outlined as follows:

1. Sample must be powdered to pass through a #200 sieve.

2. Standard solutions are prepared of 0.1N H_2SO_4 and 0.1N NaOH, and then standardized.

3. Standardization procedure for normality determination of any basic solution is as follows:

   a) Place approximately 0.9 gm. Potassium Acid Phthalate (AR) in accurately weighed beaker. Weigh both to determine exact amount of Phthalate.

   b) Add approximately 50 ml. of hot distilled water.

   c) Titrate with unknown basic solution. Use phenolphthalein indicator (5 or 6 drops).

   d) Calculate normality:

$$\frac{\text{Titre} \times 0.81688}{\text{Wt. of Phthalate}} = A$$

$$\frac{40}{A} \times 0.1 = \text{True Normality}$$

4. Take approximately one gram of pure clay and weigh accurately on an analytical balance.

5. Place sample on a filterpaper in a Buchner funnel and attach to a vacuum line.

6. Slowly wash sample with 200 mls. of 2N Ammonium Acetate in 4 or 5 portions, allowing all the solution to be completely filtered before adding the next portion. (This is best done with a wash bottle). Save the filtrate for cation determination.

7. Wash the clay thoroughly 3 or 4 times with neutralized methyl alcohol (pH 7).

8. Transfer filter paper and clay to standard Kjeldahl distillation apparatus (fig. 12).

9. Place end of condenser in beaker containing 25 ml. of standard Sulphuric Acid, making sure condenser tip is immersed in acid. Methyl orange may be used as indicator (5 drops).

10. Run approximately 25 ml. of concentrated (6N) Sodium Hydroxide onto the clay. Make sure sample is completely submerged.

11. Distill for 5 minutes. Temperature should be kept as close to boiling point as possible as overheating will cause carryover of base droplets into acid.

12. Back titrate excess acid with standard Sodium Hydroxide. If pH meter is used, titrate to pH = 3.80.

13. Calculation:

$$\frac{25\text{-Titre}}{\text{Wt. of Sample}} \times \text{Normality of base} \times 100$$

= TEC in milliequivalents per 100 gm.

14. Filtrate can then be placed in flame photometer to determine the cations that were originally present.

Several hints may be offered here. First, it is advisable to include a standard nitrogen trap (fig. 12) in each Kjeldahl apparatus. This allows only vapor to escape into the condenser. Secondly, greater confidence can be placed in experimental results if each sample is run

in duplicate. Any discrepancy can be settled by a rerun of two additional samples. Thirdly, the titration point of 3.80 pH was determined by comparison with clays of known TEC provided by the University of Illinois. It may be advisable to recheck this endpoint from time to time in case fluctuations occur either in the pH meter or elsewhere in the analytical system. Furthermore, the pH meter should be periodically standardized at pH = 4.0 with a commercial buffer solution to check for drift due to room termpature and humidity changes.

In the TEC calculations the figure 25 represents 25 ml. of 0.1N Sulphuric Acid. This figure must be adjusted accordingly as the standardized solution varies from this normality. If a large number of samples are anticipated, it is advisable to prepare 4 or 5 liters of standard base and acid at one time and to keep them stored in closed jars provided with silica gel desiccator tubes (fig. 12).

Variation in exchange capacity of clay minerals (table 4) is caused by differences in the availability of exchange sites, that is, the position of negatively charged spots on the clay lattice, and by the chemical composition which causes the charges to develop. Variations in grain size and irregularities in structure appear to increase the exchange capacity by providing a greater number of exchange sites on the particle edges. This is particularly true for kaolinite and halloysite which have very little interlattice

Figure 12. Equipment used for exchange capacity determinations.
A. Standard acid and base containers
B. Silica gel moisture trap
C. Ammonia distillation apparatus
D. Water circulation pump
E. Voltage control for heat pods
F. PH meter

substitution and hence few negatively charged areas within the structure. For these clays the exchange capacity increases as the grain size decreases because of the increase in surface area and in the number of broken bonds. Hendricks (1945) has shown that the exchange capacity of kaolinite increases from about 2 meq per 100 gm. with a specific surface area of 10 square meters per gram., to 8 meq per 100 gm. with a specific surface area of 40 square meters per gm. Reduction in grain size together with disordered lattice structure tends to produce a mineral amorphous to X-rays. Such minerals have higher exchange capacities than larger, better crystallized grains of similar composition because of increased surface area and more broken bonds. Materials like silica gel have exchange capacities in the range of 70 to 100 meq/100 gm. (Carroll, 1959). However, this kind of exchange is probably related more to surface adsorption than to true cation exchange.

Ion exchange takes place when a solution containing cations comes into contact with a clay mineral surface. The kind and amount of exchange that takes place depends largely upon the chemical composition of the structure. Carroll (1959) has summarized the structural causes for cation exchange as,

1. Unsatisfied valence produced by "broken bonds" at surfaces and edges of particles.

Table 4. Base Exchange Capacities of Common Clay Minerals (After Carroll, 1959)

Mineral	Structural Control	TEC (meq/100 gm.)
Kaolinite	Unsatisfied valences on edges of structural units	1-15
Halloysite ($2H_2O$)	Unsatisfied valences on edges of structural units	5-10
Halloysite ($4H_2O$)	Unsatisfied valences on edges of structural units and on internal surface between layers	40-50
Montmorillonite Group	Substitutions in the octahedral and tetrahedral units giving excess negative charge; unsatisfied valences on edges of unit	70-100
"Illite"	As in montmorillonite plus deficiency of K^+ between layers	10-25
Vermiculite	Replacement of interlayer cations, substitutions in the units, and unsatisfied valences on the unit edges	100-150
Chlorite	Data poor. Possible deficiency of charge due to substitution in brucite layer	10-40?
Glauconite	As in "Illites"	11-20

2. Unbalanced charges caused by isomorphous substitution of cations -- for example, Al^{+3} substituted for Si^{+4}.

3. Dissociation of structural OH^- radicals the H^+ of which may be replaced by metallic cations.

4. Accessibility of structural cations other than H^+ which become exchangeable under certain conditions -- for example, at low pH values Al^{+3} ions move from the octahedral units to the exchange positions.

Hence the principal cause of cation exchange in the 2:1 clays, montmorillonites, illites, vermiculites, is isomorphous substitution, whereas in the 1:1 clays, Kaolinite, halloysite, "broken bonds" are more important.

Additional considerations are discussed by Robinson (1962) who outlines the factors influencing cation exchange as:

1. Binding forces -- the forces that affect the stability of an ionic crystal include (a) electrostatic, or coulomb forces whose attraction between ions falls off with the square of the distance; (b) Van der Waals forces with attraction diminishing according to the seventh power of the distance; and (c) inter-atomic repulsive forces also diminishing rapidly with the distance.

2. Accessibility of the lattice ions -- a single cation may be adsorbed by a clay mineral with a wide range of bonding energies, and this is related to the position of the silica-aluminum packet at which the cation is adsorbed, therefore, on basal surface, edges, or corners.

3. Ionization of adsorbed cations -- only a small proportion of adsorbed cations is likely to be ionized depending upon the particular clay, the concentration of the clay-water system, the nature of the cations, the relative concentration of the cations, and the nature of the adsorbed anions.

4. Relative size of ions -- for ions of equal valence, the smaller ions are held less tightly than the larger ones.

5. Temperature -- generally has but a small effect on cation exchange.

6. Valence -- the higher the valence of a cation, the greater its replacing power, other things being equal. Hydrogen, which behaves more like a divalent or trivalent cation, is cited as an exception.

7. Atomic weight -- for elements of the same valence, replacing power of cations tends to increase with atomic weight.

8. Concentration -- in general, the replacing power of a cation increases with increasing concentration of the cation in solution. The common metallic cations found in exchange positions in clay minerals are Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+}. At low pH values, H^{+} replaces other cations. The order of replaceability of the common cations has been found to be Li<Na<K<Rb<Cs and Mg<Ca<Sr<Ba.

9. PH -- cation exchange capacity is a function of pH and at a given pH the exchange capacity is a definite quantity for a given sample.

Jonas (1963) has demonstrated that two kinds of hydrogen are exchangeable on the surface of H-saturated montmorillonite. At low pH there is more titratable hydrogen in a fine-size fraction of the clay than there is in a coarse fraction. This indicates neutralization of H^{+} adsorbed at the crystallite edge. The H^{+} adsorbed on the interlayer flake surface is neutralized at a higher pH, where there are more titratable hydrogen ions for the coarse fraction than for the fine. This implies some degree of correlation between charge density and particle size.

Realizing the variety of factors which are at play in determining the kind of cations that occupy exchange positions, it becomes somewhat less than speculative to suggest why Ca^{+2} and K^{+} are associated in the particular manner that they are in K-bentonites. Geologically, Ordovician K-bentonites in Kentucky, Ohio, and Indiana, are associated almost entirely with limestone sequences, having only minor shale breaks present to suggest any influence of detrital material. In such a sedimentary environment, the most prevalent cations in solution during devitrification of volcanic material would be Ca^{+2} plus those ions released during the alteration process in the ash beds. Mg^{+2} is only a very minor constituent in the limestone as shown by diffractometer tracings of carbonate peaks.

Alteration of acid to intermediate feldspars and ferromagnesian minerals will contribute primarily Si^{+4}, Na^{+}, Al^{+3}, Mg^{+2}, Fe^{+2}, K^{+}, and Ca^{+2}. Following the exchange series mentioned above, Ca^{+2} and Mg^{+2} have been shown to be preferentially retained compared to Na^{+} when montmorillonite is soaked in sea water (Kelly and Liebig, 1934). However, under conditions of high concentration reverse replacement may occur and, in the case of K^{+}, a certain amount of "fixation". Such a situation would occur for clays forming on the bottom of a carbonate sea by the alteration of K-rich

minerals and it might be expected that a K-rich clay would form to the partial exclusion of a Ca-rich one.

In the eastern United Sates, Ordovician K-bentonites are found in sedimentary sequences characterized by abundant detrital components (Ross, 1928; Kay, 1935). The additional source of K^+ from weathered micas contributed from nearby land areas might conceivably affect the Ca/K ratio of K -rich clays. Weaver (1953) reports a basal (001) spacings of 10.8-10.9Å, indicating 75% collapsed and 25% expandable layers compared to 65-70% and 35-30% here. This could be interpreted as a reflection of the depositional environment since some variability in fixed potassium content can be shown for K-bentonites.

The total exchange capacities for the less-than-two micron fraction of 37 K-bentonites are listed in table 5. Values range between 38 and 53 meq/100 gm. with a majority occuring between 45 and 50 meq/100 gm. Each sample shown was run in duplicate to insure greater accuracy. In most cases the error between the two initial trials was less than 6%. Those that exceeded this amount were subjected to additional trails until good agreement was reached. Of particular interest is the order of magnitude of these K-bentonites in comparison with published values for montmorillonites and "illites" (table 4). Montmorillonites typically have exchange capacities in the range from 70 to

Table 5. Table of Total Exchange Capacities for K-bentonites

Sample Number	TEC (meq/100 gm.)
KB-1AT	45
KB-1BT	43
KB-1BM	44
KB-1BB	42
KB-1CT	47
KB-1D	47
KB-1EM	41
KB-1EB	38
KB-1F	50
KB-1H	50
KB-1I	49
KB-2B	47
KB-2D	39
KB-2ET	45
KB-2EM	49
KB-2EB	46
KB-2F	38
KB-2GM	43
KB-2H	50
KB-2I	48
KB-3B	46
KB-3C	50
KB-3E	43
KB-3FT	45
KB-3FM	50
KB-3FB	50
KB-3H	48
KB-4I	49
KR-9T	41
KR-9B	53
KR-9-2	43
KR-9-3	50
KR-10	52
KR-11	41
KR-13	43
KR-14B	45
KR-15	45

100 meq/100 gm. indicating a large number of unsatisfied charges between and on the edges of octahedral and tetrahedral sheets. Weaver (1958) has suggested that those in the lower portion of the range represent montmorillonites derived from the alteration of non-layer silicates such as volcanic debris in which isomorphous substitution has occured primarily in the octahedral layer. Consequently the seat of residual negative charge is located in the octahedral layer and is further from the interlayer exchange position. Bonding forces then are not quite as intensive and ion exchange occurs more easily. On the other hand, montmorillonites derived from the degradation of "illites" and muscovites are represented by the higher TEC values. Normal muscovites and "illites" are characterized by greater Al^{+3} for Si^{+4} substitution in the tetrahedral layer than is found in most montmorillonites (Grim, 1953). Thus the seat of residual negative charge is concentrated close to the interlayer area and exercises greater bonding force on exchange ions in that position. Exchange capacities for "illites" (hydrous micas) given in the literature range between 10 and 25 meq/100 gm. This range is lower than that for montmorillonites because the majority of negative charges has been satisfied by non-exchangeable potassium with only a few exchange vacancies remaining. Muscovite, which has even a greater portion of tetrahedral silica

substituted for by aluminum has practically all available sites occupied by potassium and at the most has only a weak exchange capacity.

The intermediate position of K-bentonites might appear to merge with the values given for "illite" and encourage the interpretation as merely a transitional stage between montmorillonite and hydrous mica. Weaver (1953) suggests that this in fact is the case and that only additional substitutional changes in the K-bentonite lattice are required to completely collapse the structure to a 10 angstrom spacing. However, although many writers have considered that there is no sharp line of demarcation between the micas proper, the hydrous micas (meaning "illites" and mixed-layer minerals), and the montmorillonites and vermiculites, Yoder and Eugster (1955) have shown that most minerals that have been called hydrous micas, "illites", hydromica, and hydromuscovite are in fact mixed layer structures of "montmorillonite" and various mica polymorphs. These have been called monomineralic structures primarily because the polymorphic mechanisms operative in layer-lattice silicates have not been fully appreciated until recently.

In figure 11 several anomalies appear in cation exchange data which are unexplainable with the available data. Samples KR-9M and KR-11 show only a very moderate collapse with K^{+} adsorption and a weak expansion with Ca^{+2} and Na^{+}. It is possible that, considering the ionic radii

of Ca^{+2} and Na^{+} (.99Å and .95Å) and for K^{+} (1.33Å), some additional cation is being held in the exchange position and effectively preventing collapse or expansion on the order of magnitude observed in other K-bentonites. During preparation of specimens for TEC determination, all exchangeable cations are flushed out with ammonium acetate. Although attempts were not made to determine what these cations were, information of this sort should be useful in explaining some of the data anomalies. It is possible for instance that Mg^{+2} is present to a greater extent in some samples since, like Ca^{+2}, it is held preferentially to Na^{+} in the exchange position. Bulk chemical analyses alone offer no additional information since octahedral magnesium cannot be distinguished from interlayer magnesium without a complete structural analysis.

Those TEC values listed in table 5 represent clay particles less than two microns in diameter which were prepared initially by settling according to Stoke's Law and finally concentrated by high speed centrifugation at 8000 rpm. Consequently the effect of particle size on the total exchange capacity is not given consideration.

There is a noticeable tendency for specimens from the centers of some of the thicker horizons to have a slightly higher exchange capacity and a slightly lower total adsorption of calcium compared to the outer portions. Generally speaking, the properties of Ordovician K-bentonites

do not vary appreciably from the top to the bottom of any one horizon. Those changes that do occur appear to be only local ones and do not bear any consistent variation either laterally or vertically. However, in samples KB-1B, KB-2E, and KB-3F exchange capacities are several units higher for the center portions and seem to correspond with lesser expansion by Ca^{+2} adsorption on the order of 0.1 to 0.2 angstroms. Increased interlayer charge would cause greater difficulty for calcium ions during exchange reactions, and total expansion would be retarded. Such an increase would also be reflected by a higher TEC value provided that no additional K^{+} fixation occured to satisfy the charge vacancies. This feature is not accorded great importance since the TEC increase is still within the limit of error of 6% mentioned earlier and because other thick beds indicated no such variation.

DIFFERENTIAL THERMAL ANAYLSIS

The technique of Differential Thermal Analysis (DTA) has been shown to be extremely valuable in the study of fine-grained minerals such as the clay groups. Although the method is moderately simple and date are fairly easily obtained, a large amount of detailed information can be gained concerning structural properties of minerals. Early studies by Ross, Grim, Rowland, Kerr, Hendricks and others have developed the instrumental and interpretative techniques to their present status.

Basically, under the influence of temperature substances experience fundamental structural changes which proceed with attendant exothermic and endothermic reactions. In DTA the temperature difference between an inert material and the sample is measured as both are being heated at a constant rate. Slight differences in temperature are measured by the use of a dual-terminal thermocouple, one end of which is placed in the sample while the other is placed in the inert standard. Any temperature increase or decrease outside that imposed by the furnace will cause an imbalance which is picked up by a sensitive recording device. The resultant graph is interpreted in terms of positive and negative peaks representing exothermic and endothermic reactions respectively.

As the chemical bonds of minerals are of many different strengths they will oxidize, decompose, and change phase at different temperatures. Thus these temperature

peaks become diagnostic for the bonding relationships that characterize various mineral groups.

Since clay minerals are hydrous silicates, they undergo several prominent changes in the range 0° to 1000°C, the normal working range for most DTA equipment. For a majority of 2:1 clays, the differential thermal curve can be subdivided into two main portions for interpretation: (1) the adsorbed water region in the temperature range 100° to 300°C; and (2) the dehydroxylation region in the temperature range 500° to 1000°C. In the second range structural breakdown and eventual recrystallization occur.

Hydrated clay minerals give pronounced endothermic peaks between 100° and 300°C. X-ray diffraction shows that over this range d(001) decreases from about 15.5Å for Ca-saturated montmorillonites to 10Å with no further decrease at slightly higher temperatures. Hence it is assumed that this reaction represents loss of interlayer, non-structural water (Grim and Rowland, 1942). The size of the peak is at least partially dependent upon both the exchangeable cations present and the relative humidity at which the sample was equilibrated.

MacKenzie (1957) gives several curves for various cation-saturated monmorillonites. Potassium-treated montmorillonite reacts with a single peak at 190°C and calcium montmorillonite is characterized by two maxima at 170°C and 210°C. The double peak reflects the hydration

properties of divalent calcium where the first water is "free" in the interlayer positions and the second is taken up by a 6-fold arrangement of water molecules surrounding each calcium ion. The somewhat stronger bond of hydrated water is broken at a higher temperature than that which removes the interlayer water.

Figure 13 shows differential thermal curves for six untreated K-bentonites. Samples were run at a resistance of 50 ohms and a millivolt range between 0.12 and 0.14 mv. The less-than-two micron fraction of K-bentonite was used for analysis since this fraction is sufficiently coarse-grained to yield distinct reactions and yet does not contain enough impurities to seriously impair accurate interpretation of the thermograms.

A primary low temperature peak lies between 150°C and 180°C with a secondary reaction occuring near 230°C in samples KB-10_4, KB-2B, KR-9M, and KR-9-3. The intermediate position of the main peak represents the influence of both K^+ and Ca^{+2} in the interlayer position while the secondary peak must undoubtedly be related to calcium alone. Ross (personal communication, 1962) has found minor occurences of gypsum in some of the Kentucky K-bentonites from Highbridge, so it may be that the variations in intensities of the secondary peaks are related to minor sulfate content. Unidentified "fibrous" aggregates found in electron micrographs would lend some support to this interpretation.

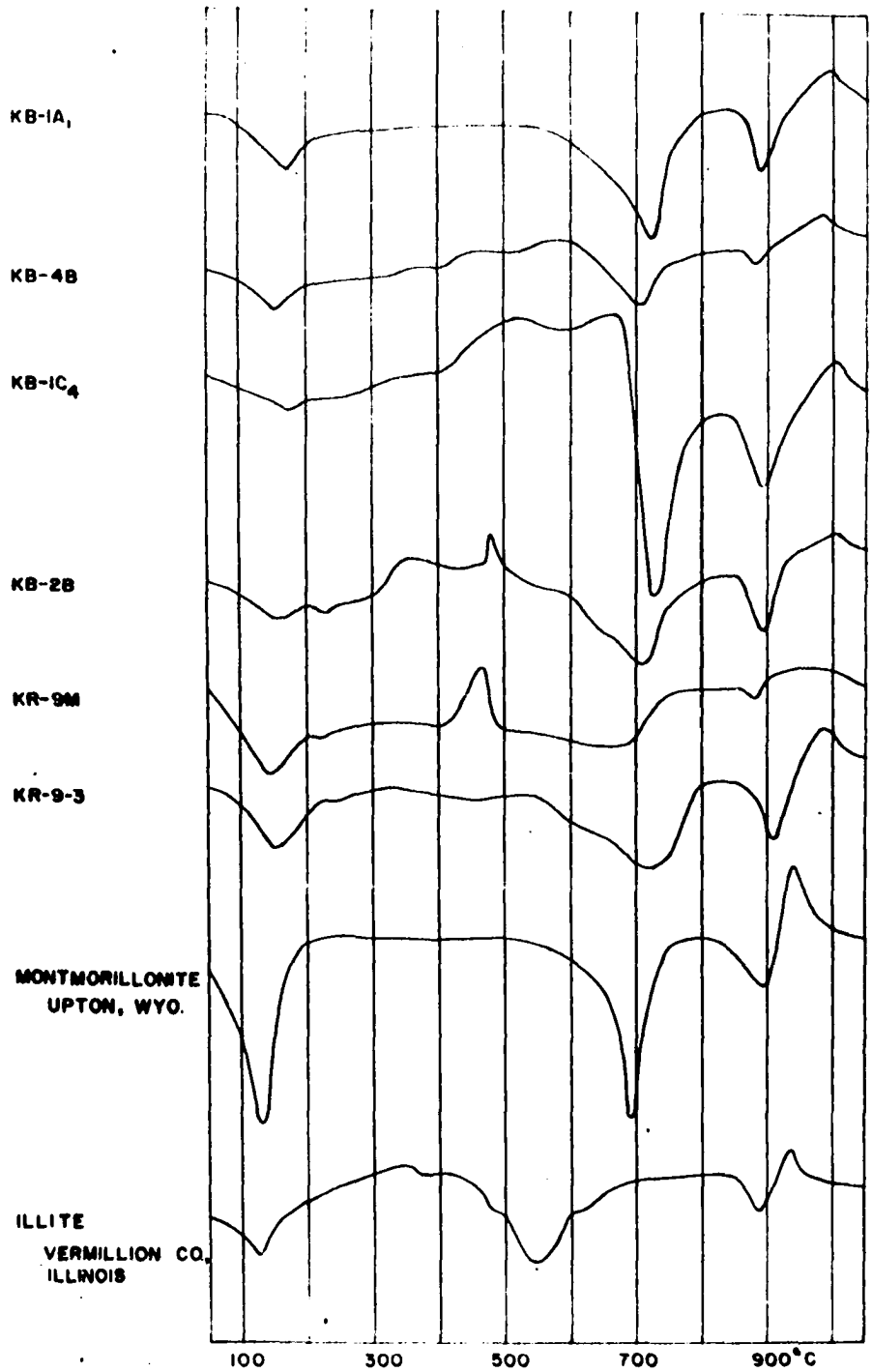

Figure 13. Differential thermal curves.

The size of the endothermic peak in the 150-250°C range could be related to octahedral chemistry of the layer-lattice silicates also. Foster (1953) has suggested a correlation between decreased swelling properties of montmorillonite with increased substitution in the octahedral layer.

MacKenzie (1957) summarizes data for the dehydroxylation of several montmorillonite group members and points out that while montmorillonite gives two endothermic reactions in the 700°C and 900°C region with an exothermic peak around 1000°C, both beidellite and nontronite have primary reactions around 500°C with secondary peaks near 700°C and 850°C. Exothermic reactions follow at 900°C. He points out further that all except montmorillonite give their main dehydroxylation peak in the 500° region and all except montmorillonite owe their silicate-layer charge predominantly to tetrahedral substitution. Thus it would seem logical to correlate the two, particularly since other montmorillonite group members containing little iron or magnesium and showing mainly tetrahedral substitution give a primary dehydroxylation peak near that of nontronite. Correlation of the 500° peak with tetrahedral substitution must still be further substantiated however as other workers have found no such direct relationship over short compositional ranges (Earley, Osthaus and Milne, 1953).

For "illite" the first hydroxyl endothermic peak falls at about 600°C (fig. 13). While this position is probably a function of the octahedral cation-hydroxyl bond, the next endothermic reaction falling in the 850°-900°C range both for "illite" and montmorillonite reflects the complete destruction of the basic lattice and so must be related to substitution in either the octahedral or tetrahedral layer.

It would seem then that octahedral composition is largely responsible in influencing the overall structural relationships in the 2:1 clays. From examination of published DTA data, aluminum-hydroxyl bonds appear to be stronger than either the iron-hydroxyl or magnesium-hydroxyl bonds since pure aluminum clays possess higher dehydroxylation temperature.

In figure 13 the main dehydroxylation peak for K-bentonite lies generally between 700°C and 750°C, slightly higher than most montmorillonites and much higher than "illite". The third peak reflecting complete collapse of the clay lattice is located in the range from 880° to 910°C and is not substantially different from other 2:1 clays. The position of the first high temperature maximum, if correlated with the amount of substitution in the octahedral layer would indicate a predominance of Al-OH bonds over those with Mg and Fe, just as higher substitutions in

montmorillonite and "illite" are reflected by the lower temperatures of the peak positions.

Bassett (1960) has shown by infrared spectroscopy that the hydroxyl bond angles for dioctahedral muscovite are inclined to the (001) cleavage plane (fig. 14), whereas for trioctahedral biotite and vermiculite the OH bond angles are directed perpendicularly to that plane. Thus, for muscovite the H-proton is farther removed from the exchange site in the tetrahedral layer, allowing closer association of the negative oxygen and positive exchange cation (in this case, potassium), while for biotite and vermiculite the proton is placed closer to the tetrahedral layer and hence reduces the strength of the force holding the exchange ions in place. This relationship was used to explain the greater susceptibility to weathering and cation-loss in the trioctahedral micas.

On the basis of the present data it is wondered if the same reasoning might not hold true for cation-hydroxyl bonds in the expandable clays and particularly in K-bentonites. The possibility has been suggested (Kerr, et al. 1951) that if there is selective (non-random) replacement of cations in the octahedral layers than those certain cation positions to which hydroxyls are attached might remain filled by Al^{+3} while substitution occured in other cation sites. In this way a highly substituted lattice might still show a relatively high temperature primary hydroxyl peak because the hydroxyls

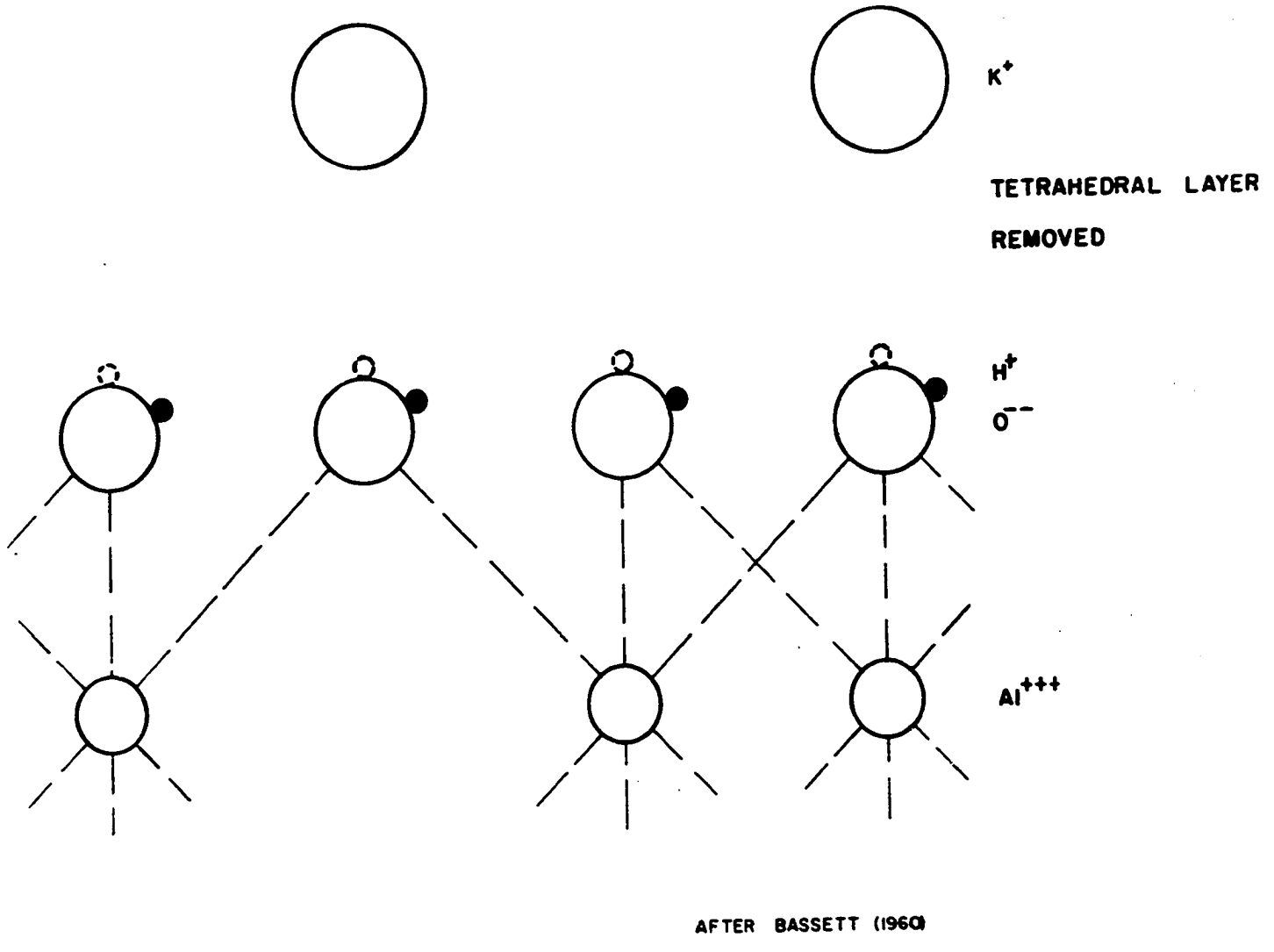

Figure 14. Hydroxyl inclination in dioctahedral (solid) and trioctahedral (dotted) micas.

would still be bound to aluminum cations. The problem of order versus disorder in octahedral coordination will be discussed later in light of recent analyses of the structures of layer-lattice silicates, but it seems possible that the angle of inclination of the OH bond while affecting the "fixation" of the interlayer cation might also affect the temperature at which dehydroxylation occurs. If this were so, then the higher temperature peaks of K-bentonite would reflect stronger cation-OH bonds than in montmorillonite. For "illite" the higher degree of tetrahedral substitution may cause greater distortion in the ionic position in the octahedral layer (Veitch and Radoslovich, 1963, pt. III), and hence weaken the cation-OH bonds. In this case, the primary hydroxyl loss would occur at a lower temperature, which in fact it does.

Exothermic reactions near 450°C in some K-bentonites (fig. 13) may be due to minor organic or sulphide contamination and are not considered to be related to the clay structure.

ELECTRON MICROSCOPY

The development of electron microscopy has lead to a renewed interest in the study of clay mineral morphology. By utilizing extremely short electron beam wavelengths and objective lenses with numerical apertures of the order of 0.01 angstroms, resolution of distances less than 15Å and magnifications up to several hundred thousand times are possible.

In order to show the thickness of particles and the contrast of particles against the background, a metallic shadowing method was employed. This method consists of depositing clay from an aqueous suspension on a piece of film such as collodion at room temperature, and then shadowing the sample with finely divided platinum dust. The angle of shadowing used varies from 30° to 10°, depending upon the average particle size and the amount of contrast desired. Specimens used for electron diffraction could not be shadowed since any contamination would show up in the diffraction patterns, so these were photographed at right angles to the plane of the sample without any preparation. Initial handling of the samples consisted of moderate mechanical breakage followed by disaggregation in an ultrasonic vibrator. Subsequent settling produced the desired upper limit of grain sizes. It is felt that no substantial damage has occured to the clays as a result of these

procedures and that the photographs represent essentially unaltered K-bentonite.

Among the clay minerals montmorillonite generally shows the least evidence of crystallinity in electron micrographs (Kerr, et al., 1951), although Ross and Hendricks (1945) show one example of Wyoming bentonite which has a fairly sharp particle outline suggesting good crystallinity. "Illites" and muscovites generally show well formed flakes, although variations in chemical composition preclude a single definitive description for the clay micas.

Sample KB-1A

Figures 15 and 16 show photographs of K-bentonite KB-$1A_2$ taken of both the less-than-two micron bulk sample and of the uppermost portion of the clay remaining suspended in water after 24 hours. The bulk sample is seen to be composed of both thin plates having sharp, well defined outlines and aggregates of plates with fuzzy outlines more like true montmorillonites. The clay is extremely fine-grained with the smallest particles being less than 1/8 micron diameter. The shadow casting photos give some idea of the thickness of the individual plates and aggregates by comparison of the lengths of the shadows formed. The plates are probably less than .002 microns in height which is about c-axis dimension, while the paskets are several

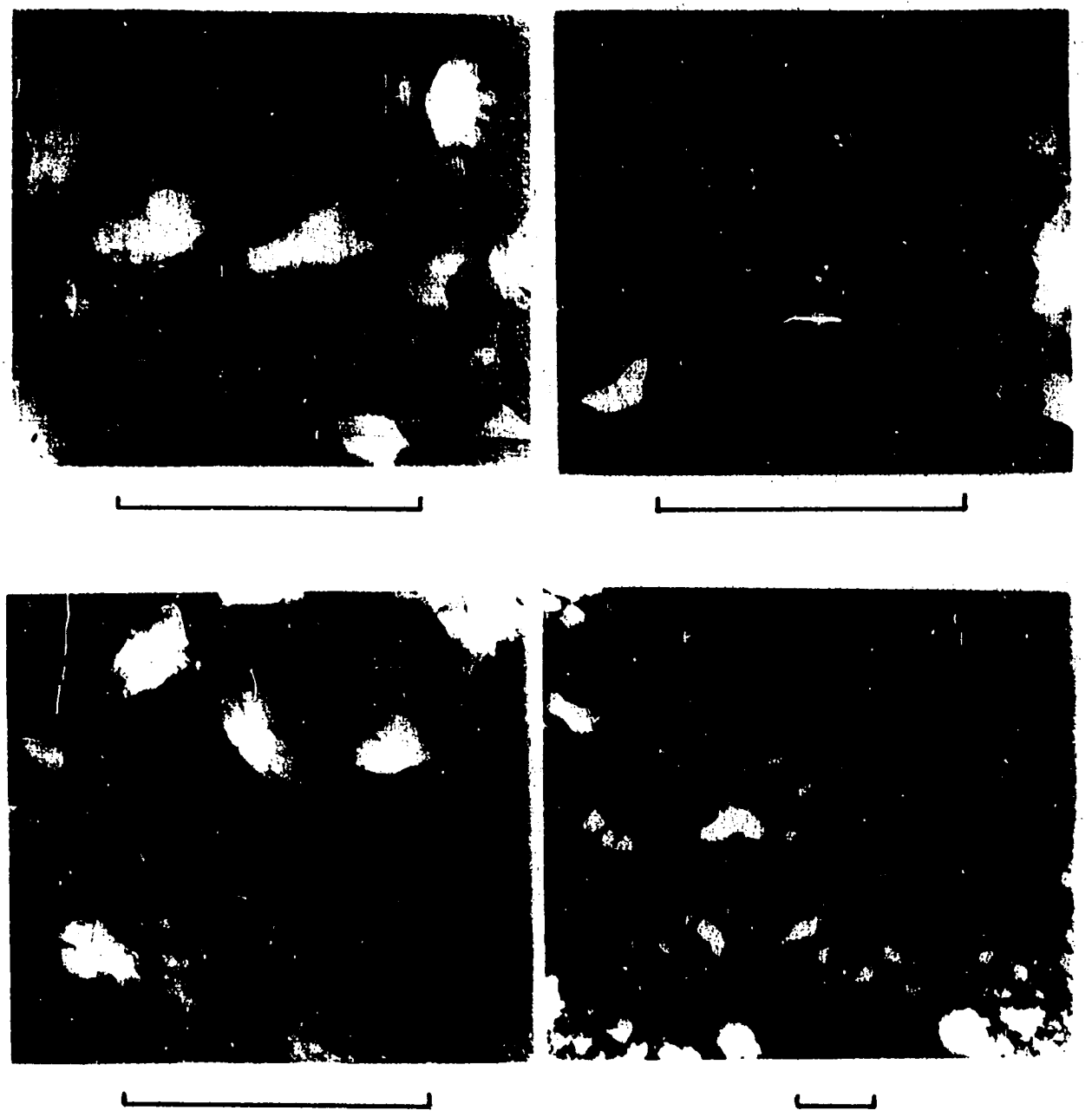

Figure 15. Electron micrographs of sample KB-1A$_2$. Line represents one micron.

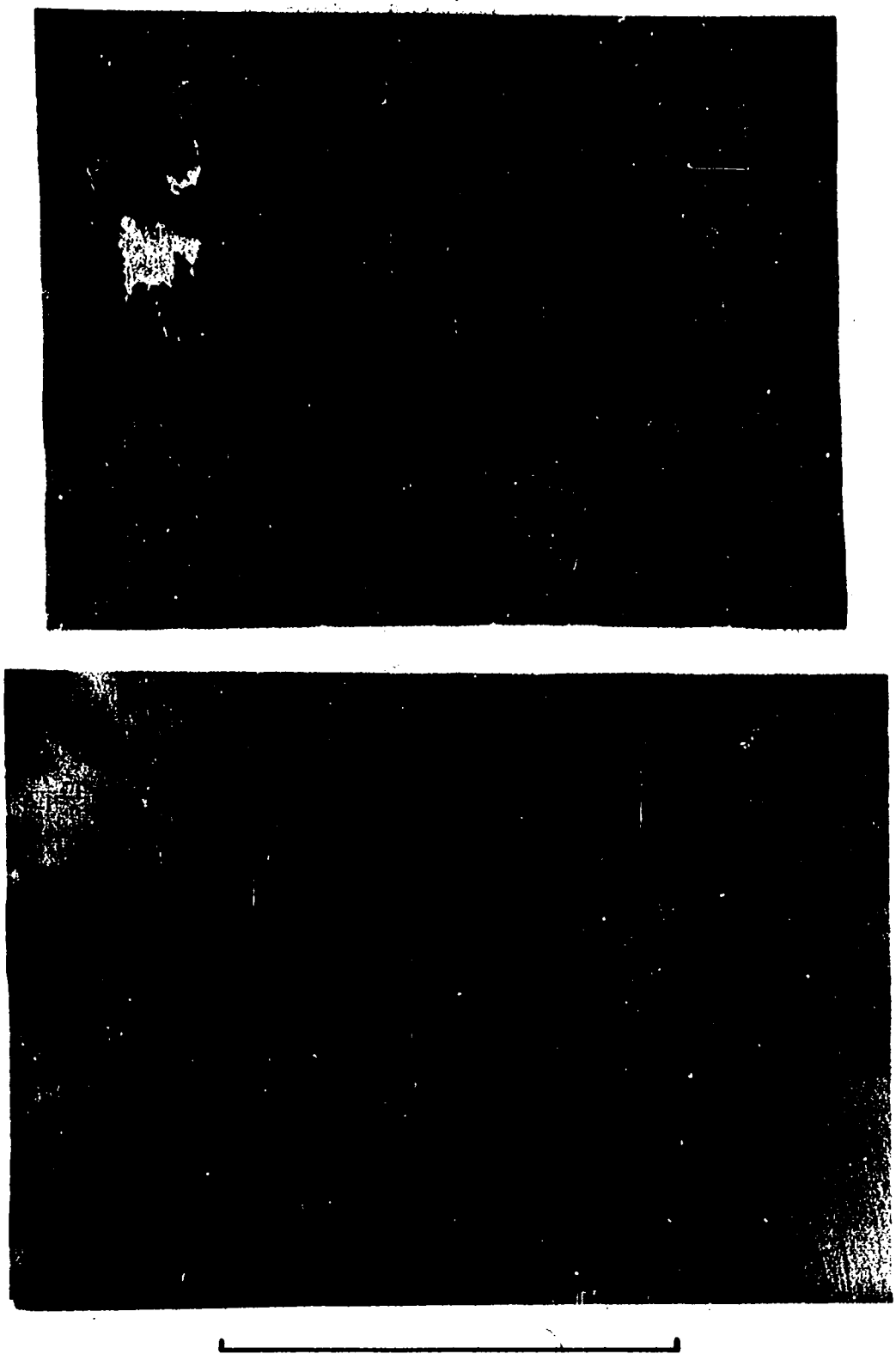

Figure 16. Electron micrographs of KB-1A_2: above, bulk sample; below, particles suspended after 24 hours.

hundred angstroms high. The bulk sample at 40,000 magnification shows that many of the plates are actually split up into sharply terminated lath-like segments in some cases and irregularly broken ones in others. These laths occur both as discrete fragments and as partially split portions of larger plates, suggesting a prominent cleavage direction perpendicular to the basal plane. This type of cleavage may be similar to that of muscovite which, in addition to the basal cleavage, has planes of secondary cleavage parallel to (010), often yielding narrow strips or thin fibers. That this phenomenon is not observed in low tetrahedrally charged montmorillonites suggests that the large size of the interlayer potassium in K-bentonite produces a strain within the crystal lattice resulting in a structure with potential cleavability perpendicular to the layer-lattice plates. Hendricks and Ross (1945) and Kerr, et al. (1951) refer to several instances in the literature mentioning a similar phenomenon in tetrahedrally charged montronite and hectorite. The laths are easily seen even at 6940X magnification and are common features in the bulk sample.

At 40,000X striations are clearly seen on thick aggregate patches of clay plates and occasionaly on the thinner stacks in the bulk sample. In the center of the photo, the striations, known as Moiré-lines, are parallel to the cleavage sides of a stack of plates which terminate roughly in a 60° corner caused by the intersection of

the striations. On the left side of the photo Moiré lines are also seen on an aggregate stack but appear to form more of a mosaic pattern. It is not evident how many of these striations are from the uppermost plate and how many are from the lower ones, but in general they are caused by the repeated stacking of a series of geometrical patterns which produce a sort of magnification only if the patterns on one level repeat those on levels above and below in their linear dimensions. In other words, the presence of Moiré lines reflects well organized and well crystallized clay layers whose stacking is arranged in a certain definite sequential progression.

Sample KR-9-3

This specimen, in addition to the flat plates described above, has several small clusters of a fibrous substance which do not appear in the other samples. These clusters do not have the appearance of clay minerals and are probably due to contamination by gypsum, zeolites or similar secondary mineralization. KR-9-3 was shown by elemental analysis to contain more iron than other samples due perhaps to partial weathering on the outcrop, hence additional contamination might easily be suspected.

Under shadow casting these photos show abundant flat needle-like laths which are broken and terminated by 60° and 120° angles on the ends similar to KR-1A_2. Moiré

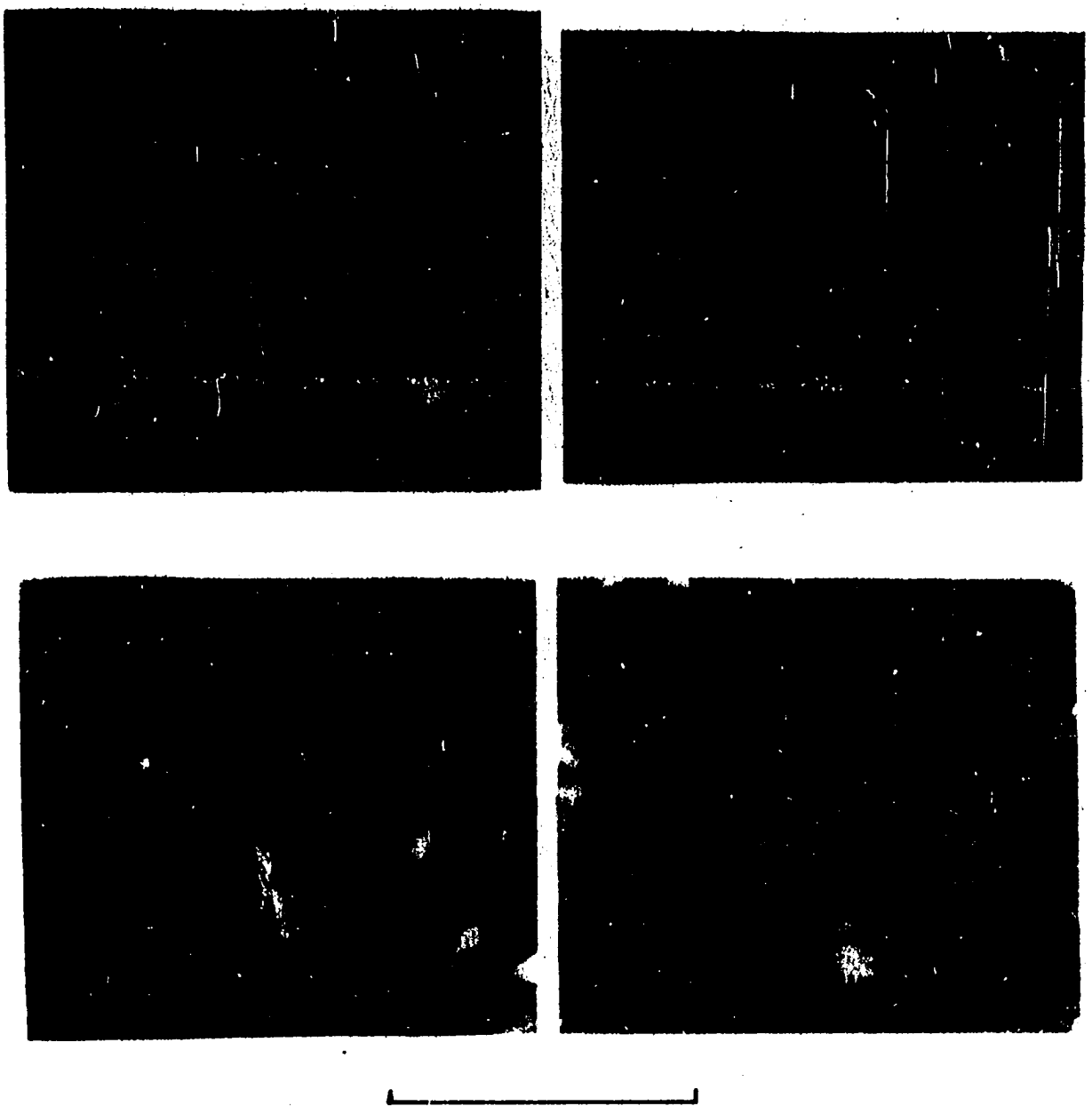

Figure 17. Electron micrographs of sample KR-9-3.

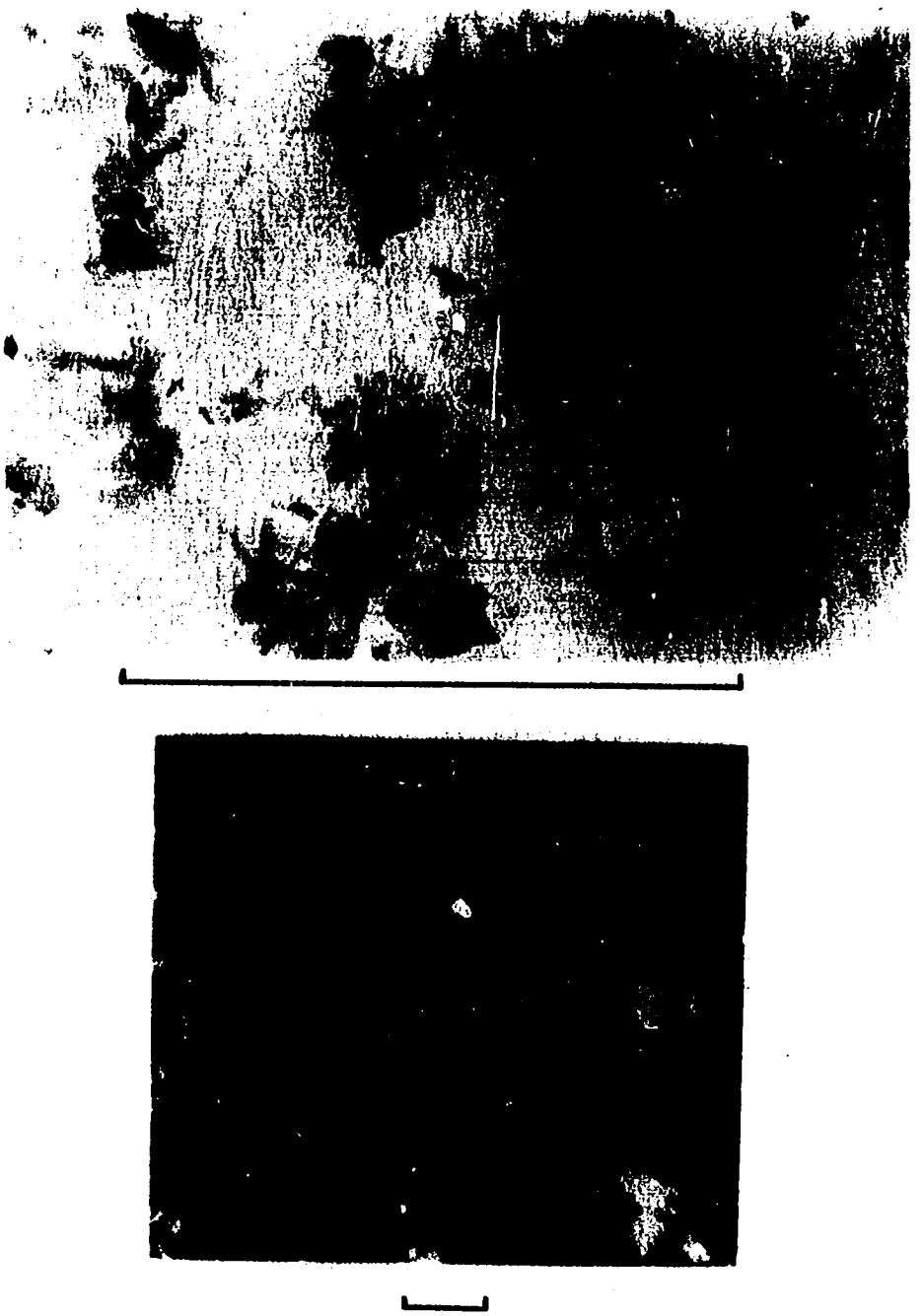

Figure 18. Electron micrographs of sample KR-9-3.

lines parallel the straight edges of a few groups of stacked plates. These are most easily seen at 40,000X magnification.

Sample KB-11

Hexagonal plates and terminated laths are common in these photographs of a bulk sample suspension. Although many plates are overlapping one another, numerous individual ones can be seen reflecting pseudohexagonal symmetry and showing well developed lattice structures. The individual plates in some of the packets in the 40,000X photograph appear to be arranged in a definite crystallographic order with respect to each other, and, as in KB-$1A_2$ possibly represent a certain ordering of plates in the c-axis direction which is responsible for the overall mosaic pattern of 120° and 60° striae interceptions seen in these samples. In several instances the upper plates are partially stripped away revealing the same pattern in the directions of the straight edges of the successive plates below. These stacks would probably show optical continuity perpendicular to the plane of the plates.

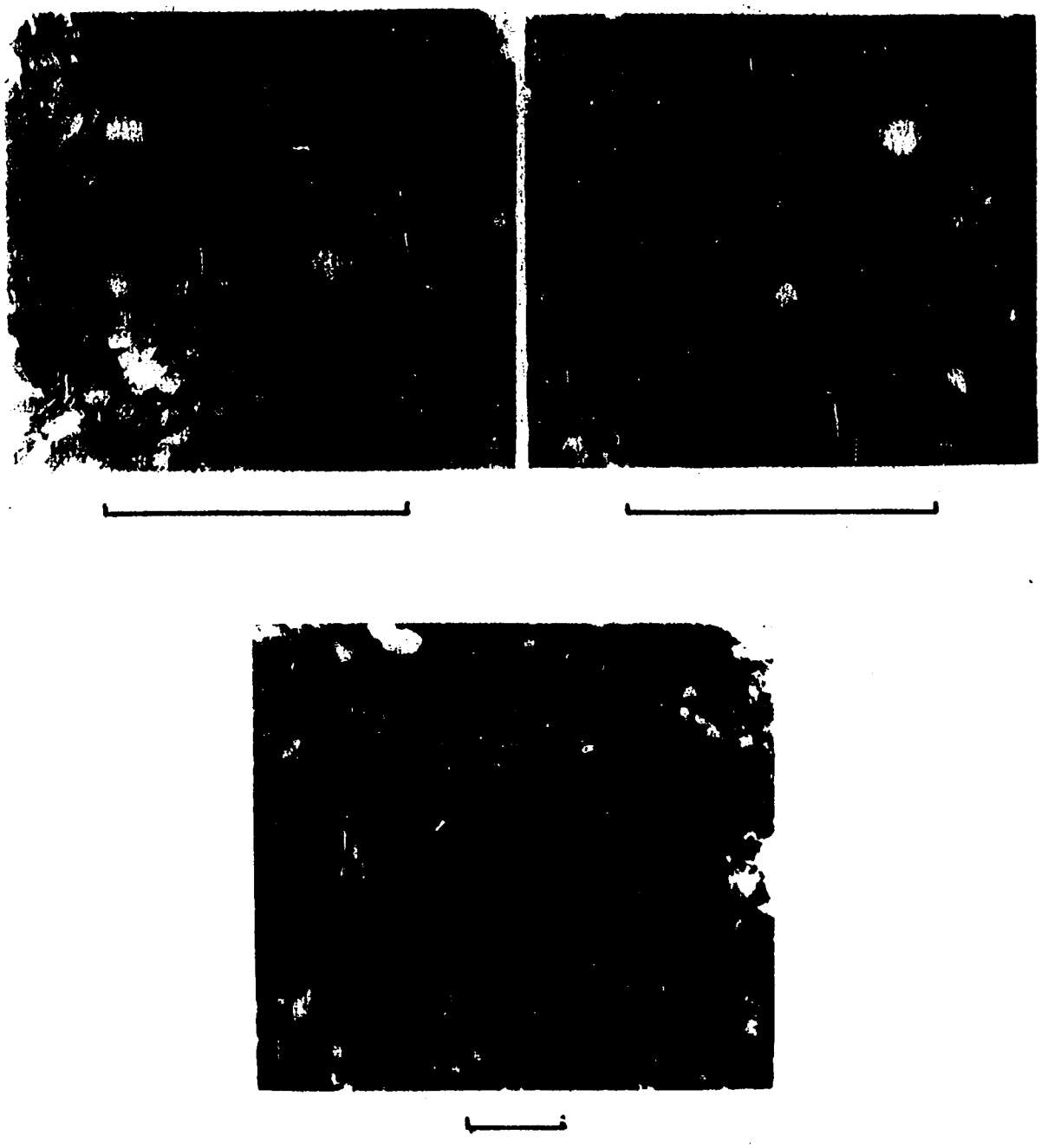

Figure 19. Electron micrographs of sample KR-11.

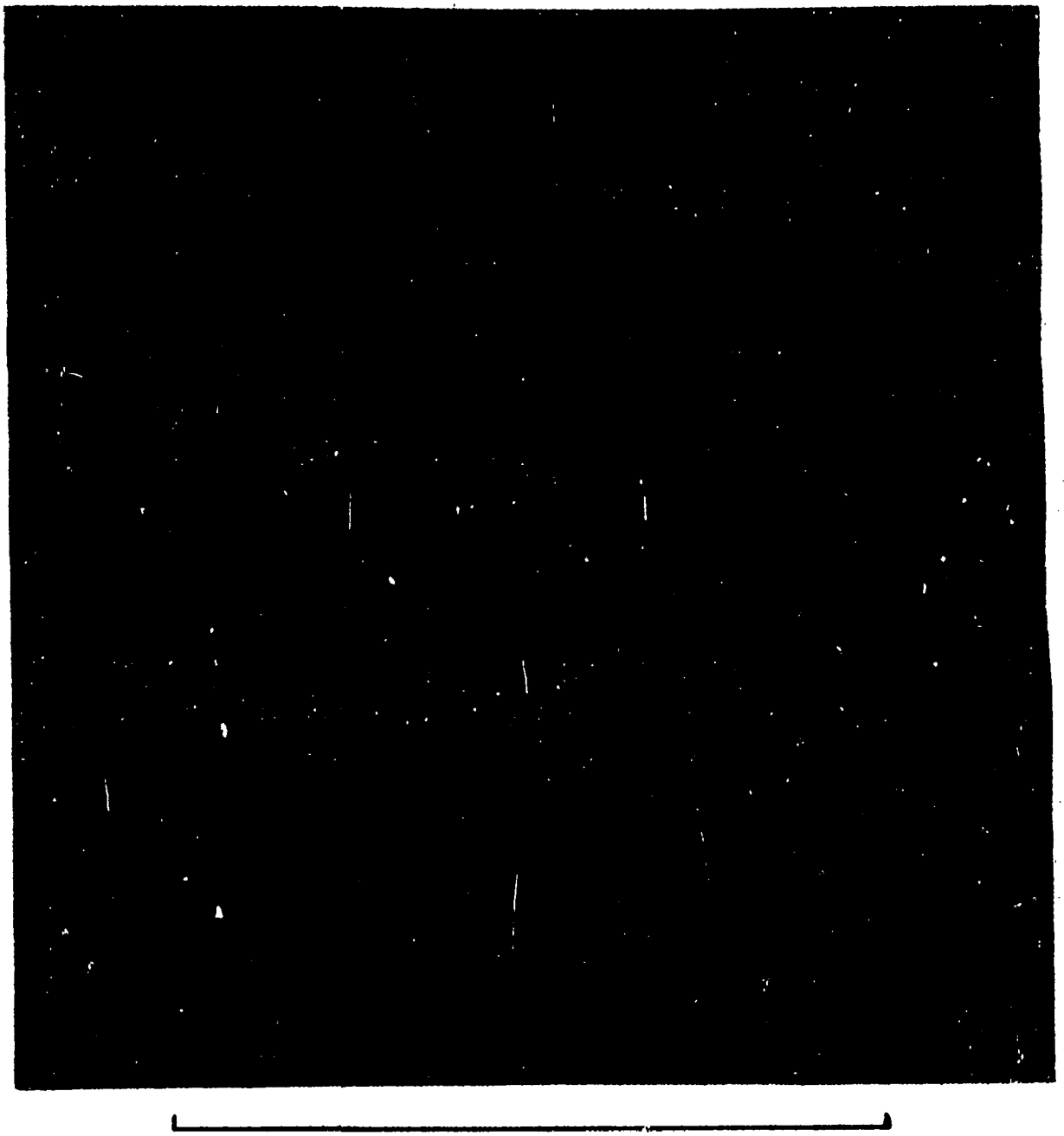

Figure 20. Electron micrograph of sample KR-11.

STRUCTURAL CONSIDERATIONS

Experimental work previous to this study on the ion exchange properties of various expandable layer clays has shown that for the most part only a limited amount of fixation of potassium can be imposed under laboratory conditions of temperature and concentration (Barshad, 1948, 1954; Weaver, 1958). Barshad (1954) interprets his data to indicate that "fixation" is a function of the amount of total interlayer charge. He shows that an expanded lattice with an interlayer charge of 150 or more meq/100 gm of material heated to 1000°C will contract to 10.4Å when saturated with K^+, whereas lattices with a charge of 110 or less meq/100 gm have an expansion equivalent to one molecular layer of water (12.4Å). So lattices with interlayer charges greater than 150 meq/100 gm experience "fixation" well over 50% of the total exchange capacity with the highest interlayer charge probably represented by muscovite which Barshad (1954) gives as 262 meq/100 gm. Weaver (1958) reports that maximum "fixation" occured with the Wyoming bentonite where fixed potassium reduced the TEC by 22 to 28%, while Barshad (1954) using a mild treatment was able to "fix" less than 4% NH_4^+ and less than 8% K^+ in montmorillonite.

Thus it would appear that substantial "fixation" of potassium occurs only under the most extreme conditions of temperature. However, montmorillonite in experimental

studies (Roy and Roy, 1955) is shown to be stable only up to 480°C, so high temperature fixation studies above this level must be interpreted with some care. Additional explanations have to be found, then, to account for the apparent collapse of 60 to 80 per cent of the layers of K-bentonite and the attendant "fixation" of a large percentage of potassium in randomly alternating layers. It appears that whatever the mechanism is operative in K-bentonite, it must be stronger in the collapsed layers than in the expandable ones since only a very moderate fixation of potassium was detected for the expandable layers with concentrated solutions of KOH.

Recent work by Radoslovich and Norrish (1962) and Radoslovich and Veitch (1963) strongly suggests that the ideal structure for muscovite is inconsistent in terms of the b-axis formula and in terms of the influence on it contributed by the octahedral and tetrahedral layers and by the interlayer cations. Realizing that original calculations of the structure did not account for the misfit of "free" tetrahedral and octahedral layers, they have proposed a new structural model based on the rotational "distortion" of the tetrahedral layer. Basically, the network of "silica" tetrahedra, ideally hexagonal, is shown to be distorted to a ditrigonal surface symmetry, by the opposed rotation of alternate tetrahedra. Hexagonal symmetry still remains in the octahedral layer

however. The amount of rotation varies from a few degrees to near the theoretical maximun of 30°. Thus the strain due to the misfit of a larger tetrahedral layer onto a smaller octahedral layer is relieved partly by expansion of the octahedral layer, with an accompanying contraction in thickness, and partly by contraction of the tetrahedral layer through rotation of the basal triads.

On this basis they propose (Radoslovich and Norrish, 1962) that the tetrahedral layers play only a secondary role in determining the b-axis, not the dominant role previously assumed. Furthermore, the cell dimensions appear to be controlled largely by the octahedral layer and the interlayer cations in such a way that for dioctahedral micas the interlayer cation (especially the large K^+) effectively stretches the octahedral layer. That this stretching does not occur for trioctahedral micas leads to the suggestion that initial tetrahedral displacements are due to the partly-filled character of the octahedral layers in the dioctahedral micas. Similarly, Burns and White (1963) have noted that treatment of muscovite with molten lithium nitrate at 300°C will remove a large portion of the interlayer potassium with an accompanying decrease in the b-axis dimension. The contraction of the b-dimension results in an effective decrease in the size of the ditrigonal opening in the planar surfaces with a consequent increase in the d(001) spacing upon resaturation with

potassium. Once the unit cell has contracted slightly, presumably by rotation of the tetrahedra, the size of the opening in the oxygen surface, initially occupied by potassium, decreases and potassium cannot fit down into the opening as far as it did initially. The result is a slight increase in d(001) from 9.96Å to 10.00Å when potassium was again added.

Since the a-dimension is related to the b-dimension by the relationship $a = b/3^{\frac{1}{2}}$, it will be affected in the same manner as the b-dimension.

The implication of this would seem to be that K-fixation involves a pre-tetrahedral rotation phenomenon, which diminishes greatly after tetrahedral-octahedral adjustments are accomplished. Any subsequent potassium contributed to the structure would be less likely to be as firmly held and could more easily exchange. This opposes the concept of a diagenetic alteration of montmorillonite to "illite" through slow K-adsorption.

Further considerations on the relationship of the OH bond to the interlayer cation (Bassett, 1960; Yoder and Eugster, 1955) indicate that the directed bonds for phlogopite are perpendicular to the sheets and inclined at a low angle for muscovite, thereby shortening the oxygen-cation distance and providing a stronger charge seat for the interlayer cation. Hence the tetrahedral configuration due to rotation is related to the degree of potassium penetration and to the orientation of the octahedral OH bonds.

For K-bentonite the high temperature of the primary hydroxyl DTA peak indicates a stronger OH-cation bond in the octahedral layer. The adsorption of K^+ must be partially controlled by the inclination of the directed OH bond rather than by tetrahedral substitution, since the lack of a prominent 500°C endothermic peak and the one angstrom increase in interlayer spacing due to Ca-adsorption preclude a high charge seat close to the interlayer cation. Ultimately the realtionship between the octahedral cation and adjacent hydroxyl must be linked to the nature of octahedral substitution. Radoslovich (1962) has shown by multiple regression analysis that for montmorillonites a slight increase in "b" occurs with the substitution of magnesium and iron octahedrally. But K-penetration (i.e., fixation) controlling largely the distortion of the tetrahedral layer adds an additional strain on the octahedral layer causing further stretching in the direction of the b-axis, so that, at least for a restricted range of potassium content, the amount of potassium present is directly related to the length of the b-axis (Radoslovich and Norrish, 1962, pt. 1).

A mitigating influence on the interlayer strain relationships exists if it is considered that octahedral cation sites are of two different sizes and that Al^{+3}, Mg^{+2}, and Fe^{+2} enter these sites preferentially. In other words, subsitutions within the octahedral layer appear to be ordered, and hence limits are placed on the amount and

kind of substitution that can occur (Radoslovich, 1963, pt. III). Radoslovich (1963a) further suggests that for muscovite, about 80 per cent of the octahedra must be occupied by Al^{+3} in particular, in order to maintain a stable muscovite-type structure. Possibly the degree of aluminum substitution in the K-bentonite lattice places similar maximum and minimum limits upon the amount of potassium that will be fixed in the exchange position and that varying K-adsorption within these limits accounts for the mixed-layering observed by X-ray diffraction. Future investigations of the b-axis parameter and OH bond inclination would be most revealing in this respect. It would be particularly interesting to find out whether or not the K-bentonite structure adjusts to the tetrahedral-octahedral mismatch over a distance of several structural layers rather than within each layer, that is, some individual layers being over-compensated and others under-compensated but with a net result of structural stability. If so, such an interplanar network of forces, if randomly centered, would produce a layer-lattice mosaic structure with some portions collapsed more than others, and having the appearance of a randomly interstratified clay mineral. This network would occur only in those expandable clays with high octahedral charge, since high tetrahedral charge (i.e., nontronites, etc) would induce different strain relationships as outlined by Radoslovich and Norrish (1962).

It is suggested that these considerations, if confirmed, would necessitate placing K-bentonite as a separate structural type within any major structural-chemical classification of clay minerals. The controlling forces involved would not occur in a continuum between montmorillonite and "illite" but rather define a distinctly separate structure with unique lattice parameters and physical-chemical properties.

ADDITIONAL DATA ON K-BENTONITES AND ASSOCIATED LIMESTONES

Insoluble Residues of Limestones

Insoluble residues of limestones adjacent to two different horizons were studied to find what gradational changes take place between the limestone and ash beds. Approximately 200 gm of limestone were taken at two foot intervals up to six feet away on either side, crushed to fragments 3/4 inch in diameter and dissolved slowly in weak (less than 10%) HCl. The residues were washed several times with distilled water, weighed and percentages calculated on the basis of the known weight of the original sample.

Figure 21 shows the extent to which insoluble content decreases away from the K-bentonite beds. Examination shows that chert constitutes practically all the insoluble material adjacent to the beds with slightly more present below than above. The formation of chert is a consequence of the devitrification of volcanic ash whereby released silica replaces nearby calcium carbonate volume for volume. In hand specimens, the chert zones appear to be discontinuous above and below the K-benonites, but thin section examination reveals a much more consistent pattern of distribution. Several writers have discussed in detail the problem of the release of silica from volcanic material and consequent deposition as chert in nearby carbonates (Fox and Grant, 1944; Ross and Hendricks, 1945; Siever, 1962).

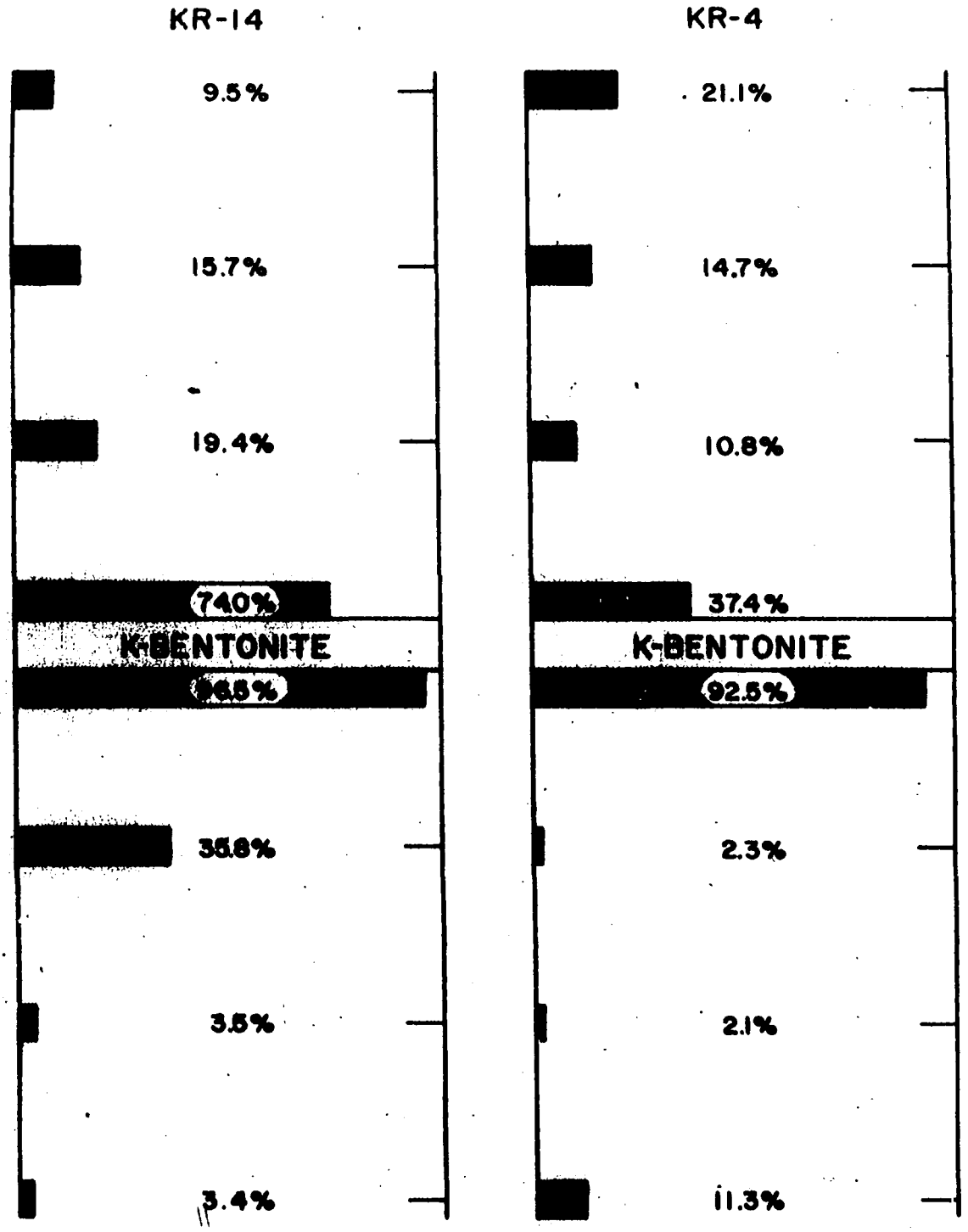

Figure 21. Vertical change in insoluble residue content at two K-bentonite localities.

Insolubles of samples between 2 and 6 feet away are composed primarily of clay with minor amounts of feldspar (orthoclase). In addition to a regular 10Å sequence, both 14Å and 7Å reflections, characteristic of chlorite, are found in the insoluble clays. Glycolation showed expansion effects only on clays taken between 0 and 2 feet away from the ash beds, indicating the vertical extent of K-bentonite gradation into the carbonates. Further away the 14Å and 10Å series were dominant as detrital micas form a major portion of the clays. Heating for two hours at 550°C did not shift the 14Å peak noticeably, a characteristic reaction for chlorite (Warshaw and Roy, 1961).

In sample KR-4 the soluble content increases at the bottom of the section as another K-bentonite horizon is approached. The higher readings at the top of the section probably reflect differences inherent in the lithologic change from Tyrone to Curdsville limestone.

Heavy Mineral Analyses

Heavy mineral studies of K-bentonite 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 practically absent

in others. The uppermost horizon in the Black River is normally characterized by an abundance of biotite (fig. 22) concentrated in zones within the bed and can usually be distinguished from other ash beds on this basis. The concentration of biotite within individual K-bentonite horizons and the variability in grain diameter (.2 to 1 mm) indicate that the mica is primary in origin and not an authigenic constituent.

Colorless apatite crystals, 0.05 to 0.3 mm in length, account for as much as 30 per cent of heavies in several samples and show a variety of morphological 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. Leucoxene crystals range up to 50 per cent of the total heavies in a few instances, but generally it is a minor constituent.

Colorless zircon crystals varying from 0.03 to 0.4 mm in length are present as a minor constituent. Habits are similar to those described by Larsen and Poldervaart (1961) for batholithic zircons which include euhedral, doubly terminated, prismatic crystals with simple and complex forms; singly terminated, subhedral crystals; and anhedral crystals with irregular forms (fig. 23). Although the appearance of apparently rounded or broken crystals within a K-bentonite horizon might seem to indicate a detrital origin, it should

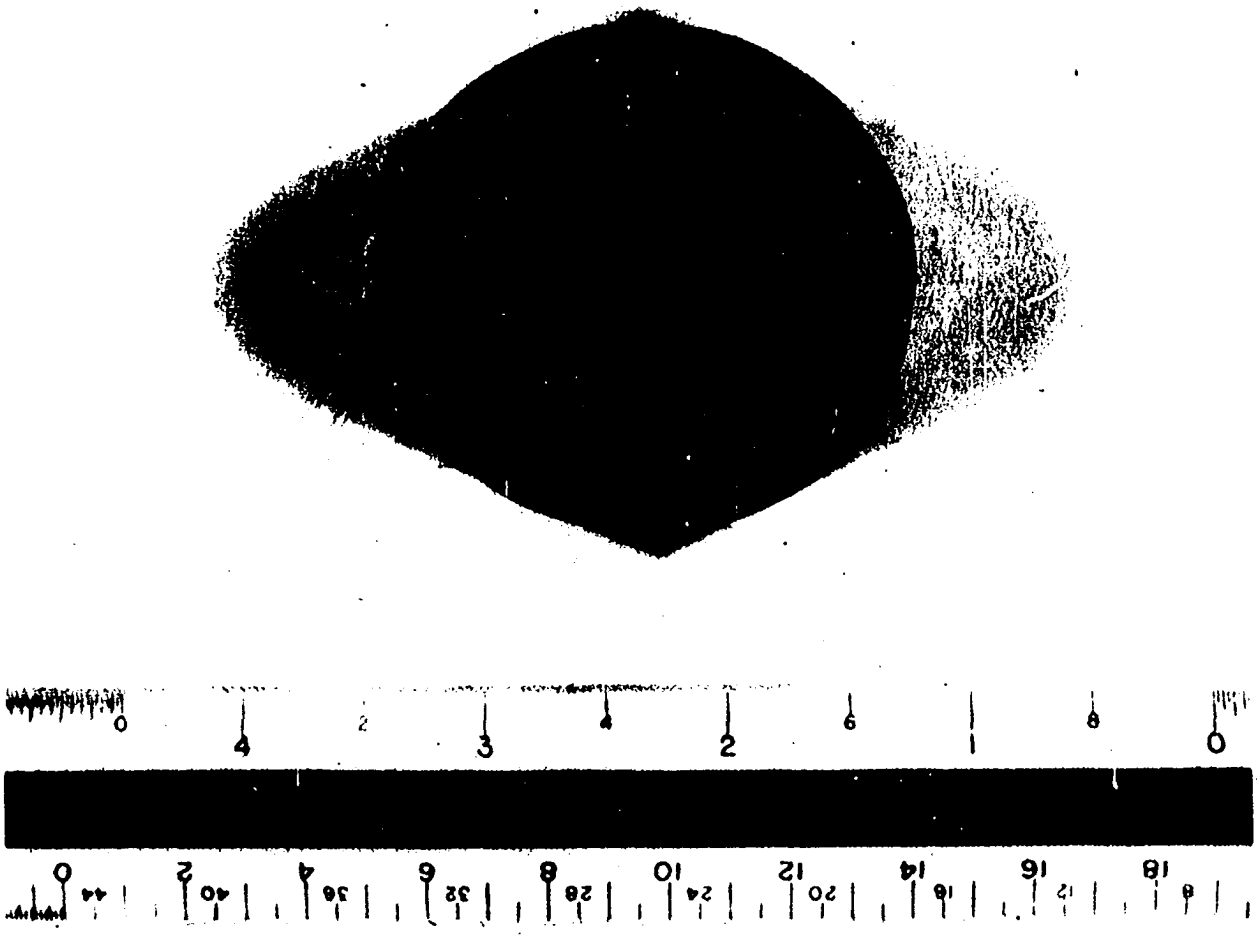

Figure 22. Biotite flakes in sample KB-1D. Upper scale in inches and lower scale in centimeters.

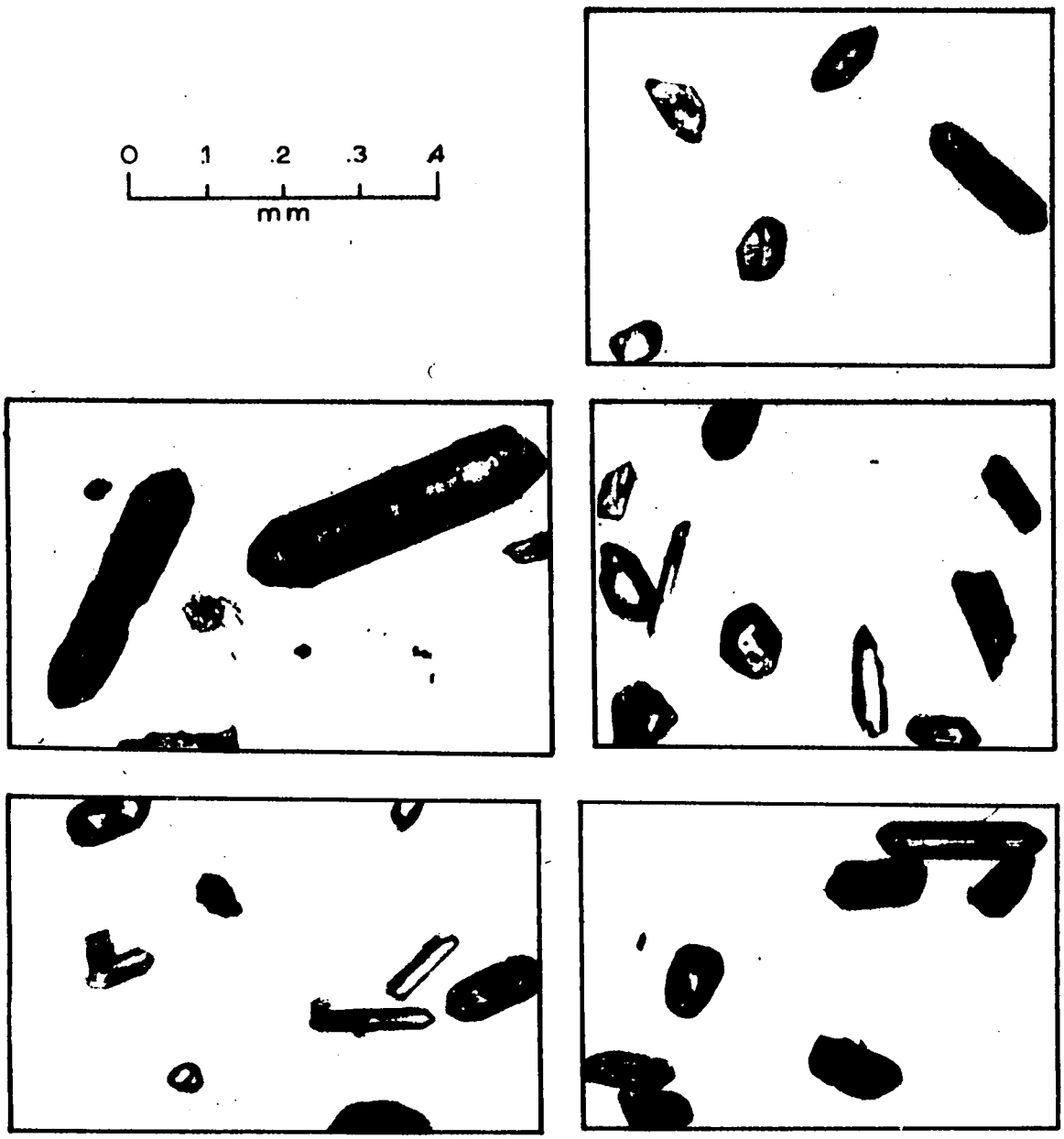

Figure 23. Typical zircon habits in Ordovician K-bentonites.

be pointed out that alternative interpretations are possible. Larsen and Poldervaart (1957) have shown that the irregular forms on zircons from granodiorites and tonalites of the Bald Rock batholith near Bidwell Bar, California, are not a result of mechanical abrasion or impact, but rather are products of incomplete crystallization. The rapid decrease in heavy mineral content in adjacent limestones further supports the idea of initial pyroclastic origin.

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 mineral suite. 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 volcanic rocks and their abundance here only attests to the pyroclastic origin of these beds. Hematite and fluorite, abundant in the insoluble residues of adjacent limestones, are detrital. No characteristic physical properties of the heavy minerals was found to be consistently useful for stratigraphic correlation.

Trace Element Study

Elemental analysis by X-ray fluorescence spectroscopy provides both a quantitative and qualitative evaluation of compositional variations in minerals to a high degree of accuracy. By bombarding a specimen with a beam of X-rays, the specimen itself takes the place of the target metal in normal X-ray diffraction. Characteristic radiation from the sample can then be analyzed by first passing it through the crystal lattice of any one of several substances, and then recording the widened spectrum as it is sensed by a flow-proportional counter tube. The results appear in graphical form as a series of peaks, each representing the energy of a particular wavelength emitted by the various elements. By comparing the peak heights with standard mixtures quantitative results can be obtained.

A General Electric X-RD-5 X-ray unit adapted to fluorescence spectroscopy with a chromium tube was used for this study. The apparatus operated at 50 kv and 40 ma with a 2 second time constant and 500 counts per scale. A lithium fluoride analyzing crystal was used for most of the work. During these analyses proper equipment was not available for work in a helium atmosphere required for many of the lighter elements on the periodic chart. Consequently, data for Ca, Mg, Na, K, Si, or Al are not presented, although this certainly would be useful information.

Over the energy range studied the most characteristic peaks belong to Cr and Fe. The first is a function of the chromium X-ray tube and so is present in all patterns. Some iron contamination is also contributed from the tube and must be subbracted from the total Fe content. Iron was not measured for comparative purposes because it was felt that the slightest degree of weathering might effectively change the iron content and prevent it from being a reliable parameter for K-bentonite correlation.

Titanium proves to be the most useful trace element for study since it is present in great enough quantities to be detected easily and yet is not subject to easy mobilization. Figure 24 shows several patterns superimposed one on another for comparative purposes. Intensity measurements in terms of scaler counts per 10 second intervals are given in table 6 and can be considered to indicate relative proportions of Ti in each sample. For more quantitative control, a 1 per cent mixture of TiO_2 (AR) and K-bentonite was prepared and the TiKa peak intensities measured to show the degree of peak height contributed by a known amount of titanium. TiO_2 powder was first mixed with water to insure a homogeneous distribution in the sample and then thoroughly mixed with an accurately weighed amount of K-bentonite that had been lightly ground to pass through a #200 screen. This process was repeated five times with five different K-bentonites

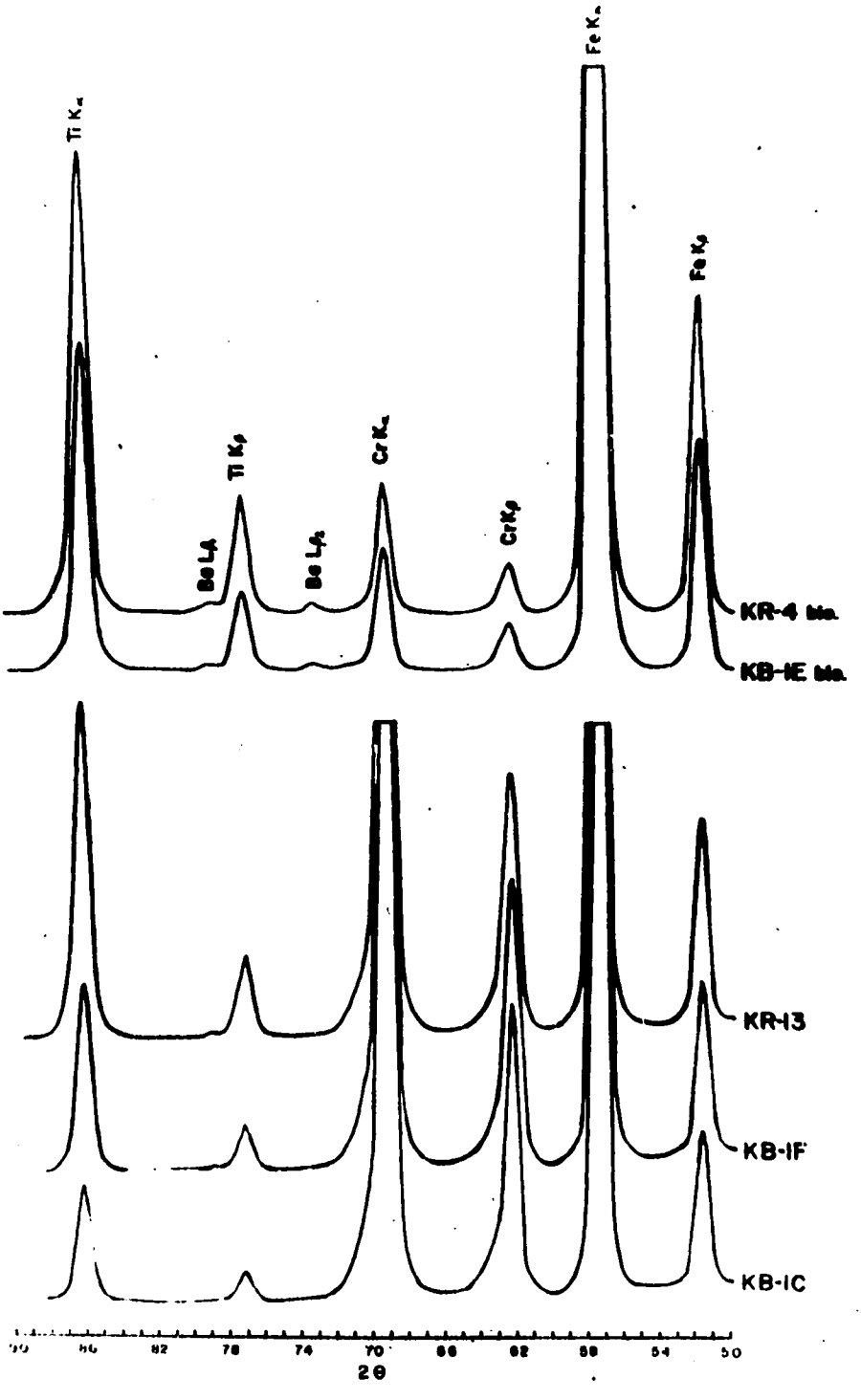

Figure 24. X-ray fluorescence patterns.

Table 6. X-ray Fluorescence Spectrographic Data

Sample No.	TiKα Intensity (counts/10 sec.)	%Ti
KB-2A	178	0.31
KB-1B	238	0.42
KB-2B	300	0.53
KB-3B	330	0.58
KB-4B	285	0.50
KB-1C	160	0.28
KB-2C	308	0.54
KB-3C	290	0.51
KB-1D	272	0.48
KB-2D	255	0.45
KB-2E	305	0.54
KB-1F	250	0.44
KB-3F	307	0.54
KB-1G	330	0.61
KB-2G	260	0.46
KB-3G	137	0.24
KB-1I	150	0.26
KB-2K	296	0.52
KB-3H	286	0.50
KB-1I	153	0.27
KB-2I	230	0.40
KB-4I	246	0.43
KB-1J	130	0.23
KR-4T	313	0.55
KR-6	305	0.54
KR-8	235	0.41
KR-9M	240	0.42
KR-9T	200	0.35
KR-9-3	215	0.38
KR-11	250	0.44
KR-13	405	0.71
KR-14B	332	0.58

and the additional counts per 10 seconds in the TiKα peak at 86.2° 2θ were averaged. Allowance was made for the oxygen contribution from TiO_2 and a figure of 570 was calculated for the number of counts in 10 seconds represented by 1 per cent titanium (table 7).

On this basis fourteen K-bentonite specimens were chosen from the uppermost horizon in the Tyrone limestone over a distance of approximately 120 miles from Hamilton, Ohio, to Camp Nelson, Kentucky, in Jessamine County. Quantitative calculations were made and are shown in figure 25. The most noticeable feature is a consistent increase in the amount of Ti going from north to south (fig. 25). Not enough samples were analyzed to give a more definite directional trend than "southerly", but at least it does seem to be consistent with, and to substantiate, the inferences made by earlier authors that the source for Ordovician volcanic ash was in the southeastern part of the United States. It is to be expected that the ferromagnesian minerals will decrease in abundance away from the volcanic source, while the lighter particles will be carried much farther. Similarly the proportion of trace amounts of elements carried by the heavy minerals should reflect this regional trend. Additional work along this line is needed to delineate more accurately the source direction.

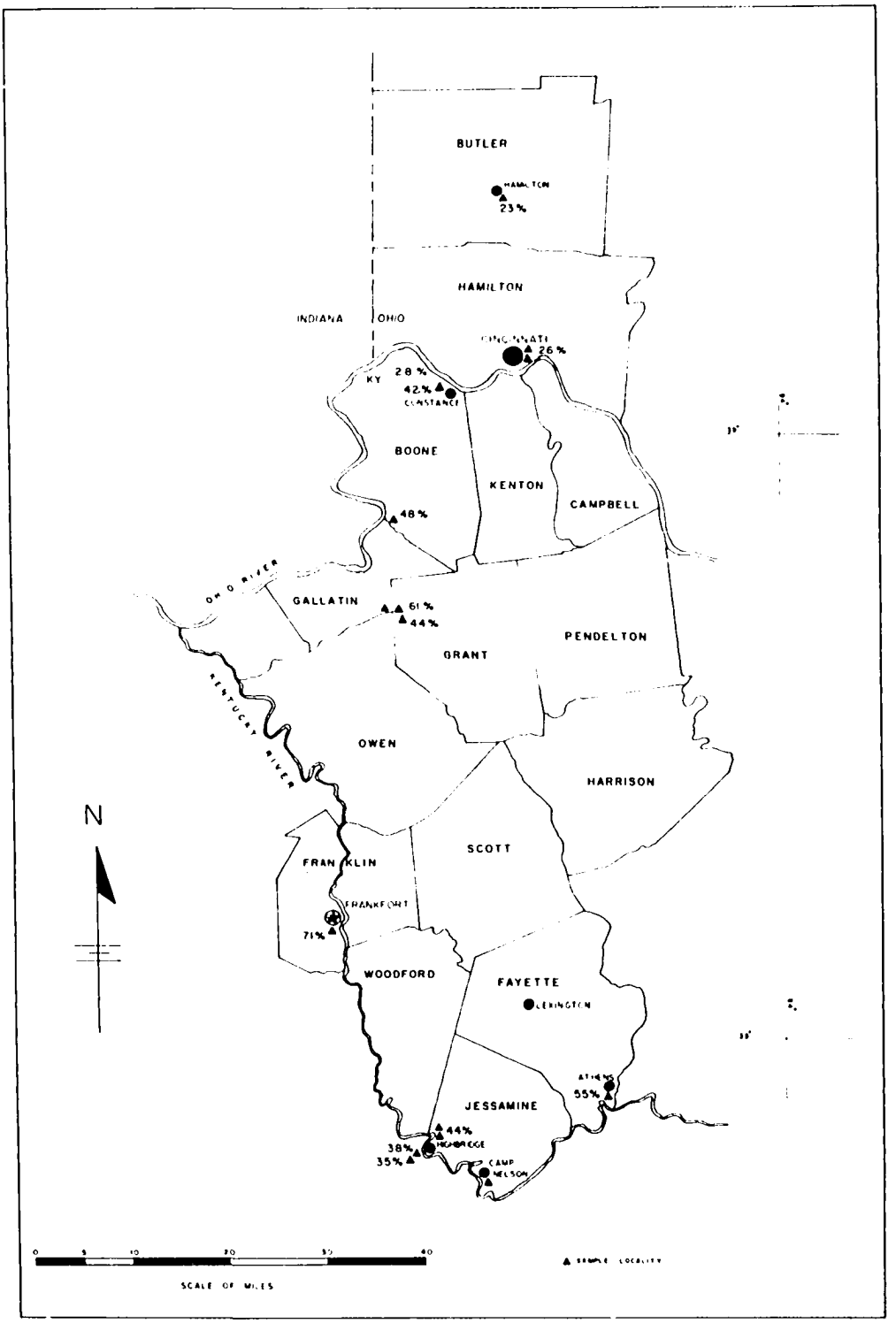

Figure 25. Map showing distribution of titanium in uppermost K-bentonite horizon.

Table 7. Intensities of Ti Kα peaks measured in counts per 10 seconds due to addition of 1% TiO_2.

Sample No.	Normal Count	2 gm + 1% TiO_2	Difference
KR-9T	200	1008	808
KR-11	250	1074	824
KB-1I	153	996	843
KB-1H	150	980	830
KB-1C	160	1013	853

Average = 832 counts per 10 seconds for 1% TiO_2.
Correction for amount contributed by pure Ti only gives equivalent average count of 570.

In order to find where the titanium was being released in the samples, biotite from the same horizon but 90 miles apart were examined for titanium content (fig. 24). The Kα peak of KB-1E has an intensity of 2230 counts, and for KR-4, 3140 counts. This is a substantial increase over the clay samples and indicates a considerably larger titanium content. Furthermore, for the biotites, the proportion of Ti (5.51% for KR-4 and 3.91% for KB-1E) is roughly equivalent to the trend observed in the clays. Hence, the trace amount observed in the clay structures is a reflection of the overall distribution in biotite. Undoubtedly, leucoxene also contributes in a similar fashion.

Ti is not an exchangeable ion in the clays as attempts to remove it with ammonium acetate were unsuccessful, but rather is contained somewhere within the clay structure

itself. It is suggested that a separate study of the trace element distribution in the heavy minerals might be even more revealing in terms of the source direction of ash, since the percentage of titanium is much larger and less subject to small sampling errors.

Herrin (1957) has correlated Cretaceous bentonites in Texas over short distances using Ca:Mg and Si:Al ratios. There is no reason why this kind of approach could not be taken here.

ORIGIN OF CLAYS

The devitrification products of volcanic ash are known to vary in composition depending upon the balance of geochemical factors in the environment of deposition. Kimpe, Gastuche and Brindley (1961) have shown that low temperature and pressure synthesis of aluminum and magnesium silicates produces various proportions of gel and crystalline phases. With aluminum, the gel phase is the more abundant and identification of the crystals is possible only by electron diffraction; with magnesium the yield in crystals is much higher and X-ray diffraction can be used. The properties of the gels influence the kinds of crystals synthesized, with the main factors being pH, salt concentration, and the ratio of aluminum or magnesium content to the silica content. For aluminum, the change from a six-fold coordination to a four-fold coordination increases with pH. Kaolinite appears at low pH, where the six-fold coordinated structure of aluminum is stabilized. At higher pH values, a "mica-like" clay mineral appears, while the four-fold coordinated aluminum increases in the gel structure. Apparently the low yield in crystalline phase is controlled by the solubility of silica as is the formation of a 1:1 or a 2:1 lattice.

In the geologic record it is noticed that K-bentonites are recognized primarily in the Paleozoic while montmorillonitic

bentonites characterize later periods. Some exceptions are noted (Zen, 1959) but are rare. Weaver (1953) suggests that the predominance of carbonate sequences in the Paleozoic compared to the Mesozoic indicates a longer exposure to sea water for the older clays and hence more opportunity to retain potassium from an environment saturated with calcium. For the younger bentonites a more active geologic environment would induce more rapid deposition and hence less susceptibility to K^+ adsorption. However, not all K-bentonites in the Paleozoic are preserved in carbonate sequences, indeed in Virginia, K-bentonites are found within the Martinsburg shale and in similar clastic sequences farther south (Ross, 1928, 1955; Kay, 1935) and in the upper Mississippi Valley (Kay, 1931).

It appears doubtful that a majority of potassium could have been added diagenetically after the clay had formed, since under these conditions one would expect to find the permeability of the clay a factor in determining K^+ adsorption and hence a definite change in the expandable: non-expandable layer ratio through the vertical section of a single bed. Similarly, for a large amount of potassium to have replaced divalent calcium would require a rather high concentration of potassium locally. It is suggested that this could arise only as a result of potassium contribution from the volcanic material itself, and could not be dependent upon the "normal" concentration of K^+ in sea water.

CONCLUSIONS

The following conclusions and suggestions are drawn:

1. K-bentonite found in middle Ordovician rocks varies considerably from other 2:1 clays in both mode of origin and physical-chemical properties. It is essentially a dioctahedral 2:1 clay composed of randomly inter-stratified swellable and non-swellable layers in proportions varying between 2:3 and 1:3, the former with calcium in the exchange position and the latter containing potassium derived from the devitrification of volcanic ash. K-bentonite is easily recognized from hydrous micas, montmorillonites, and "mixed-layer" degraded micas by X-ray diffraction, DTA, cation exchange, and electron micrograph properties.

2. K-bentonite appears to be a fairly stable structure with additional K-adsorption limited to less than 10 per cent. Cation exchange data indicate low tetrahedral substitution and high octahedral substitution. Disagreement of analytical data appears most reasonably explained in terms of recent structural re-evaluations of 2:1 layer lattice silicates. It is suggested that K-bentonite does not represent one stage in a continuum between montmorillonite and "illite" but rather is

confined to a narrow compositional range between these two and distinct from them representing the type of material initially formed through devitrification, and hence should be considered for classification as a separate unit in a general classificiation of the clay materials.

3. Correlation on the basis of clay mineralogy alone is not promising since regional consideration shows vertical consistency in properties from one horizon to another but slight lateral change in layer ratios. K-bentonites are distinguishable from detrital clays however. Heavy minerals show no substantial stratigraphic parameters with the exception of biotite concentration in the uppermost horizon in the Tyrone limestone. Trace element study may offer the best hope for development of correlation parameters.

4. A southerly increase in titanium content correlates with an increase in the thickness of K-bentonite beds in that direction and is consistent with earlier suggestions of a southeastern source direction.

5. Future investigations should concentrate on trace element analysis and detailed structural investigation of the clay mineral structure.

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