The Pennsylvania State College

The Graduate School

Earth Sciences Department

Division of Mineralogy

MINERALOGY AND PETROLOGY OF SOME PALEOZOIC CLAYS FROM CENTRAL PENNSYLVANIA

A thesis

by

Charles Edward Weaver

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January 4, 1952 — T. F. Bates, Mineralogy Division

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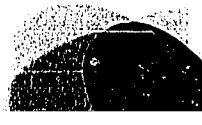

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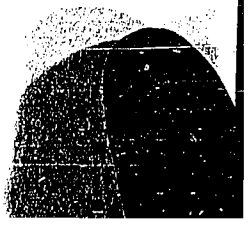

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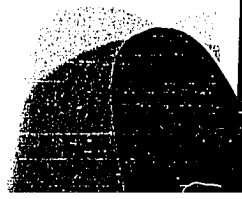

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ABSTRACT

The literature of the dioctahedral 2:1 clay minerals is briefly reviewed. A classification of the 2:1 minerals is presented in which the percent of total replacement which occurs in the octahedral and tetrahedral sheets is considered to be of primary importance. The secondary division is based upon the degree of expansion and the nature of the external cations.

22 samples of the Ordovician K-bentonite were examined by the use of size analyses, differential thermal curves, x-ray diffraction patterns and electron micrographs. The less than one micron fraction of two typical samples was studied in more detail. It was established that the K-bentonite consists of randomly interstratified expanded and non-expanded 2:1 layers in the ratio of 1:4. Many of the samples contain packets of chlorite. The chlorite was found to cause an endothermal peak on the differential thermal curves which was formerly believed to be due to illite. Chemical analyses of the two samples show a direct correlation between the percentage of K present and the percentage of non-expanded layers.

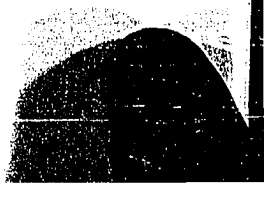
The nature of the heavy and light minerals indicates that the clay altered from a volcanic glass. It is believed the clay first formed as an expanded 2:1 mineral and later obtained K which caused 80 percent of the layers to become non-expanded.

27 samples of the limestone on either side of a

series of K-bentonite beds were examined in detail. The heavy and light minerals indicate that the insoluble residue is composed of both volcanic and non-volcanic material. The non-volcanic material is largely a non-expanded dioctahedral 2:1 clay; the volcanic material altered to form chlorite. The chlorite and volcanic heavy minerals increase in abundance as the K-bentonites are approached from above or below. It is believed that the ash altered to chlorite because of the availability of Mg. The availability was probably enhanced by the presence of the calcite ooze.

Four samples of bedding plane clay were collected from the Ordovician limestone. The light and heavy minerals reflect both volcanic and non-volcanic sources for the material. The non-volcanic clay is a non-expanded dioctahedral 2:1 clay, whereas the volcanic material altered to an expanded dioctahedral 2:1 clay. It is not known whether the expanded clay formed directly from the ash or from the alteration of a partially non-expanded clay.

Samples of the Oswego and Juniata graywackes and pure clay beds occurring in the Oswego were examined. The light and heavy minerals indicate that the clays were in all cases detrital. The clay minerals are predominantly the non-expanded dioctahedral 2:1 variety though small amounts of halloysite are sometimes present. Electron micrographs show that much of the non-expanded clay is lath-shaped. The clay beds are believed to have been formed by a winnowing of the coarser graywackes.



Two clay beds in the Devonian shales were examined. One, the "Tioga Bentonite" was found to be identical to the Ordovician K-bentonite. The other contains largely non-volcanic heavy minerals. The predominant clay is the non-expanded dioctahedral 2:1 variety. Minor amounts of chlorite are also present. The data suggest that the clay in this bed was probably concentrated by a winnowing action.

MINERALOGY AND PETROLOGY OF SOME PALEOZOIC CLAYS FROM CENTRAL PENNSYLVANIA

INTRODUCTION

NATURE OF STUDY

This study concerns the mineralogy and petrology of some rocks from the Palezoic (mainly Ordovician) of central Pennsylvania. The clay minerals in these rocks were investigated in detail. The majority of the clay minerals investigated were the 2:1, dioctahedral variety, i.e. illite and montmorillonite. As the concepts and nomenclature of these clays are at present in a state of crepuscular confusion a brief discussion of the evolution and present trends plus the author's own ideas on nomenclature are presented.

MONTMORILLONITE

Nomenclature

Ross and Hendricks (1945) have given a detailed discussion of the montmorillonite nomenclature. In the present paper only the high lights and particularly pertinent material will be discussed. Damour and Salvetat (1847) first proposed the name montmorillonite for a particular clay mineral having the formula $4.2SiO_2.Al_2O_3.7.4H_2O$. The name beidellite was given by Larsen and Wherry (1925) to a montmorillonite having a 3:1 silica:alumina ratio. Wherry,

Ross, and Kerr (1930) found that the majority of the montmorillonites had a SiO_2: Al_2O_3 ratio of 4:1 but that many had ratios as high as 5:1 and as low as 2:1 without change in structure. Ross and Kerr (1931) gave several members for the montmorillonite clay group: montmorillonite, beidellite with a SiO_2: Al_2O_3 ratio of 3:1, an unnamed member with a 2:1 ratio, nontronite with a SiO_2 Fe_2O_3: ratio of 3:1, and saponite, a magnesium member.

Ross and Hendricks (1945), on the basis of 103 chemical analyses, listed nine structural formulas of minerals of the montmorillonite groups:

Montmorillonite $Al_{1.67}Mg_{.33}^{Na_{.33}} Si_4O_{10} OH_2$

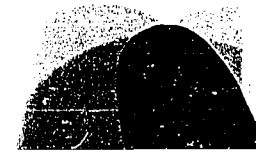
Beidellite $Al_{2.17}^{Na_{.33}} Al_{.83}Si_{3.17} O_{10} OH_2$

or $Al_{2.22}^{Na_{.33}} Al_{1.00}Si_{3.00} O_{10} OH_2$

Nontronite $Fe^{3}_{2.00}{}^{Na_{.33}} Al_{.33}Si_{3.67} O_{10} OH_2$

Nontronite (aluminian) $Fe^{3}_{2.17}{}^{Na_{.33}} Al_{.83}Si_{3.17} O_{10} OH_2$

Hectorite $Mg_{2.67}Li_{.33}^{Na_{.33}} Si_4 O_{10} OH_2$



Saponite $Na_{.33}Mg_{3.00}Al_{.33}Si_{3.67}O_{10}OH_2$

Saponite (aluminian) $Na_{.33}Mg_{2.67}Al_{.33}Al_{.67}Si_{3.33}O_{10}OH_2$

Sedletsky (1942, 1945) suggested that the montmorillonites should be named by means of an"index number", equal to twice the SiAl ratio (to the nearest whole number). Thus beidellite, with a 1:1 ratio, would be montmorillonite - 2, montmorillonite with a 5:2 ratio would be montmorillonite - 5. This classification has five stages in the montmorillonite series.

The term montmorillonite is now used in three different ways: as a group name; as a sub-group where alumina replaces silica, and as a name for minerals having the same composition as the type material (Damour and Salvetat).

MacEwan (1951) suggested that the term montmorillonoid be used as a group name. Correns (1951) suggested the term montmorin as a group name.

Structure

Pauling (1930) proposed structures for gibbsite, brucite, talc, pyrophyllite, the micas, and the chlorites. He indicated that these silicates were made up of a combination of gibbsite or brucite layers with silicate layers.

Pyrophyllite was shown to have a layer structure composed of two tetrahedral silicate layers inclosing an octahedral gibbsite layer. Pauling (1930) and Jackson and West (1933) showed that the muscovite structure was similar to that of pyrophyllite. In muscovite one-fourth of the silica in the tetrahedral layers is replaced by alumina. The excess negative charge is compensated for by potassium situated between successive tetrahedral layers.

Hofmann, Endell and Wilm (1933) proposed a structure for montmorillonite that is the same as that of pyrophyllite. They found that the a and b spacings in the plane of the cleavage are identical with those for pyrophyllite. However, the spacing characteristic of the thickness of the unit layers had a higher value for montmorillonite than for pyrophyllite. It was concluded that montmorillonite was composed of layers of pyrophyllite with variable amounts of water between them.

Marshall (1935) indicated that the montmorillonite lattice carried a negative charge which he suggested was caused by the replacement of Al for Si in the silica layers, and Mg for Al and $Fe^{"}$ for Al in the gibbsite layers. This negative charge would be balanced by Ca, Na, K and other exchangeable cations which occur between the lattice layers.

Ross and Hendricks (1945) worked out the structural formulas previously listed on the basis of these principals of substitution.

Barshad (1950) and others have shown that the

amount of water held between the layers (the degree of expansion in the "C" axis direction) is directly related to the type of cation present between the layers.

ILLITE

Nomenclature

A group of minerals related to the micas, but containing less potassium and more water, have been given a wide variety of names: hydro-micas (Galpin, 1912), hydrous micas (Bayley, 1920), potassium-bearing clay minerals (Ross and Kerr, 1931), glimmerton (Endell, Hofmann, and Maegdefrau, 1935), and illite (Grim, Bray and Bradley, 1937). Bravaisite (Mallard, 1878) is the only specific mineral name that has been proposed for a mineral of this group.

The term illite has been more widely accepted than the others. Illite is considered to have from four to eight percent K_2O and from six to twelve percent H_2O. The X-ray diffraction patterns give the same "d" values as those of muscovite though the individual lines are wider.

At the 1950 International Soil Science Congress it was agreed that the term illite should be used as a general term for mica-clay minerals (both di- and tri-octahedral types) which show no significant swelling and which give a first order, basal reflection of about 10Å

which is unaffected by mild chemical and/or thermal treatments. Hydrous mica was suggested as a general term to cover both illites and mixed-layer minerals.

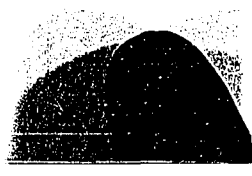
Structure

The structure of illite was suggested by Grim (1942) to be similar to that proposed for montmorillonite. He considered that replacement in the tetrahedral layer was predominant over that in the octahedral layer and believed 15 percent of alumina replacing silica to be necessary to obtain a non-expanded structure.

MIXED LAYER MINERALS

In addition to the "pure" clay minerals, mixed minerals can occur in which layers of different types alternate either regularly or randomly. Gruner (1934) pointed out that certain vermiculites had interstratified layers of mica. Hendricks and Jefferson (1938) found that many vermiculites are actually mixed vermiculite and chlorite layers. Grim and Rowland (1942) on the basis of differential thermal analysis identified several specimens as being composed of mixed layers of illite and montmorillonite. Nagelschmidt (1944) showed that by treating illite with $CaCl_2$ certain of the layers could be made to expand. This resulted in an interstratification of expanded and non-expanded layers.

Bradley (1945) has shown how, by the use of

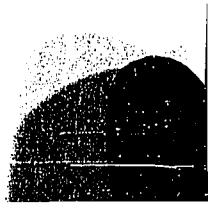


ethylene glycol, mixed layer minerals can be detected by x-ray analysis. He found that bravaisite, glimmerton, metabentonite and Grundy illite are mixed layer minerals

THE CLASSIFICATION OF THE 2:1 MINERALS

During the present study, it became apparent that the differences between illite and montmorillonite are not as great as they appear at first glance. White (1950) has shown that by treating illite with $MgCl_2$ and precipitating the exchanged potassium the illite would expand and give a montmorillonite x-ray pattern. Many of the montmorillonite minerals particularly beidellite, contain some non-expanded layers which are indicated by the presence of potassium in the chemical analyses. Caillère and Hénin (1949) have shown that by boiling montmorillonite in KOH the clay will collapse and give a 10Å illite x-ray pattern. The present work has shown that by continuously wetting and drying the K-bentonite in a solution of one normal KOH the expanded layers collapse and give a 10Å value.

It appears that many of the 2:1 dioctahedral clays contain both expanded and non-expanded layers and that it is relatively easy to change their state of expansion. The ideas given below were developed in an attempt to relate these two clay groups. Although few of the ideas are new, they have not before been organized coherently.



Except for the external cations, K, Na, Mg and Ca, the structural formulas of illite and montmorillonite are similar, and in many cases identical. The predominance of K as an external cation is characteristic of illite.

Illite, as usually defined, has a non-expanded lattice, with a "c"-spacing of 10Å. Montmorillonite has an expanded lattice, 12 to 20Å in the direction of the "c" axis.

Illite commonly gives a hydroxyl-endothermal reaction at 500-600°C., whereas the montmorillonite reaction usually occurs at 600-750°C.

These three criteria provide the fundamental means of differentiating between the two clay groups. Naturally all three were developed from a study of many clays. However, it is significant that the great majority of montmorillonites studied are those formed from volcanic ash, usually of Cretaceous and Tertiary age. The majority of the illites described are found in the Carboniferous sediments. In most cases clays of either type from other sources do not possess the properties which are diagnostic of the "type" materials.

Probably the most widely used and most reliable means of identifying the minerals of these two clay groups is by x-ray diffraction. When a 10 Å value is obtained the clay is considered to be non-expanded and is called illite. If the x-ray pattern has a value of 12Å or greater, the clay is considered to have an expanded lattice and is

called montmorillonite (assuming it is not vermiculite or chlorite). However, Caillère and Hénin (1949) and the present work have shown that K can be fixed between the montmorillonite layers such that a 10Å lattice will result. Barshad (1948) and others have shown that biotite will exchange K for Mg and form an expanded lattice with a value greater than 10Å. (Further leaching may cause replacement within the lattice itself, but it does not appear to be necessary in order to form an expanded lattice). Nagelschmidt (1944) and White (1950) have shown that, at least in part, illite can be transformed into an expanded clay. There is little doubt that these processes working in nature for any length of time will form an expanded clay from a non-expanded one and vice versa. Therefore, the concept of an expanded verses a non-expanded lattice is not based on the structure of the clay mineral, but upon the cations in interlayer positions.

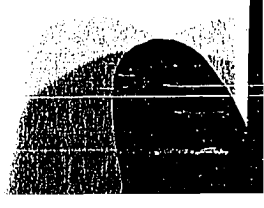
An examination of the differential thermal data shows that the characteristic hydroxyl-endothermal reaction of illite occurs between 500 and 650° C; however, this figure is determined largely from samples obtained from the Carboniferous rocks. When illites from totally different sources are examined this range can be extended, as for example in the case of the Ballater illite described by McKenzies, Walker, and Hart (1949). The hydroxyl-endothermal reaction of this illite occurs at 713°C.

The montmorillonites derived from the majority of

the Cretaceous and Tertiary ash beds have a hydroxyl-endothermal reaction restricted to a 650-700°C. range. However, Mg and Fe montmorillonites from varied sources extend this range from 500 to 800°C.

The temperature of the hydroxyl-endothermal reaction is controlled largely, if not entirely, by the various cations in the octahedral layers. As the range in temperature of this reaction for the two clays is almost identical, it would appear that the composition of the octahedral layers varies within the same range and could be identical. Further, the chemical analyses indicate that the octahedral layers for illite and montmorillonite are quite similar and in many cases the same in composition.

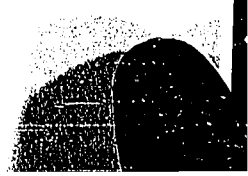
The composition of the tetrahedral layers in the two clays can only be determined by chemical analysis. Although the ranges of the percentage of aluminum replacing silicon overlap to a considerable extent, the available analyses (largely of bentonites) indicate a tendency for many of the montmorillonites to have a very small amount of aluminum in the tetrahedral layer, as compared to the known illites. However, this does not mean that a 2:1 lattice with little aluminum in the tetrahedral layers cannot attract potassium and form a 10Å lattice. It is just more probable the potassium would not be firmly held and the unstable clay resulting would tend to have the K replaced by Ca, Na, or Mg to form an expanded clay structure. Neither is the converse true. For, even if there is 15 or



20 percent replacement in the tetrahedral layer but no potassium is available, the lattice will be expanded. This can be easily appreciated by a study of the data presented by Ross and Hendricks (1945). Of the 82 dioctahedral montmorillonites analysed, 25 have nearly 15 percent or greater replacement in the tetrahedral layer. (On the basis of the chemical composition of the impure pyrophyllite lattice these 25 clays would be classed as illite but on the basis of their degree of expansion they would be called montmorillonites).

The above discussion suggests that starting with a variety of impure pyrophyllite-talc structures, x-ray patterns of either an expanded or a non-expanded lattice can be obtained depending upon the external cations attached to the lattice. The hydroxyl-endothermal reaction occurs at a variety of temperatures, depending upon the composition of the octahedral layers, and does not show any correlation with the "c" dimension of the lattice (the "a" and "b" dimensions are similar for both clays). The chemical analyses, excluding the external cations, also show no direct correlation with the "c" dimension of the lattice. (Other differences such as the asymmetry of some of the x-ray lines of the expanded lattice can be explained by the bonding strength, size, and charge of the external cations).

Although over the complete range of impure pyrophyllite-talc compositions, either an expanded or a



non-expanded lattice can be formed under a variety of conditions, there appear to be poles or compositions where one type of structure is predominant. These poles may be the result of three factors: (1) selected sampling in age, location, and variety of source rock (2) the tendency of certain cations to occur together in nature and (3) the limited stability of certain combinations of exchangeable cations and cationic substitutions in the lattice.

As more clays are being described and these poles become less sharply defined, the question arises as to whether these clays should be divided into two separate mineral groups when the distinction apparently rests entirely upon the type of external cation present, and particularly when minerals of these two groups also occur interstratified. It is believed that such a division is not a self perpetuating concept because it is based upon criteria resulting from modifying processes acting upon the clay, rather than upon the more fundamental composition of the impure pyrophyllite-talc structure which reflects more accurately the original composition of the source material.

The result of over-emphasizing the importance of the expandability of 2:1 clays has led only to confusion and as more information is acquired the confusion increases geometrically. If the existing confusion is to be alleviated the idea of expandability must be placed in the background

and all 2:1, dioctahedral, and probably trioctahedral, clays treated as one group with a breakdown into mineral species based on the chemical composition of the impure pyrophyllite lattice. The terms expanded and non-expanded (or K, Ca, Mg etc.) can be prefixed to these names to indicate the external cations present. At this stage in the development of clay mineralogy it is best to use a classification based on hypothetical end members that will include all 2:1, dioctahedral clay minerals. Figure 1 shows how all dioctahedral and trioctahedral 2:1 minerals with varying degrees of expansion can be organized into a compact classification.

The main breakdown of the 2:1 minerals is based upon the location of the replacement occurring in the impure pyrophyllite-talc lattices. The clays having greater than 75% of the total replacement occurring in the tetrahedral sheets are referred to as tetrites. Clays having greater than 75% of their total replacement occurring in the octahedral sheet are called octrites. Clays having greater than 25% of the total replacement occurring in both types of sheets are called tetoctrites.

Each of these sub-groups are further divided on the basis of whether the clay is dioctahedral or trioctahedral. The dioctahedral clays are divided into Al and Fe depending upon which is the predominant element in the octahedral sheet, the trioctahedral clays contain only Mg as the predominant element in the octahedral sheets.

The secondary classification is based upon the composition of the external cations which directly reflect the degree of expansion. The expanded clays have Ca, Na and Mg etc. as the external cations. The non-expanded clays have K as the external cation. Clays having both types of external cations are the mixed layer type containing both expanded and non-expanded layers.

Eventually names might be given to all possible combinations of the two divisions; however, for the present the use of descriptive terms will help to avoid confusion. The illite-like minerals can be referred to as non-expanded Al 2:1 clays. Where the composition is known they can be further defined and called non-expanded Al tetrites or non-expanded Al tetoctrites; glauconites are called non-expanded Fe tetoctrites; trioctahedral illites are non-expanded Mg tetoctrites. Many of the montmorillonites are expanded Al octrites; most are expanded Fe tetrites. Beidellites can be classed as expanded and non-expanded Al tetrites or tetoctrites.

It is thought that this arbitrary breakdown on the basis of the location of the predominant replacement in the lattice, will avoid the confusion caused by trying to name newly described minerals by comparing them with established species. From the name the general composition of the impure pyrophyllite lattice and the state of expansion can be inferred. And by making the state of expansion secondary and independent of composition a more realistic

approach to the origin and genesis of these clays can be used. The composition of the impure pyrophyllite-talc lattice reflects the original source of the clay mineral. The composition of the external cations, and degree of expansion reflect environment and environmental changes occurring after deposition of the clay.

2:1 SILICATES

DEGREE OF EXPANSION	EX. CATIONS	PERCENT OF TOTAL REPLACEMENT IN 2:1 LATTICE								
		>75% in TETRAHEDRAL			>25 and <75% in BOTH			>75% in OCTAHEDRAL		
		TETRITE			TETOCTRITE			OCTRITE		
		DIOCTAHEDRAL		TRI.	DIOCTAHEDRAL		TRI.	DIOCTAHEDRAL		TRI.
		Al	Fe	Mg	Al	Fe	Mg	Al	Fe	Mg
EXPANDED	Ca Na Mg									
EXPANDED & NON-EXPANDED	Ca Na Mg K									
NON-EXPANDED	K									

FIG. 1

ORDOVICIAN K-BENTONITE

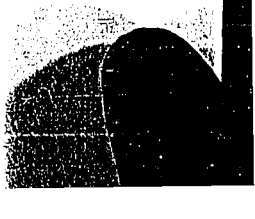
INTRODUCTION

Geological Occurrence

Bentonite (a clay formed from the alteration of glassy igneous material, usually a tuff or volcanic ash) is common in the Cretaceous and Tertiary rocks of the western United States and is usually composed of montmorillonite clay minerals. Nelson (1922) was the first to report altered volcanic ash beds in the eastern United States. These beds were found in Kentucky, Alabama, Tennessee, and Virginia. Later Bonine and Honess (1929), Rosenkrans (1933) and Kay (1931, 1935, 1944) located and described occurrences in central Pennsylvania and southern New York. Sardison (1924) and Allen (1929, 1932) reported altered volcanic ash beds in Minnesota, Iowa, and Wisconsin. These eastern occurrences are all found in the Trenton and Black River limestones of the Middle Ordovician.

The eastern beds were classed as bentonite because of their occurrence as thin, wide-spread beds and the ability of the material to slake when placed in water. Ross (1928) reported euhedral crystals of biotite, and crystals of orthoclase and albite in the material. Volcanic structure is rarely preserved and has only been noticed by Ross in a few thin sections.

Since much of the clay has been metamorphosed by



slippage along bedding planes, Ross (1928) suggested it be called metabentonite (highly altered bentonite). However, as much of the material is not metamorphosed, it would perhaps be best to refer to it as potassium bentonite (K-bentonite) to differentiate it from the montmorillonite bentonites.

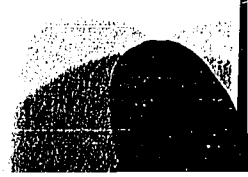
Grim and Rowland (1942) reported that the"metabentonites" from High Bridge Kentucky gave a differential thermal curve like montmorillonite and x-ray patterns similar to mica. They were not able to reconcile the apparent discrepancy. Bradley (1946) proposed that the material consists of mixed layer mineral composed of illite and montmorillonite.

Samples Studied

Twenty-two samples of K-bentonite were collected from five different localities and fourteen stratigraphically different beds in Central Pennsylvania.

The beds vary from ½ inch to 10 inches wide and average 2 to 4 inches. The color varies from tan to gray. Nearly all of the beds contain an abundance of thin layers of secondary calcite.

The fresh K-bentonite is hard and gives a semi-conchoidal fracture. This material is quite blocky and solid pieces 4 to 6 inches thick and a foot square can be obtained. The more weathered material has a shaly texture and breaks into thin chips. This grades into a highly



weathered plastic clay with no evidence of structure.

Figure 2 is a columnar section of Middle Ordovician rocks in Central Pennsylvania taken from Kay (1944). Beds of metabentonite are indicated by numbers from 0 to 7 and the letters N_1, N_2, and A to F. These beds are described in detail by Rosenkrans (1933). The location and the beds from which the present samples were obtained is given in Table 1.

Table 1

Localities and Beds From Which K-Bentonite Samples Were Collected

	Symbol For Beds
Quarry	
Oak Hall (OH)	2 0 N_1 N_2
Bell Mine Quarry (B)	A D
Bell Mine (M)	N_2 A D
Water Quarry (W)	A B C D E
Salona (S)	5 4 3 2 1 0 A F

Oak Hall (OH) is located 3 miles east of State College. The samples were collected in a quarry which is still in operation and thus the specimens are relatively fresh. Several samples were collected by Dr. C. E. Prouty of the University of Pittsburgh.

The Belle Mine Quarry (B) at Bellefonte, 10 miles

northeast of State College has not been worked for many years and the K-bentonite samples from here are highly weathered.

In an attempt to obtain fresh material 3 samples were collected from the Belle Mine (M) shaft 600 feet below the surface (about 1/4 mile east of the quarry). However, only one sample N_2 appeared to be fresh.

The Water Quarry (W) is an abandoned quarry 2 miles east of the Belle Mine. All of these beds are considerably weathered.

Eight samples were collected at Salona, 50 miles northeast of State College. Several beds are quite fresh but many are weathered to a plastic, structureless material.

Table II is a list of the samples with a brief megascopic description.

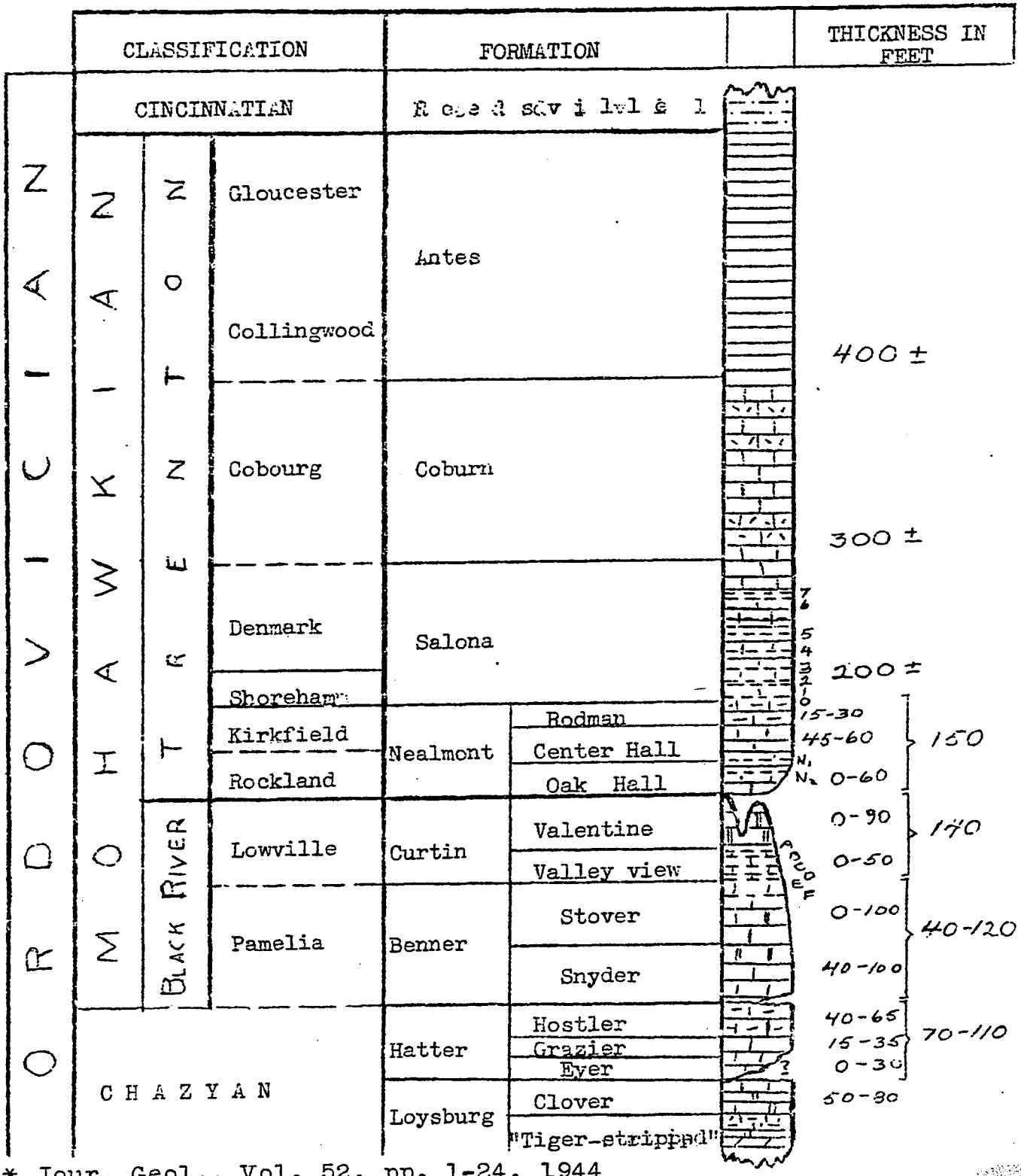
Table II

Description of K-Bentonite Beds

Sample No.	Description
S-5	Light gray, highly weathered, structureless.
S-4	Light gray, highly weathered, structureless.
S-3	Light gray and light tan, moderately weathered, shaly.
S-2	Tan, fresh, hard, blocky.
S-1	Tan, highly weathered, structureless.
S-0	Tan and gray, fresh, shaly.
S-A	Gray, moderately weathered, shaly.
S-F	Gray, moderately fresh, shaly.
W-A	Light tannish gray, highly weathered, very fine chips.
W-B	Light tannish gray, highly weathered, very fine chips.
W-C	Light tannish gray, moderately fresh, shaly.
W-D	Gray, moderately weathered, shaly.
W-E	Tan, moderately weathered, shaly.

STRATIGRAPHY OF MIDDLE ORDOVICIAN LIMESTONES

After G. Marshall Kay *



* Jour. Geol., Vol. 52, pp. 1-24, 1944

Fig. 2

Table II (cont.)

Sample No.	Description
B-A	Gray, moderately weathered, fine chips.
B-D	Gray, moderately weathered, shaly.
$M\text{-}N_2$	Gray, fresh, very hard, blocky.
M-A	Gray, moderately weathered, shaly.
M-D	Gray, moderately weathered, blocky to shaly.
OH-2	Tan, fresh, blocky.
OH-0	Gray and tan, moderately fresh, shaly.
$OH\text{-}N_2$	Gray, fresh, blocky to shaly
$OH\text{-}N_1$	Gray, fresh, blocky.
$OH\text{-}N_1$	Tan, moderately fresh, shaly.

MINERALOGY

Bulk Samples

Size Analysis

Twelve, 20 gm. portions (crushed to pea size or less) of sample B-D, were each placed in 500 cc. of water and shaken on a rotary shaker for periods of from 5 to 100 hours. 25 cc. of material of less than 1 micron size was drawn off and the amount in each sample was plotted against the shaking time. (Figure 3). From this graph it can be seen there is a break in the slope of the curve somewhere between 20 and 30 hours. Thus a run of approximately 24 hours will give the maximum amount of dispersion in the most reasonable time. The efficiency of the rotary shaker decreases considerably after twenty-four hours to equal the dispersion between 5 and 25 hours would require an additional run of 60 hours.

Twenty grams of sixteen of the K-bentonites were

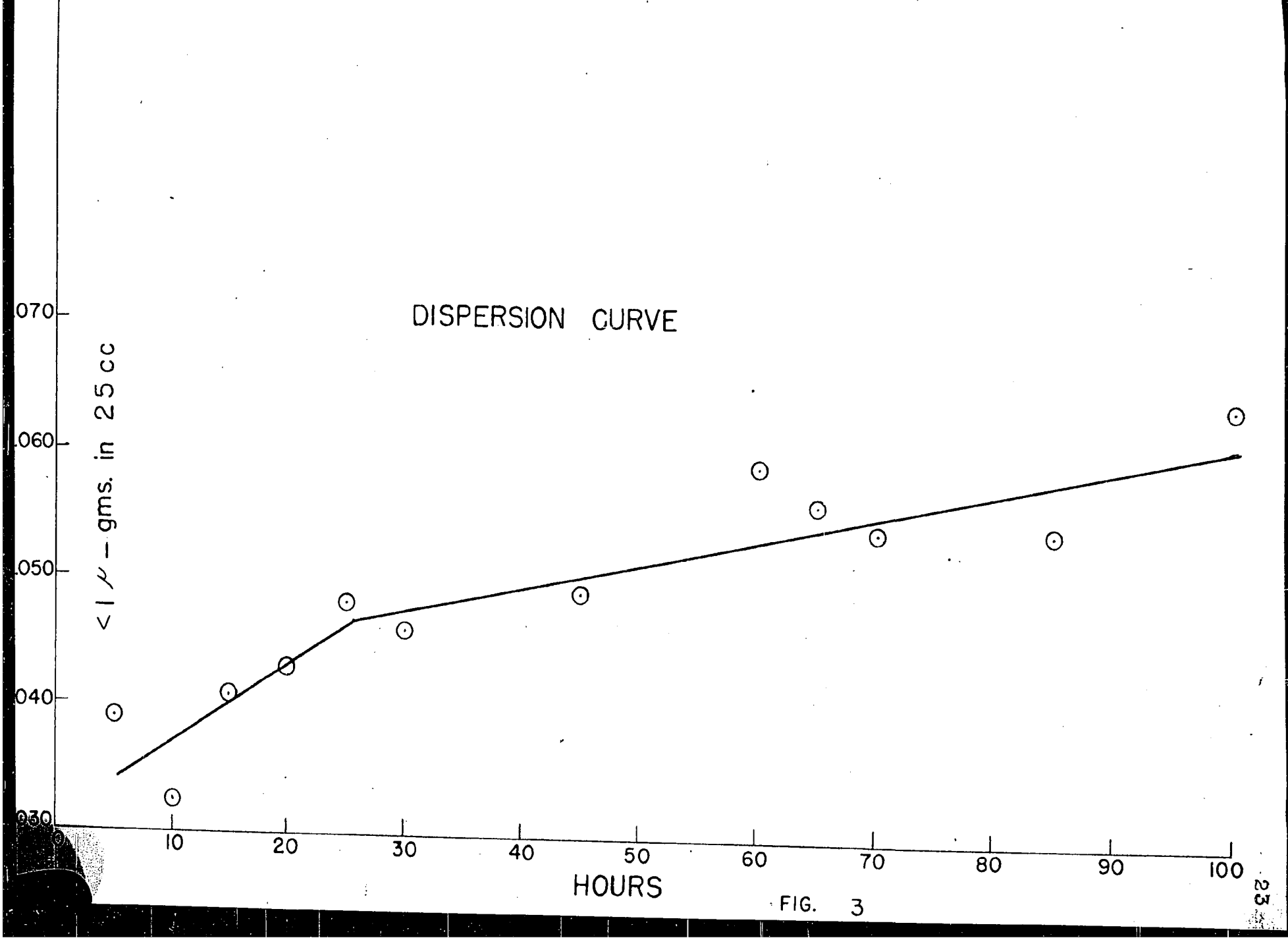


FIG. 3

placed in 500 cc. of distilled water, 8 drops of NH_4OH were added and the samples were shaken for 24 hours on a rotary shaker. The samples were then diluted to 1000 cc. and pipetted at 1 ø intervals. Cumulative curves were constructed (Figure 4 - 6) and tables drawn up showing the amount of material in each ø size. (Table 3). (The ø scale as derived by Krumbein (1934) simplifies the calculations required in statistical analyses. The logarithm, to the base 2, of the diameter is used and the log is multiplied by -1 to avoid negative numbers (phi $-\log_2$ diam. (mm)).

The cumulative curves give a graphical representation of the amounts of material in each grade size. As it is doubtful if the method used completely dispersed the clays, the curves are actually a measure of the degree of dispersion rather than of the size relationships. Of the two types of curves seen in the graphs, one is approximately a straight diagonal line between 4 and 11 ø. The other type shows a rather sharp increase in slope around 7 or 8 ø extending to 10 or 11 ø indicating that the unique frequency curve has a fairly sharp peak with a mode near 9 - 10 ø. The K-bentonites which have curves with a break in the slope are fresher than those with the constant slope with the exception of sample M-N_2, which is the least weathered metabentonite and yet produces practically a straight, horizontal curve. This exception is due to the fact that only 32.5% of the material was dispersed to finer than 4 ø (12.5% between 4 and 11 ø) and the change in slope would not be apparent.

The Percentage of K-bentonite in each Ø Size and the pH Values for the Bulk Samples

Diameters in Microns	Ø	S-5	S-4	S-3	S-2	S-1	S-0	S-A	S-F	B-D	M-N_2	W-A	W-C	OH-2	OH-0	OH-N_2	OH-N_1
62.5	4	34.7	27.5	13.2	14.0	19.5	29.2	60.0	48.0	20.7	67.5	23.7	48.7	25.5	16.2	25.0	33.5
62.5-31.2	5	5.3	7.0	2.5	2.5	9.2		4.5	3.5	10.8	1.5	9.8	3.3	4.2	1.5	6.7	5.5
31.2-15.6	6	12.5	5.0	9.7	3.0	13.8	3.3	4.2	3.0	13.7	3.7	9.5	2.7	3.8	4.5	6.0	5.7
15.6- 7.8	7	10.5	7.5	16.3	6.5	12.2	1.7	3.3	5.0	13.5	0.3	8.0	2.8	4.7	4.3	6.8	4.5
7.8-3.9	8	8.2	12.0	12.2	19.7	9.3	6.0	3.2	7.0	9.3	2.2	10.2	3.7	16.0	10.0	7.0	4.8
3.9-1.95	9	7.5	12.0	10.3	17.0	7.7	12.3	3.5	8.2	8.5	0.8	9.8	4.3	14.3	12.0	16.0	19.7
1.95- .98	10	4.5	10.0	8.0	18.0	8.0	15.5	3.5	6.8	7.7	2.0	9.5	7.7	20.0	17.5	14.2	20.5
.98- .49	11	5.3	9.7	8.2	12.3	8.0	14.0	3.3	7.0	7.3	2.2	8.2	8.8	4.7	14.7	9.3	3.5
.49	11	11.5	9.3	11.8	7.0	12.3	18.0	14.5	11.5	8.5	19.8	11.3	18.0	6.8	19.3	9.0	2.3
pH		7.05	6.85	6.00	5.25	6.95	5.45	7.50	7.25	6.50	5.8	6.50	6.30	4.4	7.75	7.95	7.20

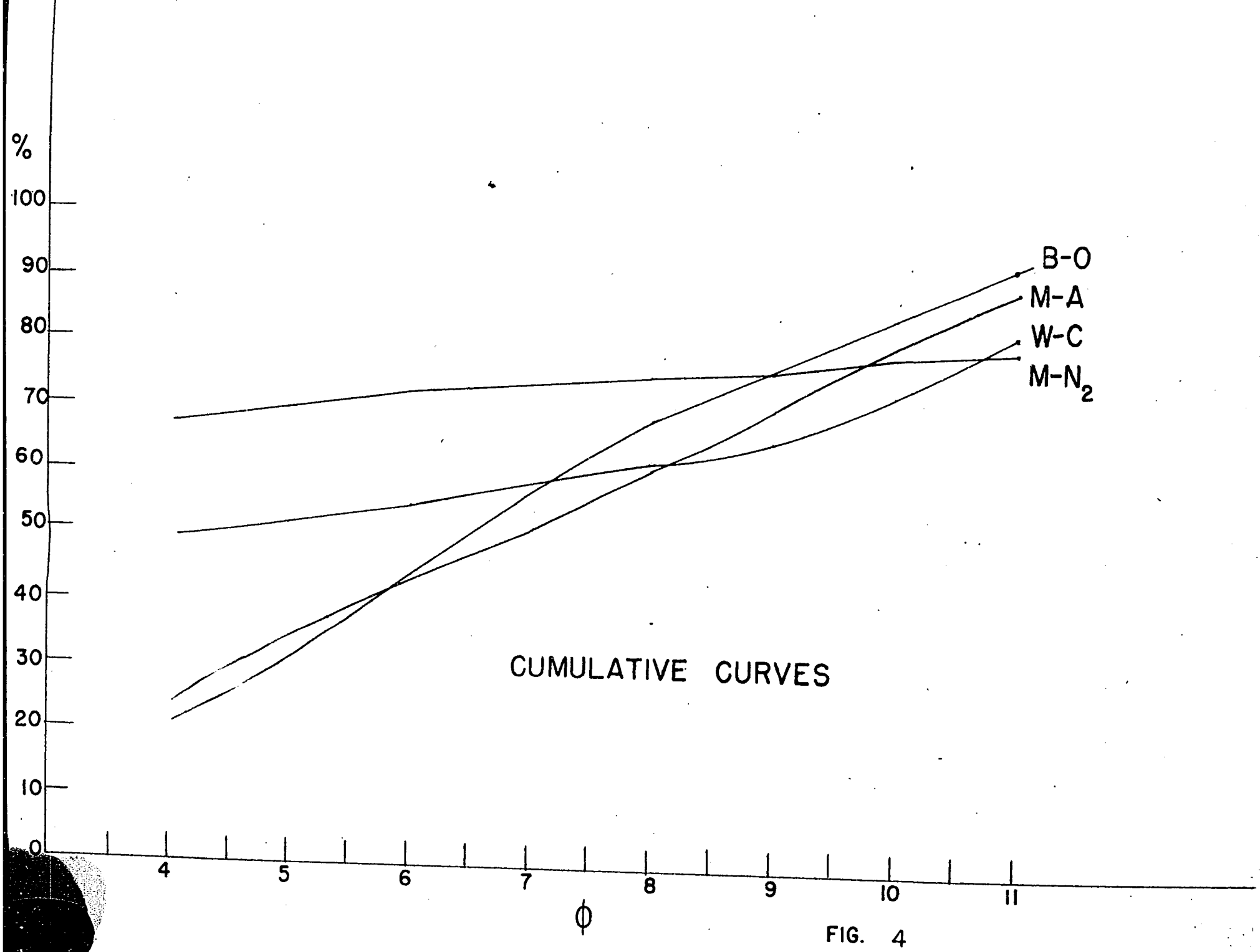


FIG. 4

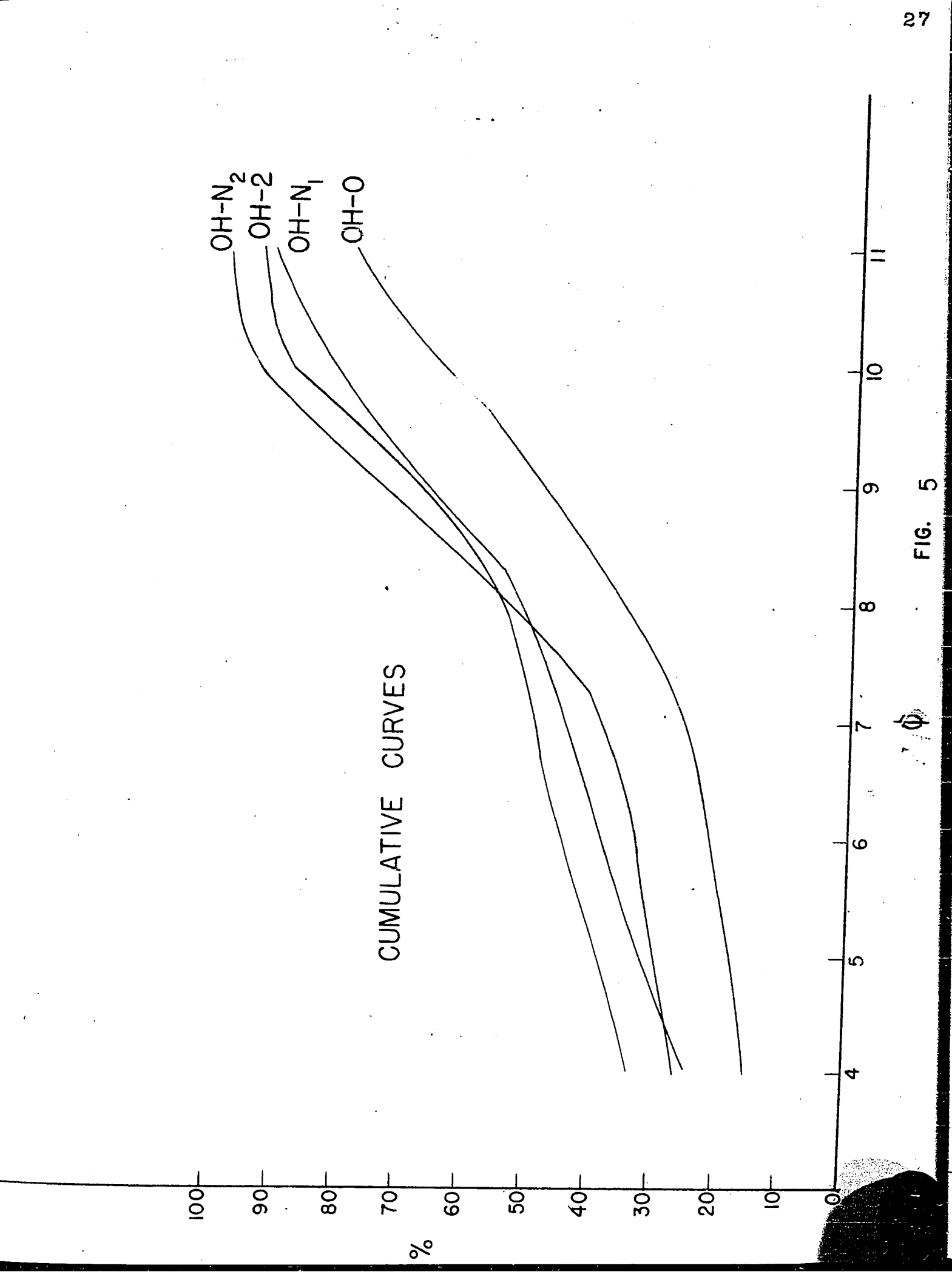


FIG. 5

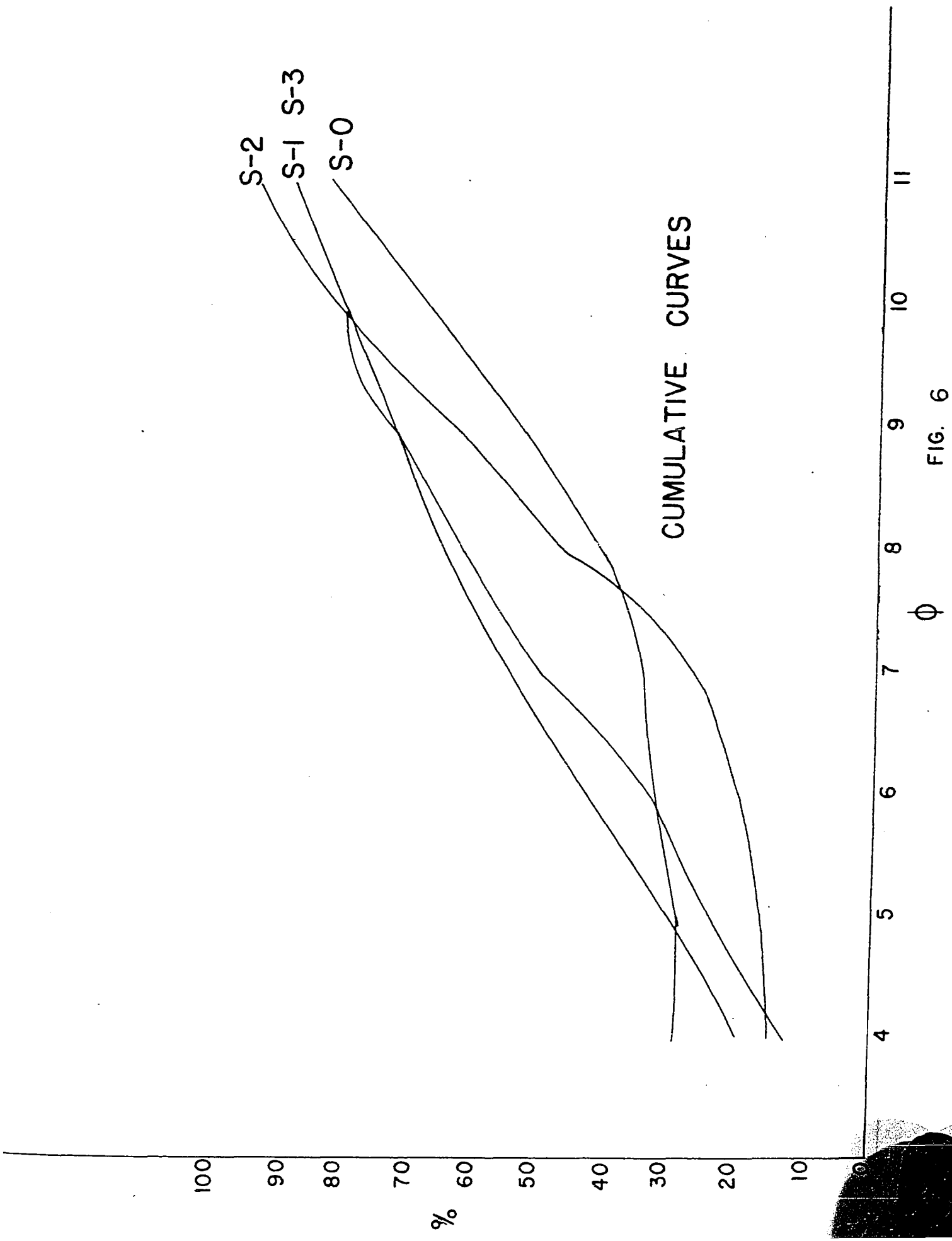


FIG. 6

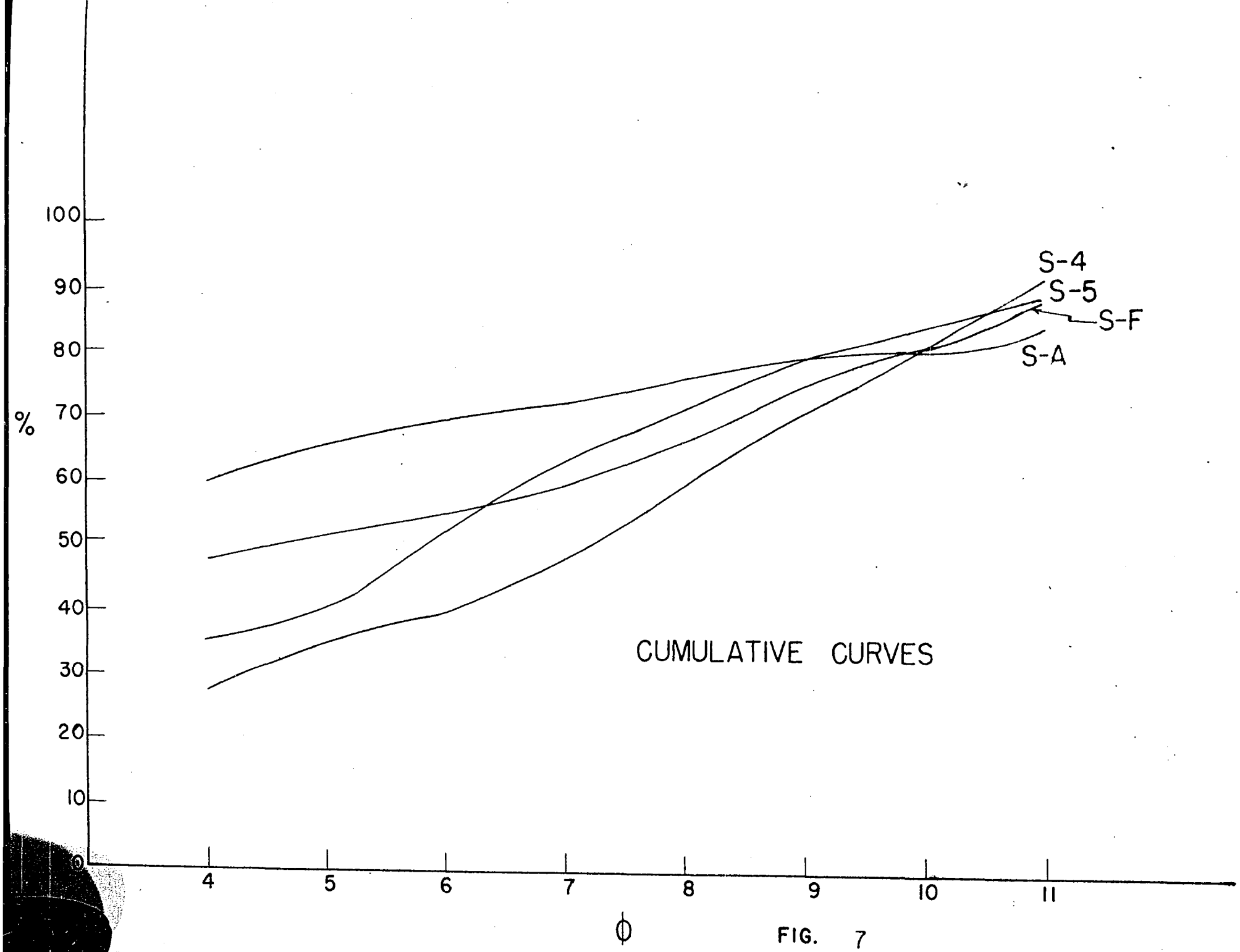


FIG. 7

$M\text{-}N_2$ has been slightly metamorphosed and as a result is much harder than any of the other K-bentonites and does not break down so readily.

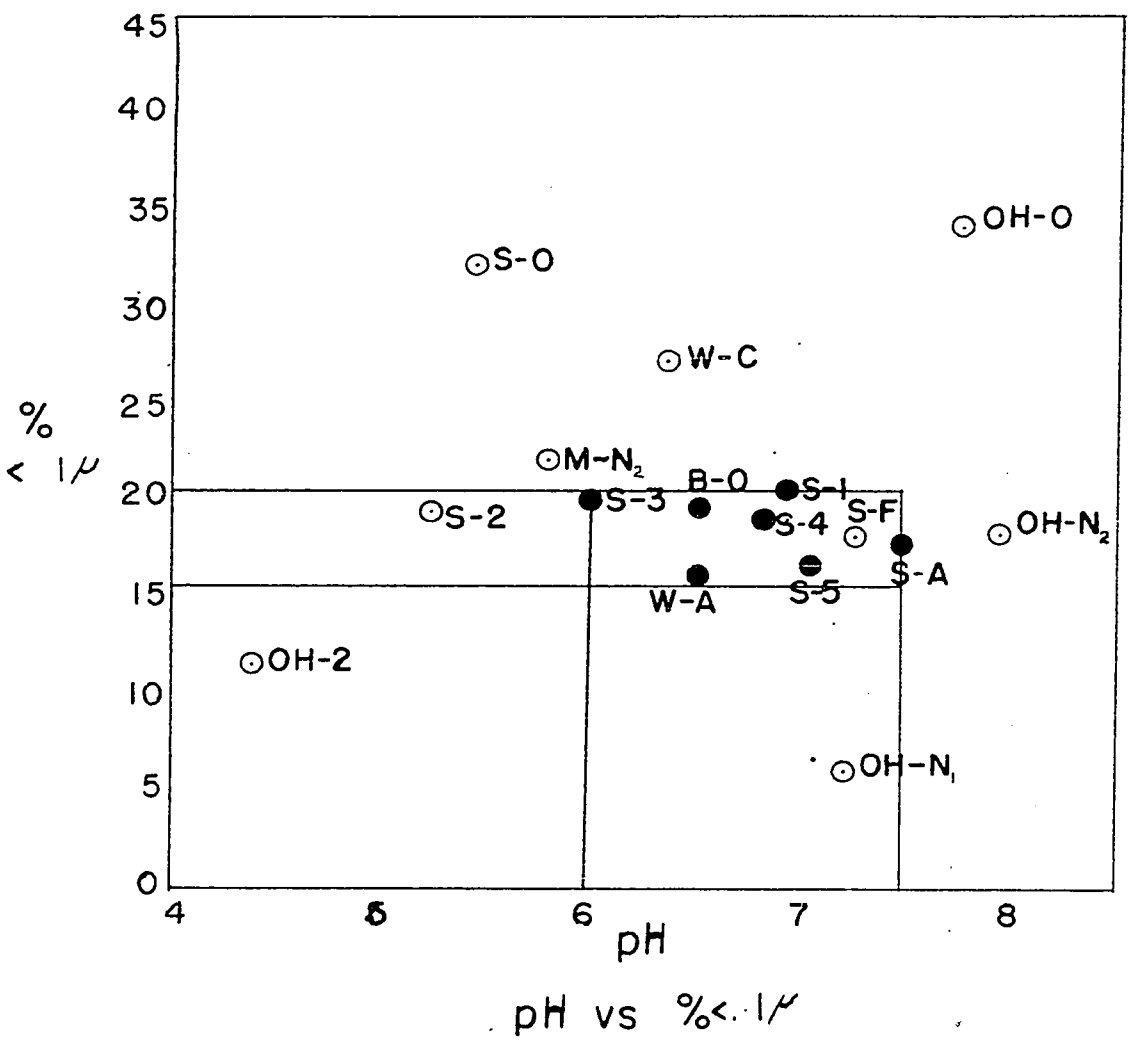
If the amount of material below 1 micron is totaled for each sample it can be seen that the moderately weathered samples show a cluster of values ranging only from 19.5 to 20.3 grams, whereas the moderately fresh and fresh K-bentonites have values ranging from 5.87 to 34.0 grams.

pH values of each of the samples were taken (Table 3). The highly weathered and moderately weathered samples have values ranging from 6.00 to 7.80; the moderately fresh and fresh specimens give values ranging from 4.4 to 7.95. Though there is no direct relationship between pH values and the amount of material less than 1 micron in size, there is a clustering of the pH values of the weathered K-bentonites similar to that of the less than 1 micron fraction (Figure 8).

It seems that weathering tends to decrease the amount of variation in several properties of the K-bentonites, as is to be expected, whereas the fresh clays show considerable amount of individual variation.

Differential Thermal Analysis Data

Differential thermal patterns were run on 21 of the samples using approximately 0.7 gms. of material sieved through a 100 mesh sieve. All samples were run in a nickel



pH vs %< 1μ

FIG. 8

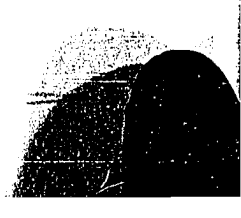
block with six sample holes. Eight of the samples were rerun one at a time using the Leeds and Northrup preamplifier to give an amplification of approximately seven times. The furnace was heated at the rate of 10° C per minute.

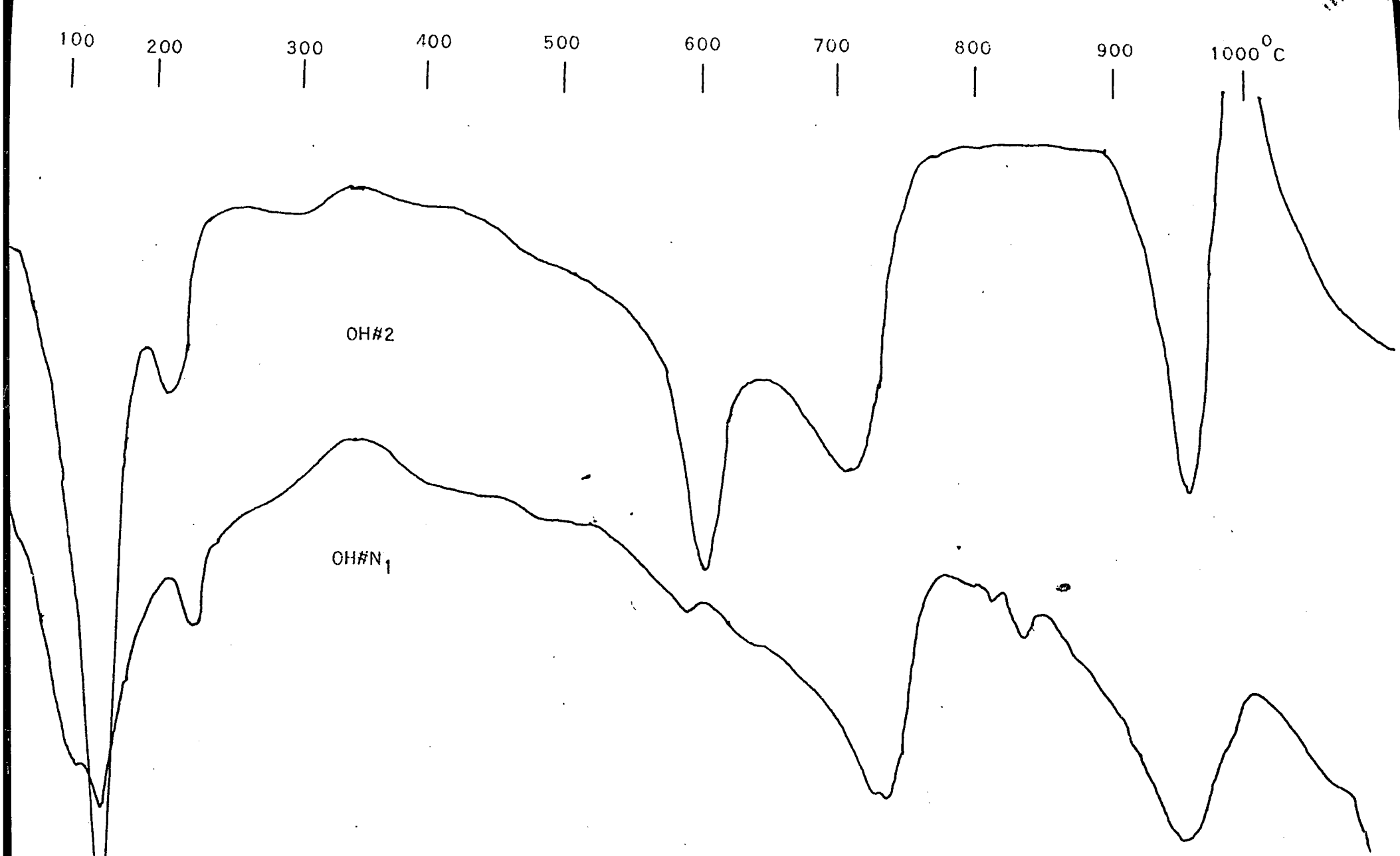
Differential thermal curves of Illinois illites, reported by Grim and Rowland (1942) show endothermic peaks at 100-200° C, 500-650° C, and about 900° C, and an exothermic peak immediately following the third endothermic peak.

Montmorillonites as reported by Grim and Rowland and by Kerr, Kulp and Hamilton (1949) have endothermic peaks at 100-200° C and about 900° C. The last is immediately followed by the exothermic peak representing crystallization of spinel. In nontronite the second endothermic peak occurs at 500° C and in hectorite it occurs at 800° C.

The first endothermic peak is caused by the loss of adsorbed water. The second, in both illite and montmorillonite, accompanies the loss of most of the water from the lattice and the third endothermic peak is interpreted as being associated with the final destruction of the 2:1 structure.

The differential thermal curves of the 21 K-bentonite samples (two of which are shown in Figure 9) show a broad endothermic peak at 100°-200° C. In many of the curves this is a double peak and is considered to be due to the loss of water of hydration from adsorbed ions, probably calcium. This peak is followed by a broad endo-





DIFFERENTIAL THERMAL CURVES

FIGURE 9

thermic swell between 500° and 700° C. Generally it starts near 500° C and slopes gradually until it reaches a maximum at 700° C where it returns to the base line rather sharply. However, several of the curves (S-2, S-3, S-4, S-5, M-A, M-N_2, OH-2, W-C,) show a break in the slope at 600° C with samples S-4 and OH-2 having a stronger peak at 600° C than at 700° C.

All of the curves have another endothermic peak between 900 and 1000° C. Calcite impurities will enlarge this peak or produce a second in this range. (The various exothermic peaks between 300 and 600° C are probably due either to organic matter or iron sulphide or both. A distinct exothermic peak occurs in all of the patterns at 1000° C and slightly higher.

Grim and Rowland (1942), Bradley (1946), and Kerr, Kulp and Hamilton (1949) have reported curves similar to these in samples of metabentonite from Kentucky and Virginia. Grim and Rowland commonly call curves of this type a mixture of illite and montmorillonite and showed that synthetic mixtures of these two minerals give such curves.

In the K-bentonite patterns the broad 100-200° C peak is characteristic of both illite and montmorillonite, though the peaks appear to be too shallow for pure montmorillonite. The gentle swells and pronounced peaks near 600° C are characteristic of illite and the peak at 700° C is characteristic of montmorillonite. The 900-950° C endothermic reaction is again characteristic both of illite and

montmorillonite, though the peak and the following exothermic peak at 1000-1020° C are both quite high for illite and for most of the montmorillonites. However, some iron-rich montmorillonites show reactions this high.

Sample S-0 after being heated to 1000° C gave a weak x-ray spectrometer pattern of spinel. A small portion of S-0 K-bentonite was heated to 1400° C and quenched. Examination under the microscope showed a matrix of glass containing abundant needle-like crystals.

Though the curves are in general similar there is considerable variation particularly in the critical 500 to 800° C range and it seems likely that the K-bentonites are not uniform in composition. The variation does not appear to show any relation to the degree of weathering.

X-ray Data

X-ray spectrometer and camera type patterns were made of each of the bulk samples. Nearly all of the patterns contained a few lines due to calcite or quartz. Later in the report a detailed evaluation is made of several x-ray patterns. In Table 4 only the (001) lines of the patterns are given.

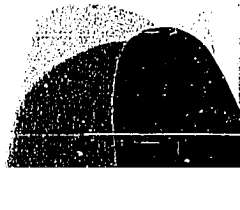
Whereas the majority of the d values check closely with those listed for illite there are many anomalous lines. All of the samples but one contain a moderately strong (001) line with a value between 10.1 and 10.5 Å. One sample has a value of 12.4 Å. Eight of the 21 samples give a very weak (001) line near 14 Å.

TABLE 4

Bulk X-ray Data - (001) Lines

Sample	d in Å	I	d in Å	I
S-0			10.2	m
S-1			10.3	m
S-2	13.9	ww	10.3	m
S-3	14.0	ww	10.2	m
S-4	13.9	ww	10.5	m
S-5	14.0	ww	12.4	w
S-A			10.3	m
S-F			10.2	m
M-A	14.0	ww	10.2	m
M-D			10.1	w
$M-N_2$	14.2	ww	10.3	m
B-D			10.2	m
OH-0			10.4	m
OH-2	14.0	w	10.6	m
$OH-N_1$			10.3	m
$OH-N_2$			10.5	m
W-A				a
W-B			10.4	m
W-C	14.0	ww	10.3	m
W-D				a
W-E			10.3	m

m = moderate
w = weak
ww = very weak
a = absent



Electron Microscope Data

Electron micrographs were taken of each of the 21 samples using the bulk material. The morphology of the material is remarkably consistent in all of the samples as can be seen in the four typical pictures, Figure 10-13.

The K-bentonites all show thin, sharply outlined flakes which are generally sub-equant and have irregular borders. The degree of weathering and the color does not appear to affect materially the morphology. Figure 10 is an electron micrograph of S-5 which is a light gray, highly weathered, K-bentonite containing impurities. Figure 11 is an electron micrograph of M-N_2, a gray, very fresh, hard K-bentonite. Figure 12 is an electron micrograph of M-A, a gray, moderately weathered sample. Figure 13 is an electron micrograph of W-D, a yellow, moderately fresh K-bentonite. The exceptionally large flake in the lower left is probably biotite. In contrast, the Fithian illite Figure 14 consists of irregular aggregates that show a "cottony" appearance. Discrete flakes are either few in number or so small as not to be resolved. Figure 15 is an electron micrograph of "metabentonite" from a well core near High Bridge Kentucky. This material consists of discrete flakes similar in morphology to the K-bentonites from Central Pennsylvania but much smaller.

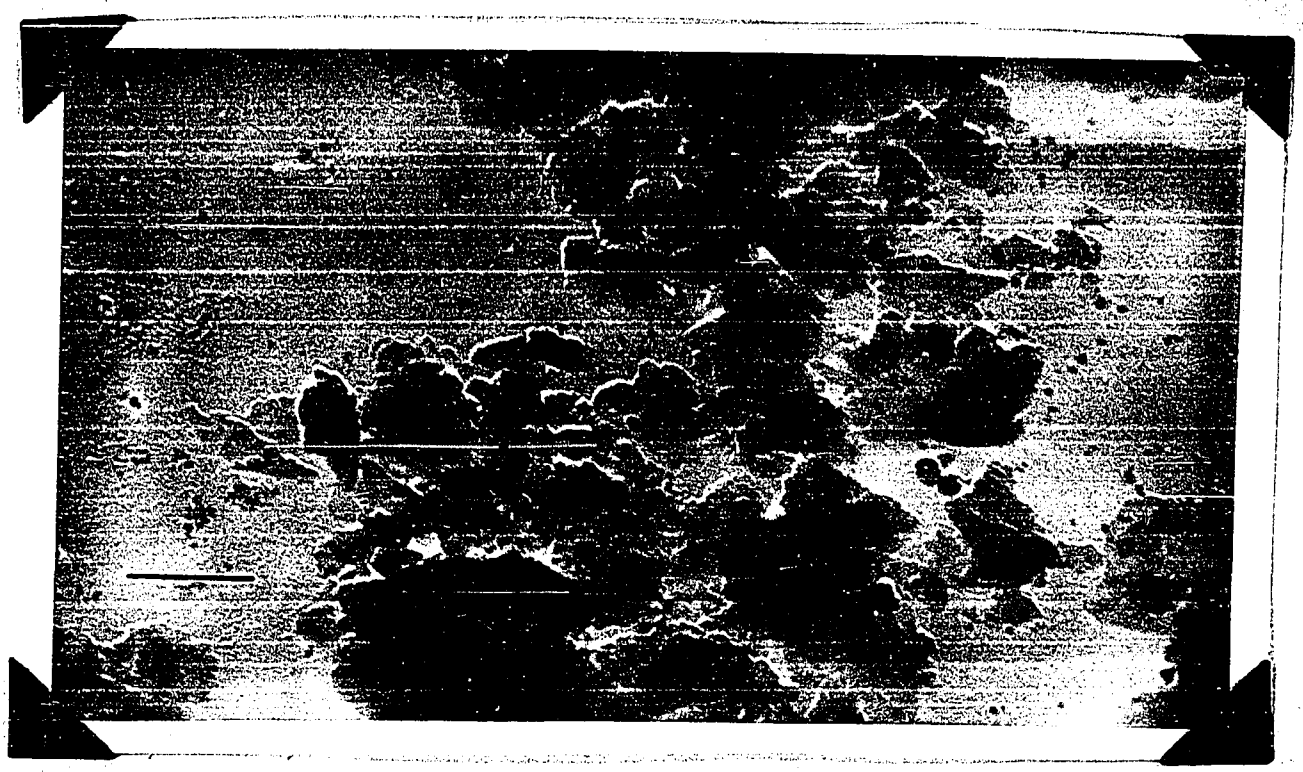


Fig. 10 - (S-5) A light gray, highly weathered, K-bentonite.
X 15,000

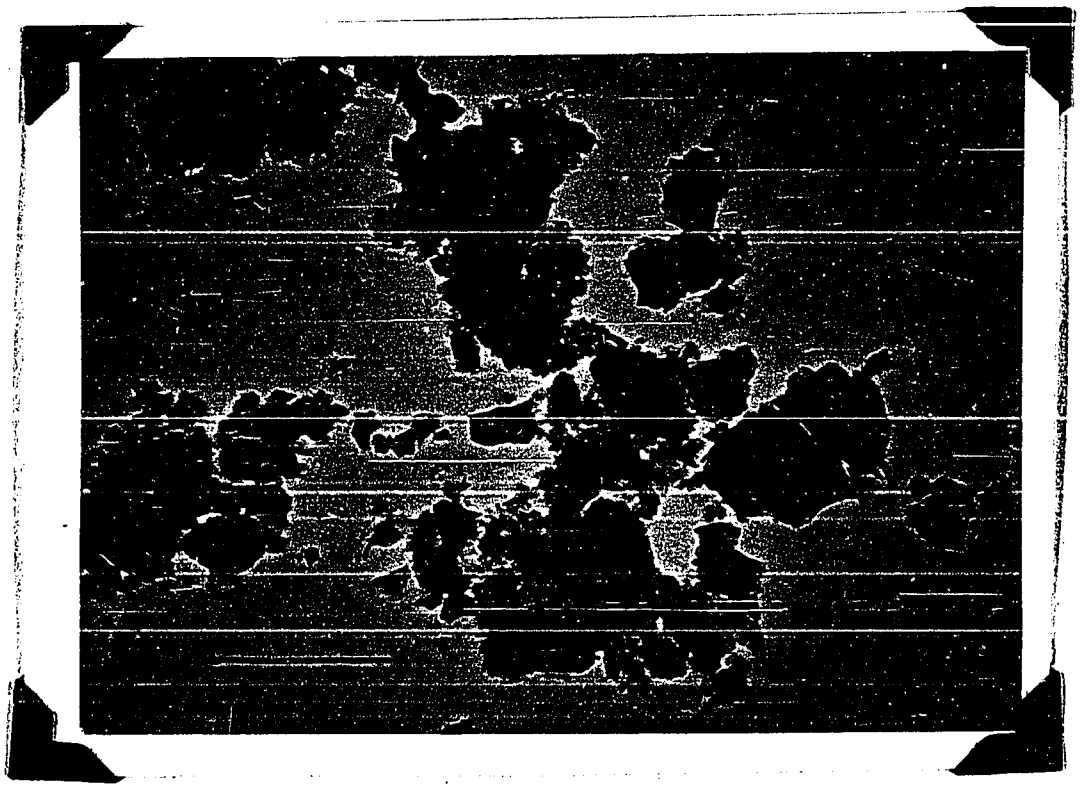


Fig. 11 - ($M-N_2$) A gray, very fresh, hard K-bentonite.
X 21,600

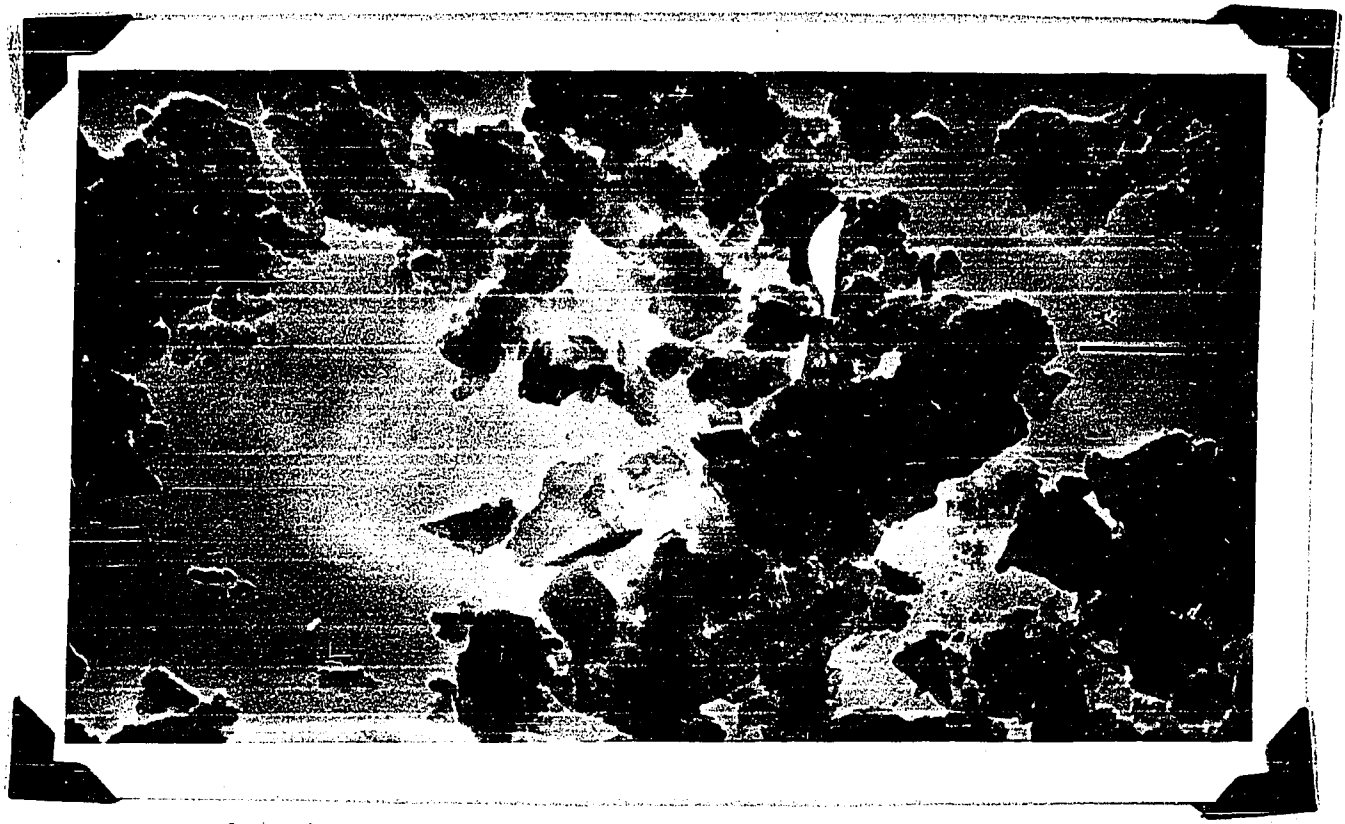


Fig. 12 - (M-A) A gray, moderately weathered K-bentonite.

X 15,000

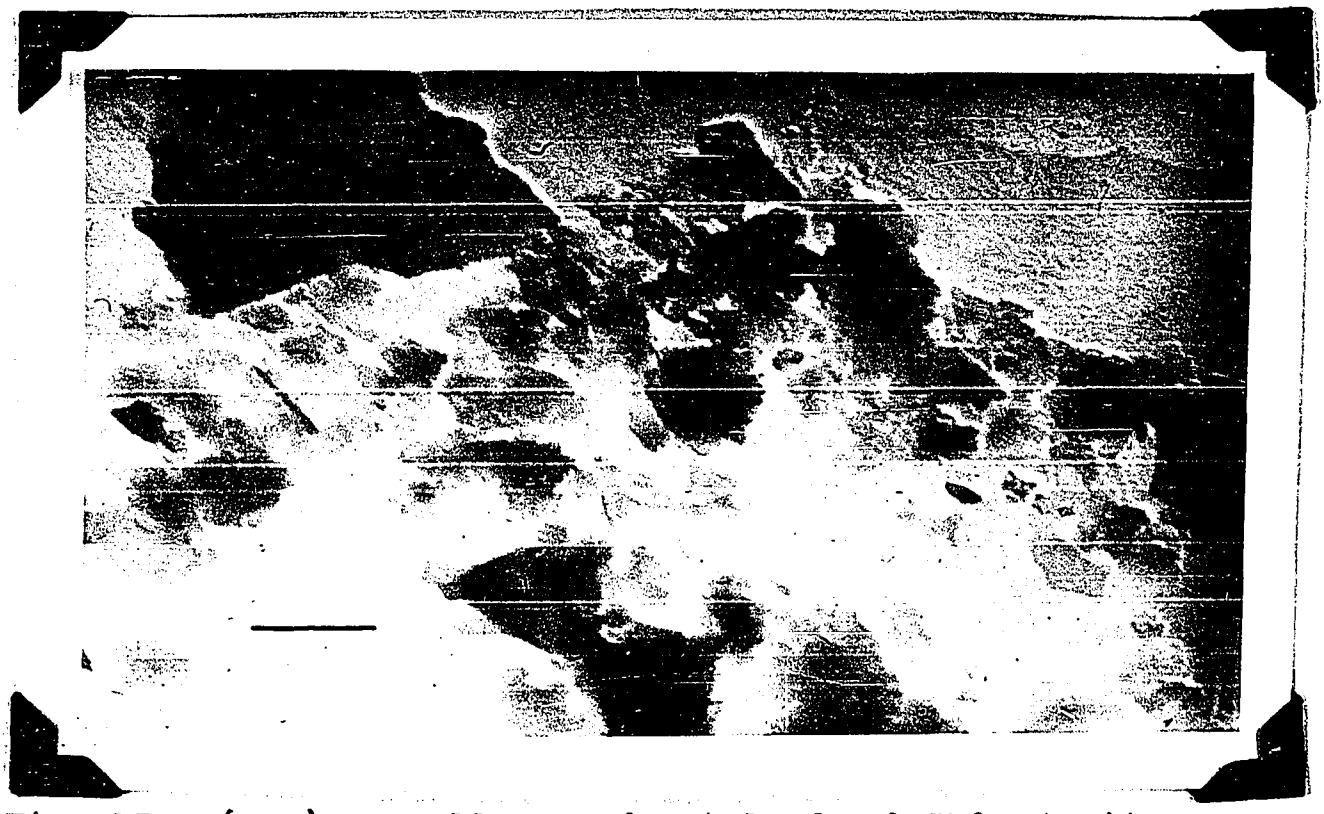


Fig. 13 - (W-D) A yellow, moderately fresh K-bentonite.

X 15,000

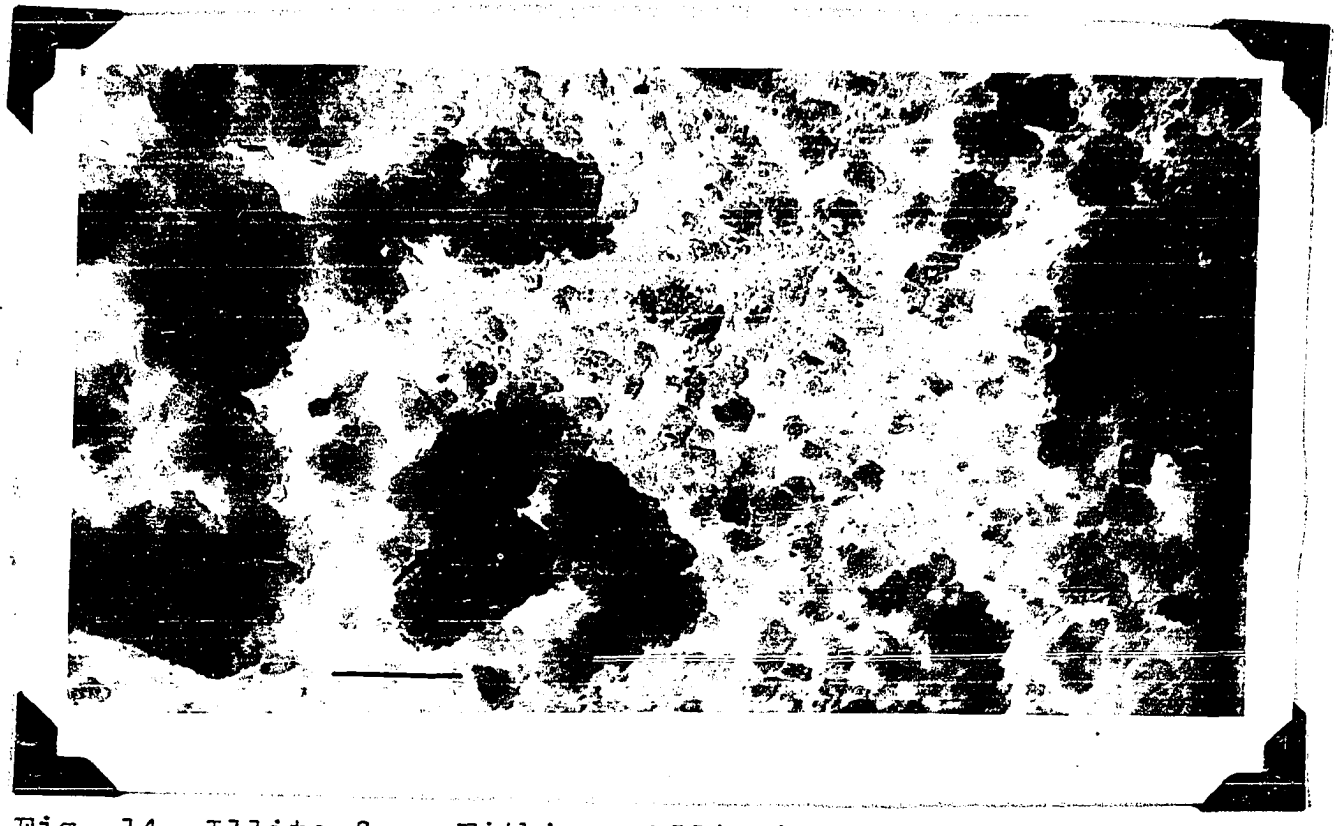


Fig. 14 Illite from Fithian, Illinois, showing irregular aggregates having a"cottony" appearance. X 15,000

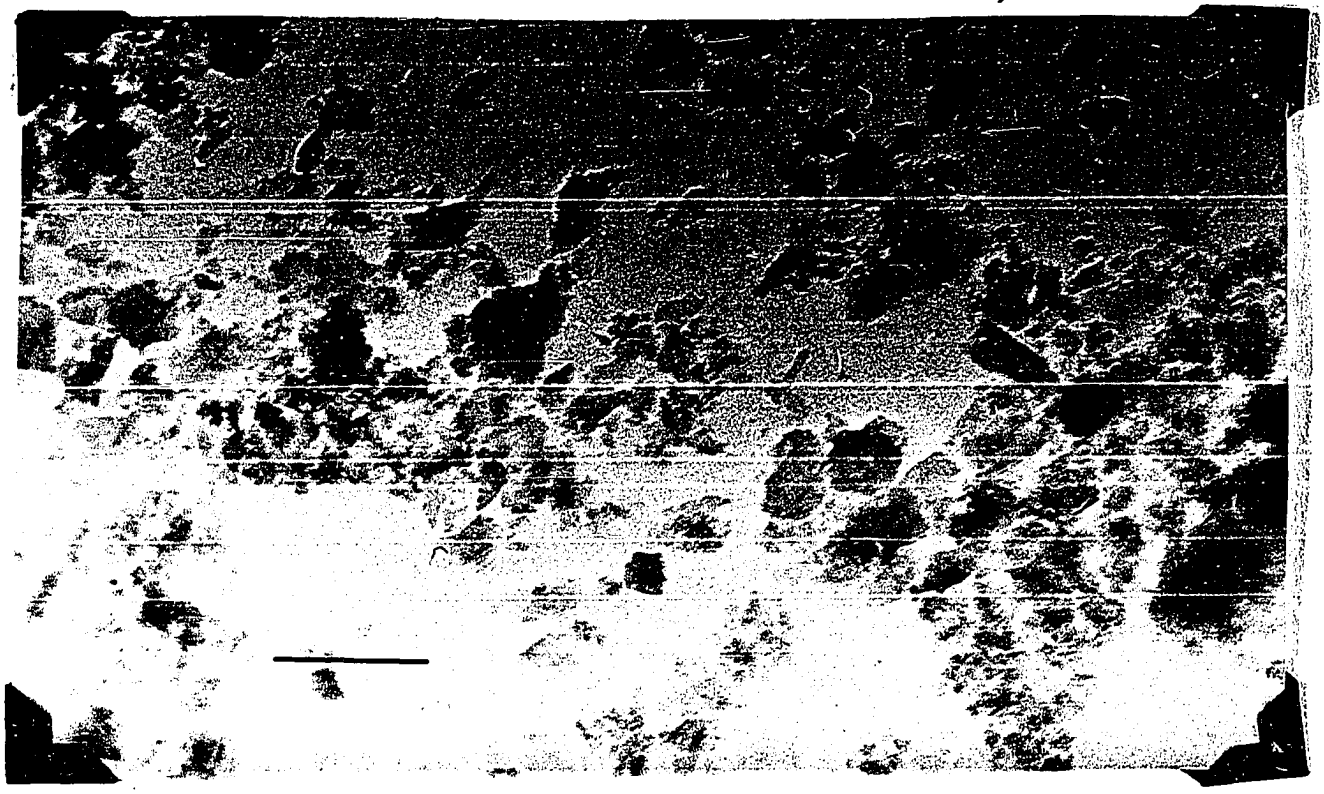


Fig. 15 "Metabentonite" from High Bridge Kentucky showing small discrete flakes. X 15,000

Fine Fraction

Introduction

On the basis of the bulk analyses the 21 clays were divided into two groups. A typical sample (OH-2, OH-N_1) from each group was chosen and investigated in detail. The differential thermal curve of sample OH-2 has both a 600° C and 700° C hydroxyl-endothermal peak whereas sample OH-N_1 has only the 700° C peak. X-ray patterns of OH-2 have (001) lines at 14.0Å and 10.6Å; OH-N_1 has only one line which is at 10.3Å. In addition both samples were relatively fresh.

Sample Preparation

Two hundred grams of crushed material were added to 1500cc of water together with eight drops of NH_4OH and the mixture was shaken on a rotary shaker for 24 hours. Sample OH-2 went into suspension but sample OH-N_1 quickly flocculated and it was necessary to add approximately 10,000cc of water to this mixture before it would remain in suspension. The less than one micron fraction was decanted six times from both suspensions.

A few drops of acetic acid were added to flocculate the less than one micron fraction, the excess water was decanted, and the clays were electrodialyzed for 150 hours to form a hydrogen based clay. At the end of 150 hours OH-2 was completely flocculated but a small portion of OH-N_1 remained in suspension. The samples were dried for two weeks at approximately 60° C.

Four gram batches of each of the electrodialyzed samples were placed in solutions of KOH, NaOH, $CaCl_2$ and NH_4CO_3. These samples were shaken for 24 hours and then allowed to stand for four weeks. They were then centrifuged three times for 20 minutes at 2000 RPM with the water decanted and fresh added each time. Some of the finer fraction of each of the four samples remained in suspension and was collected by evaporating the water.

More of the less than one micron fraction of OH-2 and OH-N_1 was removed by adding 30 grams of raw sample to 500cc of water, shaking on the rotary shaker 56 hours, decanting and drying at 60° C. This time neither sample flocculated. These samples will be referred to as untreated samples.

Following the method described by Caillère and Hénin (1949) three grams of each untreated sample were placed in 150cc of one normal KCl and allowed to stand for several days. Then the excess liquid was decanted and 200cc of one normal KOH was added to the clay. This was boiled for eight hours in an Erlenmeyer flask attached to a vertical cooling column. The material was filtered, washed, and dried for 18 hours at 60° C. This was repeated three times for both samples with a small portion of each removed after each eight hour period. In addition, sample OH-N_1 was boiled in KOH an additional 36 hours making a total of 60 hours.

Two untreated samples were placed in a 1N solution

of KOH and alternately wetted and dried ten times.

Untreated samples of both clays were also heated for a 24 hour period at temperatures of 500, 600, 640, 675, and 700° C.

X-ray Data

Approximately 50 x-ray diffraction patterns were measured and studied in considerable detail. The interpretation of these patterns is based on the work of Bradley (1946) (1950) and Brown and MacEwan (1950).

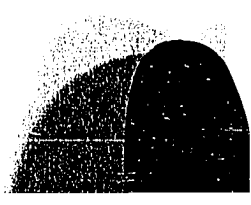
Table 5 lists the various cations with which the less than one micron fraction of the clays were treated and the measured value of the resulting (00ℓ) lines with the largest spacing.

TABLE 5

Largest (00ℓ) Spacings

	OH-2				$OH-N_1$		
Untreated	10.9Å	m	14.0Å	ww	10.8Å	m	-
H	10.9	m	14.0	ww	10.8	m	-
Ca	10.8	s	14.0	ww	10.9	m	-
Na	10.4	s			10.4	m	-
K	10.3	m	14.0	ww?	10.4	m	-
K (boiled 60 hrs)	10.4	ss	14.2	ww?	10.3	s	-
NH_4	10.3	s					
Ethylene glycol	9.5 m, 11.1 m		-		9.5 m, 11.3 m		-
24 hrs at 500°C	10.0	s	14.2	m			
" " " 600°C	10.0	s	13.4	w			
" " " 640°C	10.1	s	13.1	ww			
" " " 675°C	10.0	s	-				
" " " 700°C	10.0	m	-		10.1	s	-

ss - very strong m - moderate ww - very weak
s - strong w - weak



The (060) value of 1.50Å (not given in this table) indicates that the clay is a dioctahedral mineral. The (00ℓ) values ranging from 10.3 to 10.9Å are not characteristic of any pure clay mineral. However, such values commonly are found in randomly interstratified 2:1 clay minerals.

Hendricks and Teller (1942) devised a formula which would predict the (00ℓ) values to be expected from a random mixture of two sheet-like layers of different thickness. This formula was modified by Brown and MacEwan (1950) who constructed a series of graphs from which the (00ℓ) spacings resulting from mixtures of two different sheet structures could be read.

There are several factors which determine the (00ℓ) values of mixed layers of different thickness. The resulting (00ℓ) value will fall between two closely associated (00ℓ) values for the individual layers in a position determined by the relative closeness to one another of these values. The position of this peak will be modified further by the structure factor of the layers, by the polarization of the diffracted radiation, by the form of the specimen, and by the relative amounts of the two structures.

It can be seen from Table 5 that the untreated clay, the H based clay, and the Ca based clay all have similar values of 10.8-10.9Å. Barshad (1950) has reported that the (001) spacing for H montmorillonite is 14.5Å and for Ca montmorillonite 15.1Å. Assuming, therefore, a

random mixture of non-expanded, 10Å, dioctahedral, 2:1 layers (060=1.50Å) and either 14Å of 15.4Å expanded layers, the relative amounts of the two types of structures can be read from the graphs of Brown and MacEwan.

Table 6 shows the three values taken from the graphs and the (00*l*) lines of the individual structures which combine to give the resulting (00*l*) value of the mixed layer mineral. (f=the proportion of layers with higher spacing.) For a mixture of 10Å and 14Å layers an f of 0.25 gives a value equal to the measured value. For a mixture of 10Å and 15.4Å layers an f of 0.20 gives a value equal to the measured value. Brown and MacEwan list three (00*l*) values for each mixture. Table 6 shows that all three values for each f check closely with the measured values.

These data indicate that the clay contains 75 to 80% of 10Å layers and 20 to 25% of expanded layers, the latter having a thickness somewhere between 14 and 15.4Å.

Returning to Table 5 it can be seen that Na, K, and NH_4 based clays give (00*l*) values of 10.3-10.4Å. Barshad lists the (001) values for montmorillonite treated with these cations as: Na=11.9; K=12.0; NH_4=12.1. On the basis of the above work using an f of 0.20 to 0.25 and end members of 10Å and 12.4Å the calculated results should check with the measured values if the previous interpretation is correct. As shown in Table 6 the (00*l*) value for 10/12.4 with f=0.20 is 10.3 and for f=0.25 is 10.5; the measured values are 10.3-10.4. The other two (00*l*) spacings also

TABLE 6

Random Layer Data

10/14 f 0.25	Original Indices	10/15.4 f 0.20	Untreated H, Ca
10.9s	001/001	10.9m	10.8-10.9m
4.90m	002/003	5.08s	4.94-5.00m
3.37m	003/004	3.31m	3.25 to 3.43m broad
10/12.4 f 0.25		**10/12.4 f 0.20**	**Na, K, NH_4**
10.5s	001/001	10.3s	10.3-10.4s
5.14w	002/002	5.12w	5.11-5.19w
3.26m	003/004	3.31m	3.27-3.30s
10/17.7 f 0.25		**10/17.7 f 0.20**	**Ethylene glycol**
11.7*	-/001	11.4*	11.1-11.7*
9.5m	001/002	9.6m	9.5-9.7m
4.95 to 5.28 broad w	002/003	5.03w	4.87 to 5.13w broad (4.97w-5.23w)
3.42w	003/005	3.37w	3.34s

___-range
to-width

f - proportion of layers with higher spacing

001 - nonexpanded indices
001 - expanded indices

* diffuse

coincide.

A further check can be made by soaking the clay in ethylene glycol and expanding the 20 to 25% expandable layers to 17.7Å. The results are shown in Table 6 where it can be seen that the measured and calculated values are quite similar. The 11.4-11.7Å calculated values are broad and extend upward to larger values. It might also be noted that, whereas in the other graphs the principal (00*l*) values were obtained by a combination of the (00*l*) spacings of both structures, in the 10/17.7 spacings the principal spacing is formed by a combination of the (001) reflection from the 10Å unit, and the (002) from the 17.7Å unit (8.85Å) giving a (00*l*) value less than 10Å. A broad spacing extending from 4.95 to 5.28 is calculated for the f=0.25 value. In some of the measured patterns this line split into two distinct lines at 4.97Å and 5.25Å. The calculated values also split into two distinct lines as f is increased.

These x-ray data show that sample OH-N_1 is composed of randomly interstratified dioctahedral layers of which 75-80% are non-expanded and 20-25% are expanded. Sample OH-2 has the same type of layers mixed in the same relative proportions plus some packets of a mineral with a 14Å (001) spacing.

It should be noted here that when these clays were placed in a 1N solution of KOH and alternately wetted and dried ten times there was a complete collapse of the expanded layers and a (001) value of 10.0Å was obtained.

Table 7 contains a list of all the mixed layer lines

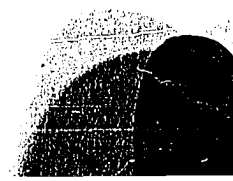


TABLE 7

Mixed Layer Spacings and Indices

Samples		Indices			
OH-2 H clay d in Å	I	Illite Calhoun d in Å	I	Muscovite	Randomly Interstratified Mineral
10.9	m				001/001
		9.98	s	002	
		4.97	w	004	
4.95	m				002/003
4.47	m	4.47	s	110	
		4.11	ww	022	
3.70	w	3.7	ww	023	
3.43	m	3.4	ww	114	
	ms	3.31	m	006	003/004 (5)
3.25		3.2	ww	114	
3.11	ww			115	
		2.98	w	025	
2.83	w	2.84	ww	115	
2.55	m	2.56	s	202	
2.495	w			008	004/005
2.45	w	2.44	w	133	
2.38	mw	2.38	m	133	
2.245	w	2.24	m	221	
2.18	w	2.18	w	223	
2.13	w	2.11	w	043	
1.97	m	1.98	m	0010	005/007

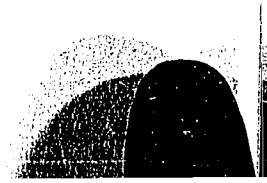


TABLE 7 cont.

Samples				Indices	
OH-2 H clay dim Å	I	Illite Calhoun dim Å	I	Muscovite	Randomly Interstratified Mineral
1.65	mw	1.65	w	310	
		1.64	m	312	
1.50	m	1.50	s	060	
1.42	ww			0014	
1.34	w	1.34	ww	335	
1.29	w	1.29	m	400	
1.265	s			402	
1.245	w	1.24	w	0016	

_____ = Indices unknown but line reported

= Uncertain if line belongs in this group

measured from a typical x-ray pattern of OH-2, together with the lines for illite from Calhoun Co., Illinois as given by Grim, Bray and Bradley (1937). The Table also contains the indices for muscovite and the randomly interstratified mineral.

Table 5 shows values of 14.Å in sample OH-2 which are not present in sample OH-N_1. Bradley*suggested that this spacing is probably due to packets of 14.0Å layers interspersed among but not part of, the predominant interstratified layers, and this interpretation has been verified.

The 14.0Å line is present in the untreated, H, and Ca clays but is either very weak or absent in patterns of the Na, K, and NH_4 clays. Since the spacing does not change to 12.0-12.4Å when the clay is treated with Na, K, of NH_4. These 14.0Å packets are not of the same material as the expanded 14.0A5.4Å structures in the interstratified material.

Sample OH-1 B, found immediately above Sample OH-2, gave an x-ray pattern containing a 14.Å line three to four times as dark as that in any of the previously examined samples. On the other hand, the mixed layer ratio was the same as in OH-2 and OH-N_1. The series of lines associated with the 14 Å spacing suggested that the material is chlorite.

Using the data of Brindley and Ali (1950) it

* Personal Communication

was possible to prove more definitely that the 14 Å reflection was caused by a chlorite mineral. These authors reported that when powdered penninite is heated to 600° C for two hours, the x-ray intensities change. They calculated x-ray intensities, using a one-dimensional Fourier analysis of the electron density distribution, for various atomic arrangements. The best agreement between calculated and measured intensities occurred when they assumed two-thirds of the brucite layer to be decomposed and the liberated Mg and O atoms to be in the hydroxyl sheets. As the chlorite is heated the first stage of dehydration consists of a loss of about half of the eight water molecules at 600° C. This is accompanied by a migration of the liberated Mg atoms into or towards the hydroxyl sheets of the brucite layer and the original 14.45 Å lattice height is reduced to 14.22 Å. At 660° C the remaining water is lost and the lattice shrinks to 14.09 Å. At 760° C the structure breaks down and most of the penninite lines disappear.

Table 8 shows the (001) values obtained by Brindley and Ali for chlorite heated for two hours and the values obtained for samples OH-2 and OH-1 B heated for twenty-four hours.

TABLE 8

Data on (001) Values for Heated Chlorite

	Brindley and Ali	OH-2	OH-1B
temperature	001	001	001
20° C. to 300° C.	14.45 Å	14.0 Å	14.0 Å
600° C.	14.22	13.4	13.6
660° C.	14.09	13.1	

The differences between the chlorite packets of the K-bentonite samples and the chlorite of Brindley and Ali may be due to inaccurate measurement and to the length of the heat treatment, but more likely may indicate that the chlorite in the K-bentonite is a different variety than the pure Mg chlorite of those authors.

Table 9 shows the relation between the observed intensities at normal temperature and at 600° as described by Brindley and Ali and those for sample OH-1B.

The comparison is not exact as the chlorite is apparently not a pure Mg variety and as the x-ray patterns of OH-1B contain overlapping lines for a mixed layer mineral and for quartz. However, the sharp increase in intensity of the (001) line and the definite weakening of the (002) and (003) lines, when the material is heated to 600° C. strongly suggests that the mineral is a chlorite.

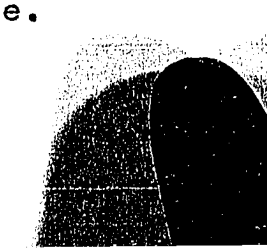


TABLE 9

The Change of X-ray Intensities of the (00ℓ) Series of Chlorite Heated to 600° C.

	Normal		600° C	
	Brindley and Ali	OH-1B	Brindley and Ali	OH-1B
001	24	m	121	s
002	67	wm	23	a
003	81	m	30	ww
004	100	wm x	100	ww
005	67	m x	186	w
006	0	w x	100	a
007	37	w	58	ww
008	11	a	0	a
009	11	w x	43	ww
0010	37	ww x	62	a
0011	0	a	40	a
0012	35	a		a
0013	0	a		a
0014	27	a		a

s = Strong
m = Moderate
w = Weak
ww = Very weak
x = Overlapped by lines of other minerals
a = Absent

The comparison is not exact as the chlorite is apparently not a pure Mg variety and as the x-ray patterns of OH-1B contain overlapping lines for a mixed layer mineral and for quartz. However, the sharp increase in intensity of the (001) line and the definite weakening of the (002) and (003) lines, when the material is heated

to 600° C strongly suggests that the mineral is a chlorite.

In Table 10 are listed the d values for OH-1B and the range of d values for twenty chlorite patterns taken from the literature. Many of the lines are overlapped by lines of other minerals but the unambiguous lines check quite closely with the chlorite values. Particularly important is the 1.55 Å (060) reflection which is characteristic of a trioctahedral mineral.

TABLE 10

Chlorite X-ray Diffraction Data

Literature d	Intensity	OH-1B d	Intensity	Index	Interfering Lines
13.1-15.0 Å	w-m	14.0 Å	m	001	
6.7-7.2	s	7.1	w-m	002	
4.5-4.8	w-s	4.7	m	003	
3.92	w	3.87	ww		-I
3.42-3.58	m-s	3.52	wm	004	
3.13	ww	3.13	ww		-I
2.83	m	2.83	m	005	-I
2.70-2.79	ww-m	2.75	ww		- qtz.
2.55-2.59	m	2.57	s		
2.38-2.46	m	2.45	w		qtz.-I
2.33	ww	2.34	w	006	-I
2.25-2.27	w	2.24	m		-I
2.00-2.09	w-m	2.03	w	007	
1.96-2.00	ww-m	2.03-1.97	w		-I
1.88-1.90	ww-m	1.86	w		
1.73-1.76	ww				
1.66-1.68	w	1.67	w		
1.55-1.58	w-s	1.55	w	009	060
1.51-1.53	w-s	1.51	w		
1.41-1.44	ww	1.42	ww	0010	-I
1.37-1.39	w				
1.30-1.33	w	1.29	m		-I

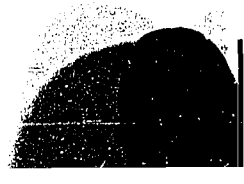
I = Mixed layer clay lines
qtz= Quartz lines

Differential Thermal Analysis Data

Differential thermal analyses were made of the untreated, the electrodialized, and the KOH, NaOH, and $CaCl_2$ treated clays. These samples were run in a nickel block with the temperature increasing at the rate of 10° per minute and with a seven fold amplification.

Differential thermal curves of untreated clays OH-2 and OH-N_1 are shown in Figure 8. All patterns contained a strong endothermal peak at 100-150° C. In addition the curves of the $CaCl_2$ treated clays contain a small endothermal peak at 225° C which was found elsewhere only on curves of the untreated clays. This would indicate the presence in the original clay, of some Ca (or possibly Mg) which was replaced in the other samples, by the K, Na and H cations.

The hydroxyl-endothermal peaks were not shifted in position though in OH-2 the amplitude of the 700° C peak relative to the 600° C peak, tended to increase in the samples treated with K, Na, and Ca. A further investigation of the hydroxyl-endothermal reactions was made by heating sample OH-2 on the differential thermal analysis apparatus, using a continuously increasing temperature. One sample was heated to 600° C and another to 700° C. These samples were allowed to stand in air for 12 days and were then rerun on the differential thermal analysis unit. The curve of the sample previously heated to 600° C had a broad endothermic swell from 500 to 600° C

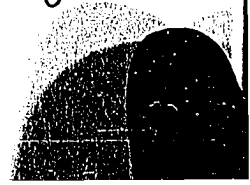


and the 700° C peak was lowered slightly to 690° C. The sample previously heated to 700° C gave a sharp peak of moderate depth at 550° C and a weaker one at 600° C and no peak in the 700° C vicinity. A sample of OH-N_1, was heated in the same manner to 725° C. After 13 days in air this sample was rerun and the resulting curve contained a weak, broad swell from 500 to 600° C.

These runs indicate that the hydroxyl ions removed by heating are partially readsorbed, but in such a manner that they are more easily removed than the original hydroxyl ions.

Samples of OH-2 were heated at constant temperatures of 600° C and 700° C for a period of 24 hours, cooled in a desiccator and run on the differential thermal analysis unit. As was to be expected after such treatment, both samples gave only the 950° C endothermic peak. This shows that the hydroxyl ions which give an endothermic reaction at 700° C when the clay is heated with a rapidly increasing temperature can be removed at a much lower temperature if the length of time of the heat application is increased.

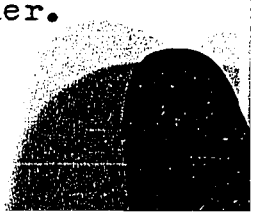
The hydroxyl ions in the illite and montmorillonite structures are bound only by the cations in octahedral coordination. Therefore the bond strength of these various cation-hydroxyl combinations should depend in large part upon the type of cation present. The strength of this bond is reflected in the endothermic peaks between 400 and 900° C



on differential thermal analysis curves. Therefore an attempt was made to correlate the percentage of the various cations in octahedral coordination with the temperature of the 400 to 900° C endothermic peak. Hectorite and chlorite, minerals with a predominance of Mg in the octahedral positions, have an endothermic peak at 800° C. Nontronite, which has Fe in the octahedral positions, has an endothermic peak at 500° C. Montmorillonites with a predominance of Al in octahedral positions, have endothermic peaks around 700° C.

These three values (Mg=800° C, Fe=500° C, Al=700° C) were used as end points on a ternary diagram, Figure 16. A survey was made of the chemical analyses of minerals in the montmorillonite and illite groups in the literature and the percentage of the various cations in octahedral coordination was computed using the method described by Ross and Hendricks. The percentages were plotted on the diagram and the temperature of the endothermic peak for each was noted. The hectorite (800° C) and nontronite (500° C) minerals separate into distinct groups. The montmorillonite and beidellite samples are clustered near the Al corner of the triangle and as a whole contain more Mg than Fe. The temperature of the endothermic peaks of this group varies only from 660 to 700° C.

The illites tend to occur on the Fe side of the montmorillonite and beidillite cluster with many of them completely outside the cluster and closer to the Fe corner.



These have temperatures of 530 to 575° C.

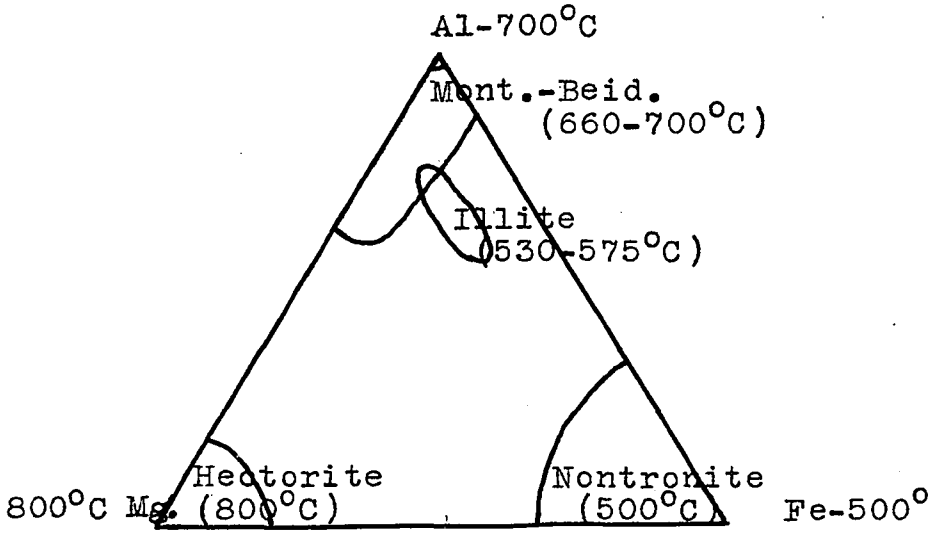


Figure 16

The separation between montmorillonite, beidellite, and illite is not distinct though there is a tendency for the illites to contain more Fe, which would account for their lower temperature endothermic peak.

As Kerr, Kulp and Hamilton (1950) suggested, the reason that there is no regular or distinct variation between temperature and composition may be because of preferential bonding of the octahedral cations, i.e., certain cations have a greater affinity to form a hydroxyl bond while others may prefer an oxygen bond.

OH-2 was electrodialized for three hundred hours removing some of the iron and magnesium and possibly some aluminum from the structure. This lowered the amplitude of the 600° C peak considerably but did not affect the 700° C peak which would indicate a preferential removal of

the iron and magnesium from the layers responsible for the lower temperature peak.

It was necessary to find if the layers which were responsible for the 600° C hydroxyl-endothermal reaction were the layers giving the 14 Å x-ray reflection. An examination of the differential thermal patterns of the twenty-two samples showed that eight of the patterns contained a 600° C peak, usually of very small size. The x-ray diffraction patterns were re-examined, and several new x-ray pictures were taken using a longer exposure time. In all cases the samples which showed a 600° C differential thermal peak gave a weak 14 Å x-ray reflection.

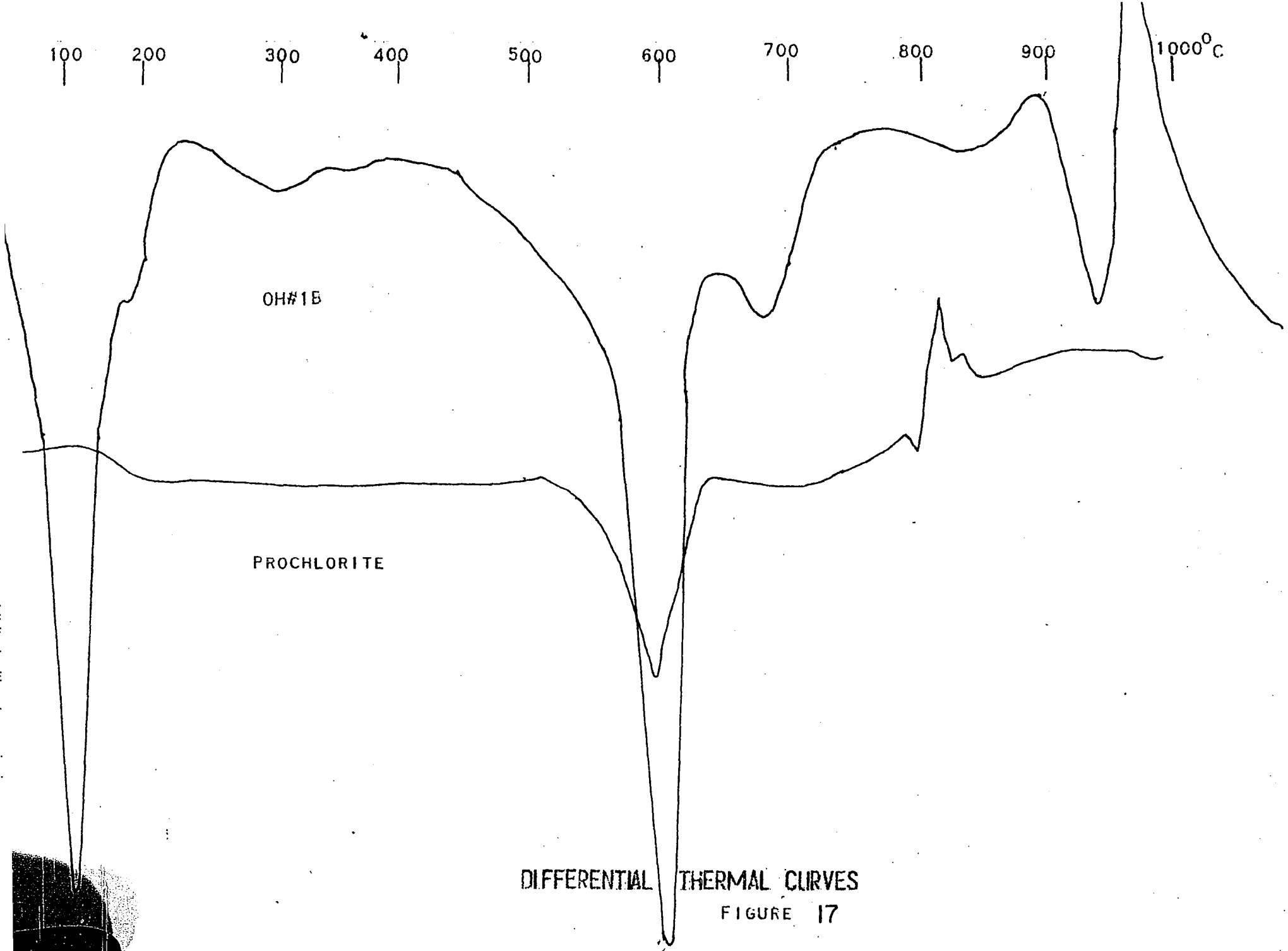
Sample OH-1B which gave an x-ray pattern containing a 14 Å line three to four times as dark as that in any of the previous samples has a differential thermal curve with a sharp 600° C endothermal peak approximately three times as large as that in Sample OH-2. The endothermal reaction is accompanied by a lowering of the lattice height to 13.8 Å which indicates that this peak is at least partly associated with a loss of water from the 14 Å layers.

A review of the chlorite literature revealed that most chlorites have a strong endothermal peak at 550-600° C and a smaller one at 800° C., followed by a weak to moderate exothermal peak. In Figure 17 it can be seen that OH-1B, in addition to the strong endothermal peak at 600° C has a weak one at 825° C followed by a weak exothermal peak. These peaks are strikingly similar to that

shown by Barshad (1948) for prochlorite from Chester, Vermont shown on the same figure. However, the true chlorite pattern shows a fairly sharp 600° C peak whereas in Sample OH-1B and OH-2, the peak begins at 400-500° C and increases gradually for 100° C before the slope changes rapidly to form a peak. This is typical of the montmorillonites, and may indicate a composite montmorillonite-chlorite reaction. These relationships indicate that the chlorite packets with the K-bentonite samples are responsible for the 600° C endothermal peaks and the randomly interstratified units, low in iron, give the single peak at 700-725° C. The reason for such a high temperature endothermal peak is not known. A survey of the literature reveals that most illites contain 5-10% iron oxides. The presence of considerable iron in montmorillonite is known to lower the endothermal peak to around 500° C. As these K-bentonites contain very little iron (0.31-1.28%), this deficiency may be responsible for raising the temperature of the hydroxyl-endothermal reaction.

In the literature it has commonly been stated that the double hydroxyl-endothermal peak found in patterns of mixed layer clays is caused by the two individual clays forming the mixture, the illite layers causing the lower peak, the montmorillonite layers the higher.

However, it is not necessary to have two hydroxyl-endothermal reactions occurring in a mixed layer clay. It may be that the curve for OH-N_1 is a single peak characteristic of a mixed layer clay, having some variation in the



DIFFERENTIAL THERMAL CURVES

FIGURE 17

composition of the octahedral layers, but with the majority of the layers having a closely similar composition. The octahedral layer need have no relation to the amounts of non-expanded illite and expanded montmorillonite indicated by the x-ray.

In the case of sample OH-2, the montmorillonite reaction, if it is present, is masked by the prominent endothermal peak caused by the admixed chlorite packets. It may be that in many of the double peaked differential thermal curves in the literature, some small, overlooked amount of chlorite is present in the clay either as individual packets or as layers interstratified with illite or montmorillonite.

Chemical Data

The chemical analyses listed in Table 11 were obtained in an attempt to find the relation of the structural formulas of these clays to others in the literature and to see what differences were caused between the two clays by the presence of chlorite in OH-2. X-ray diffraction patterns of sample OH-2 show a very weak 14 Å line, and a strong 10.9 Å line. OH-N_1 contains only the strong 10.9 Å line.

It can be seen that the low percentage of chlorite has not affected the chemical analyses appreciably. However, it is probable that the slightly greater amounts of FeO and MgO and the lesser amount of SiO_2 in the OH-2 sample as compared to the OH-N_1 sample can be explained

by the presence of a small percentage of a chlorite mineral.

The most noticeable difference between the K-bentonite and the illite analyses is the much smaller amount of iron in the former. This may be the reason for the higher temperature (700° C) endothermal peak in the K-bentonites as compared to the 500-600° C peak usually found for illite. It is of interest to note that OH-N_1, which has less iron than OH-2, has its endothermal peak occurring at a temperature approximately 25° higher.

Below are given the structural formulas computed from the chemical analyses using the method of Ross and Hendricks (1945).

$$K_{.55}\ \frac{Ca}{2}_{.11}\ Na_{.02}$$

$$\text{OH-2}\quad (Al_{1.65}Fe'''_{.06}Fe''_{.01}Mg_{.38})\quad (Al_{.55}Si_{3.45})\ O_{10}\ (OH)_2$$

$$K_{.64}\ \frac{Ca}{2}_{.10}\ Na_{.02}$$

$$\text{OH-}N_1\ (Al_{1.64}Fe'''_{.02}Mg_{.36})\quad (Al_{.45}Si_{3.55})\ O_{10}\ (OH)_2$$

The presence of the chlorite is indicated by the total of 2.10 in octahedral coordination for OH-2 as compared to 2.02 in OH-N_1. If the formula for OH-2 is corrected for the presence of a small amount of chlorite by subtraction of small quantities of magnesium and iron and the addition

TABLE 11

Chemical Analyses

	1. OH-2	1. OH-N_1	2. Illite
SiO_2	50.65	52.44	48.95
Al_2O_3	27.37	26.38	25.03
Fe_2O_3	1.15	.31	7.29
FeO	.13	.00	1.61
Mg O	3.75	3.57	3.10
Ca O	.73	.66	.29
Na_2O	.16	.16	.15
K_2O	5.89	7.39	6.03
H_2O+	5.73	4.78	7.56
H_2O-	3.47	3.07	1.70
CO_2	.06	.00	
Ti O_2	.35	.44	.51
P_2O_5	.03	.04	
SO_3	.01	.30	
Cl	.01	.02	
MnO	.002	.001	
Li_2O	.01	.01	
	99.50	99.57	102.22

1. OH-2 and OH-N_1 less than one micron fraction: Analyzed by J. A. Maxwell, Department of Geology and Mineralogy, University of Minnesota.

2. Illite: Average of five analyses, Grim et al. (1937)

of some silica the two formulas will be in close accord.

In OH-N_1, if the .02 excess magnesium in the octahedral layer is assigned to an exchange position (Foster, 1950), the total excess positive charge on the octahedral and tetrahedral layers would total .79 and the total negative charge of the exchange and "fixed" cations would be .80.

Most, if not all, of the K is probably present in a"fixed"position in the non-expanded layers, whereas the Ca, Na and Mg is probably held in exchangeable positions by the expanded layers. It seems likely that a direct relationship exists between the amounts of K and Ca, Na and Mg present, and the degree of expandability, as these latter three elements make up 20% of the total external cations and the x-ray reveals that the expanded layers form 20-25% of the total clay. 80% of the external cations are K and as 75-80% of the layers are non-expanded there is little doubt that the K prevents expansion. This close correlation between ratios obtained by x-ray and chemical data suggests that the proportion of mixed layers can be predicted from the chemical data or in turn the composition of the external cations can be predicted from the x-ray data.

On the basis of the x-ray and chemical data the K-bentonite can properly be referred to as randomly inter-stratified layers of expanded and non-expanded Al tetoctrite. These layers are in the proportion of 1:4.

Electron Microscope Data

Figures 18-21 are electron micrographs of the less than one micron fraction of samples OH-2 and OH-N_1. Two of the pictures show the clay after standing in a 1N solution of NaOH for two months; the other two pictures show the clays after a similar treatment with 1N KOH.

The electron micrographs show that the clay of both samples consists of thin, irregular, sub-equant flakes which have smooth, straight edges. Electron micrographs were taken of these two clays after each of the various treatments described previously and none showed any significant variation in morphology.

PETROGRAPHY

X-ray spectrometer patterns were made of the bulk samples of all 22 clays. Nine thin sections were examined and the heavy and light mineral separates of samples OH-2 and OH-N_1 were examined.

The heavy minerals were concentrated by crushing 30 gms. of clay, dispersing it in water, and then shaking it for 24 hours on a rotary shaker. The less than 15 micron fraction was decanted five times; the residue was dried and sieved through a 100 mesh sieve; the material passing through the sieve was placed in bromoform (Sp.G 2.88) and centrifuged at 1000 RPM for 15 minutes; the lower portion of the bromoform, containing the heavy minerals, was

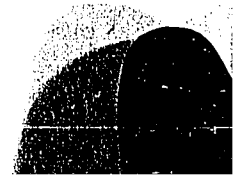


Fig. 18 - (OH-N_1) Na based less than one micron fraction.

X 15,000

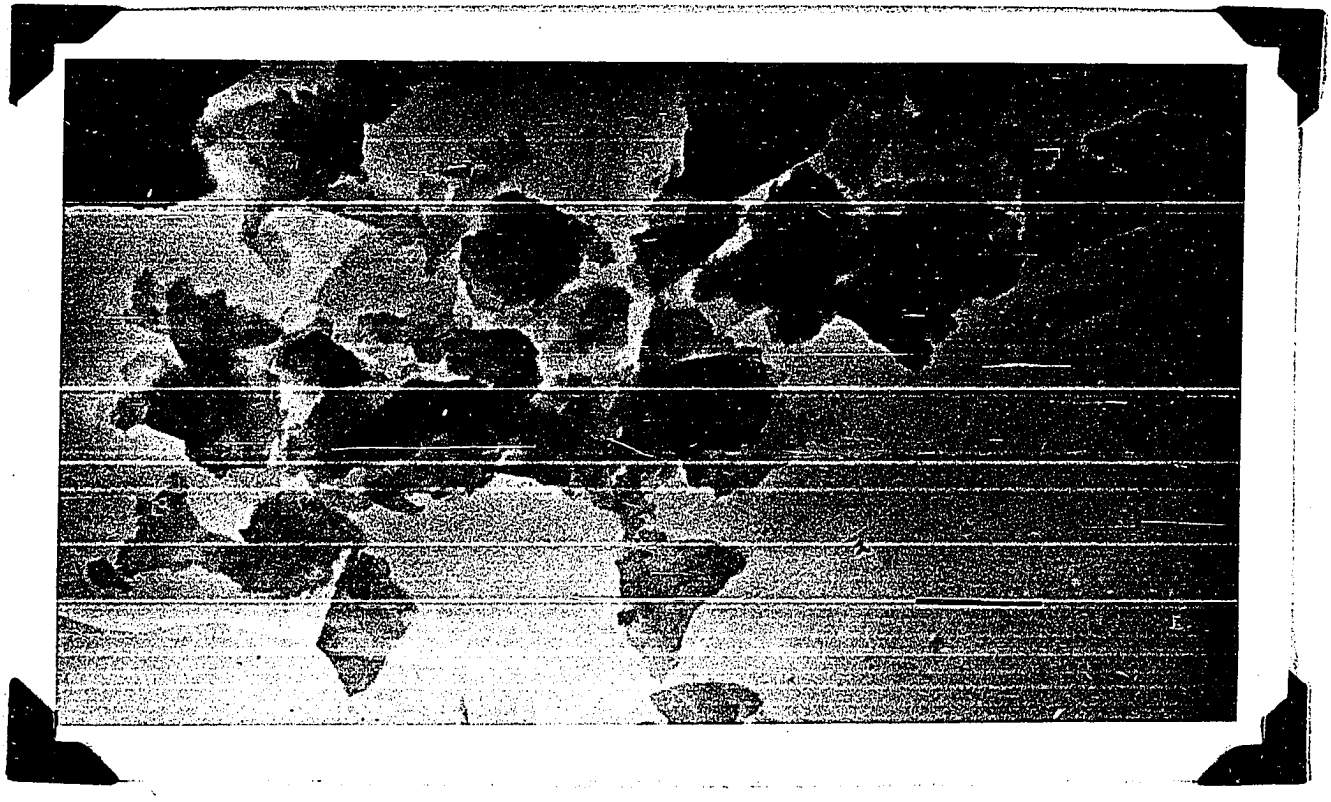


Fig. 19 - (OH-2) Na based less than one micron fraction.

X 15,000

Fig. 20 - (OH-N_1) K based less than one micron fraction.

X 15,000

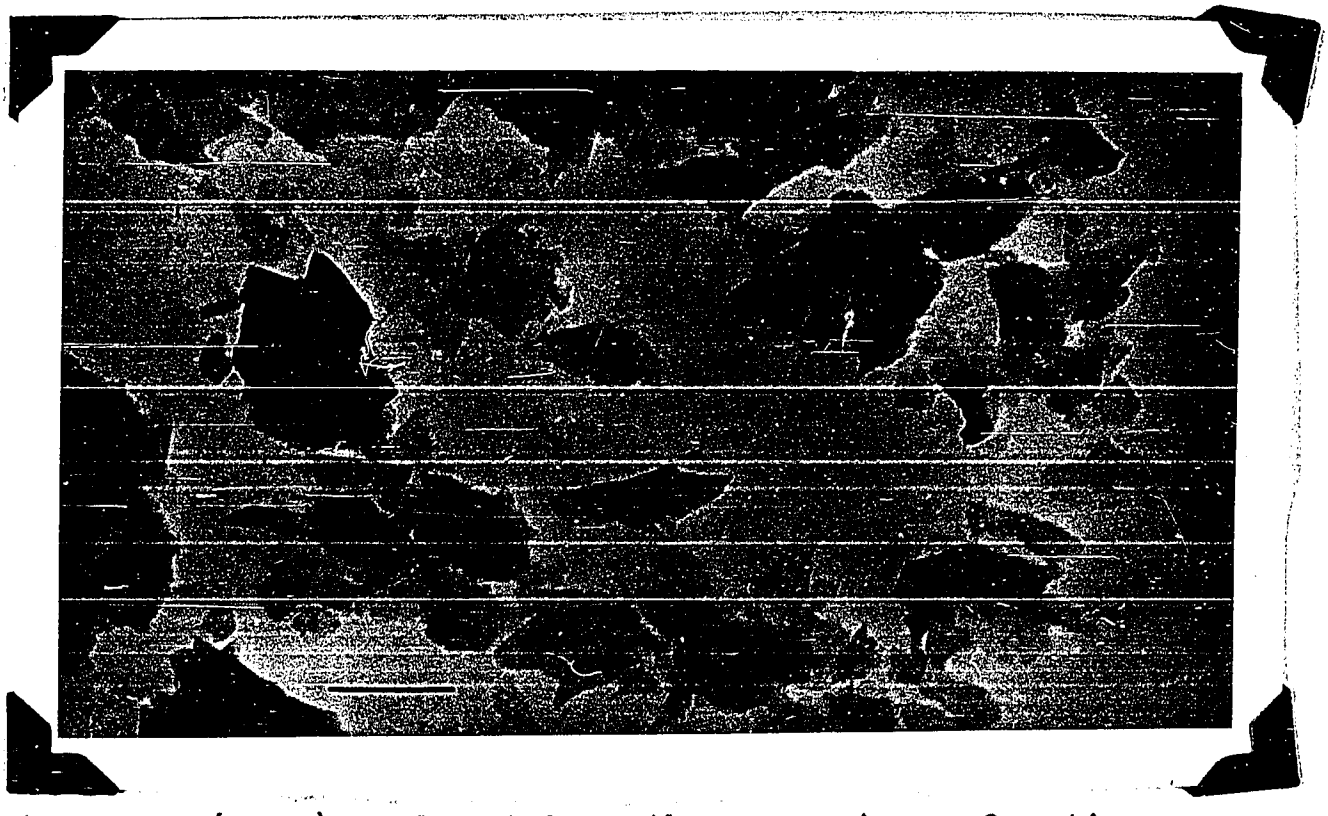


Fig. 21 - (OH-2) K based less than one micron fraction.

X 15,000

frozen and the remaining bromoform and light minerals poured off. The frozen bromoform was then thawed and the heavy minerals collected in a filter paper. A clean separation was obtained by this method.

The bulk x-ray spectrometer patterns gave, in addition to peaks for clay minerals, very small quartz peaks indicating 1-2% of this mineral.

Sample OH-2

In thin section, the clay comprises approximately 95% of the material present. The oriented aggregates show a white to yellow birefringence and have an index of refraction between 1.54 and 1.55.

The varietal minerals, comprising approximately 5% of the sample, are albite, quartz, volcanic glass, apatite, zircon, biotite, and leucoxene.

Albite: (Figure 22) A few albite peaks show up on x-ray spectrometer patterns of the light fraction. In loose grain mounts it occurs usually as angular, xenomorphic grains, although frequently hypidiomorphic, plate shaped grains are seen. The extinction angle on albite twinning, when present, varies from 12° to 17°. The grains average .05 to .1 mm. in size and range up to 0.2 mm.. They commonly contain minute calcite inclusions. In most cases the grains have rough, deeply pitted surfaces.

Quartz: Though a small amount of quartz was

indicated by the x-ray patterns, it was not noticeable under the microscope. It probably occurs as disseminated, fine grained chert.

Volcanic glass: (Figure 23) In the thin sections and in the loose mineral mounts, about 3% of the material consists of clear, isotropic, angular grains with an index of refraction of 1.55. Frequently the grains are elongated and have a shard-like appearance.

Apatite: (Figure 24) Apatite grains comprise 98% of the heavy mineral separate, and about 0.1% of the total sample. The apatite occurs in two forms. The most common type, which comprises 90% of the grains, occurs as prismatic, idiomorphic to hypidiomorphic grains ranging in length from .01 to .16 mm. They average .08 mm. in length and .02 in width. The prism sides are smooth and straight; the ends are sometimes fractured, but usually contain basal or pyramidal terminations (frequently appearing slightly rounded). Cross sections show a perfect hexagonal outline. Elongated bubble inclusions are common, usually occurring in the center of the grain. The less common type of apatite consists of xenomorphic grains equant in shape, with rough, irregular edges. The surface of the grains is pitted, rough, and shows a grayish tinge. A few contain irregular cracks. Table 12 lists the d values of the apatite concentrate from OH-2. The d values and intensities do not check

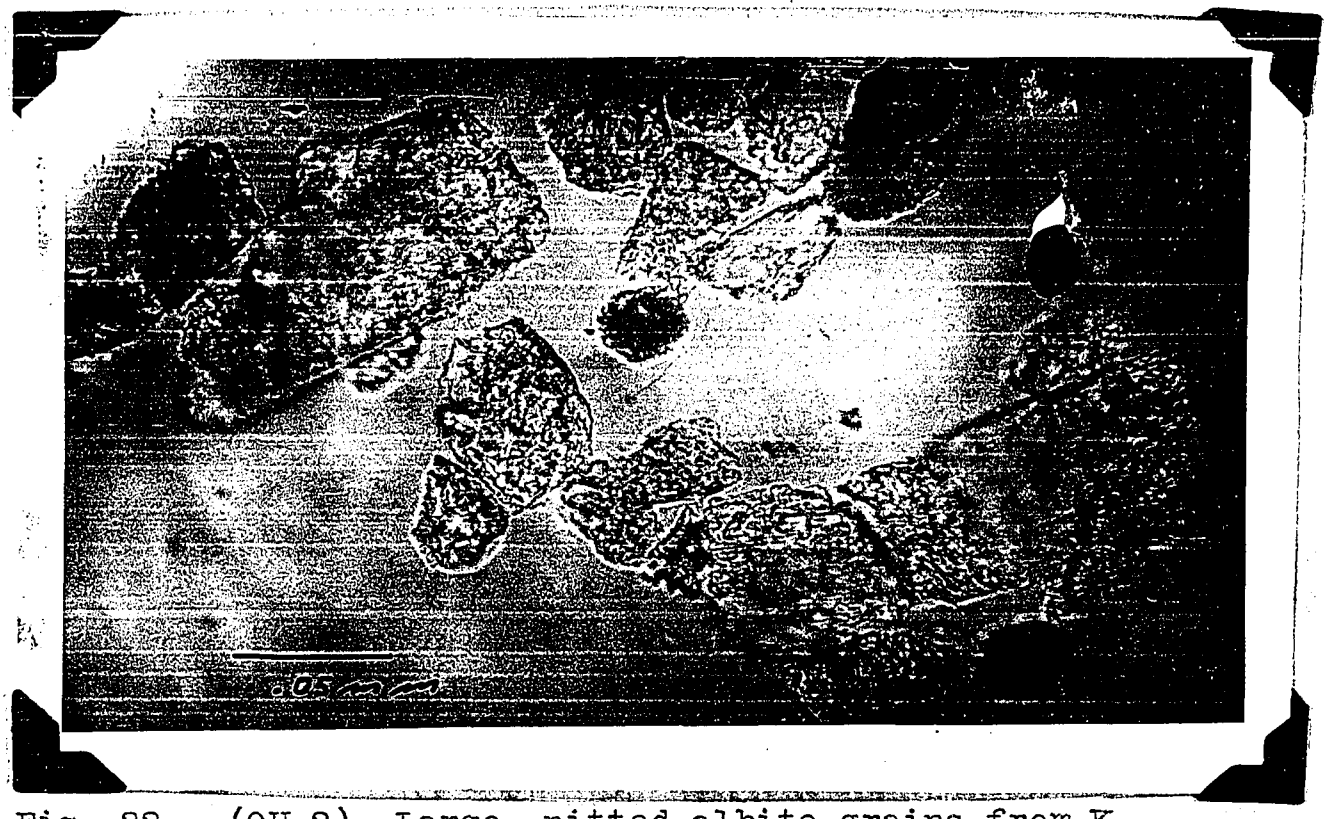


Fig. 22 - (OH-2) Large, pitted albite grains from K-bentonite. X 370

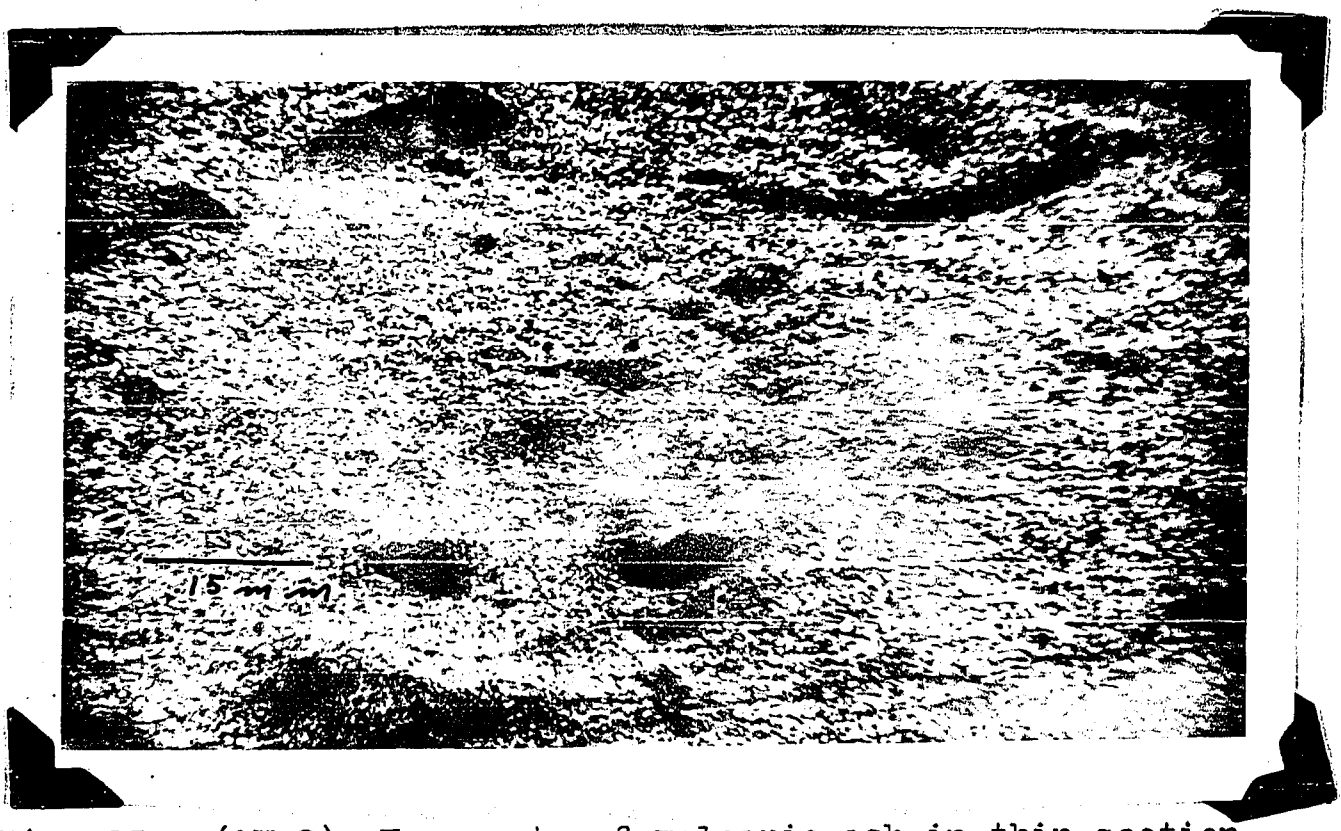


Fig. 23 - (OH-2) Fragments of volcanic ash in thin section of K-bentonite. X 150

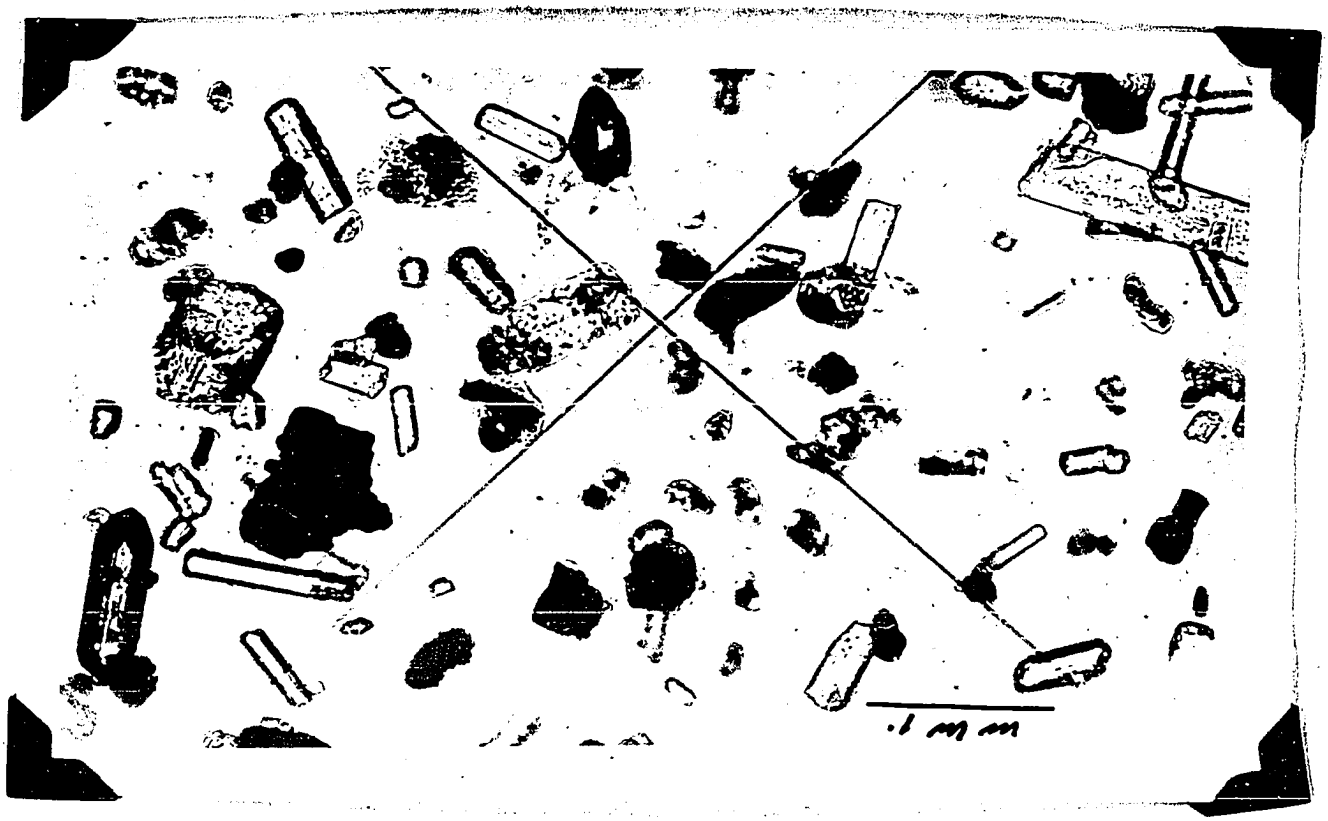


Fig. 24 - (OH-2) Idiomorphic apatite and zircon grains in heavy concentrate from K-bentonite. X 180

exactly with any of the various apatites listed in the literature. As very few apatites are alike, it is to be expected that this volcanic apatite would be a different variety than most of those previously examined.

Zircon: (Figure 24) Zircon makes up 2% of the heavy mineral separate. Most of the zircon is prismatic and idiomorphic. A few crystals are fractured. The grains are colorless and usually contain large bubble inclusions. The average length is about 0.04 mm.

Biotite: A few flakes and books of light pinkish-brown biotite can be seen. The flakes vary in shape from hypidiomorphic hexagonal to xenomorphic. Rod shaped inclusions are common and generally lie at an angle of 60^{0} to one another.

Leucoxene: About 10% of the heavy mineral separate consists of opaque, irregular, equant grains which are dull white in reflected light. X-ray patterns indicate the leucoxene is composed of anatase.

Sample OH-N_1

In the thin sections the clay is similar to that described for OH-2; however, there are a few lenses of clay, within the main mass which are characterized by the presence of disseminated, opaque, black material - probably pyrite.

No feldspar or quartz x-ray lines were obtained for this sample and no trace of these two minerals or volcanic glass was seen under the microscope. The heavy minerals, apatite, zircon, and biotite are identical in kind and relative amount, with those in OH-2. In addition, the heavy mineral separate contains about 50% of opaque minerals consisting of aggregates of pyrite and chalcopyrite.

ORIGIN

In considering the origin of the Ordovician K-bentonites, the data just presented may be evaluated with regard to the probable nature of the source material, the manner of its deposition, and the mode of formation of the clay minerals.

The presence in the K-bentonite beds of volcanic glass, biotite, and idiomorphic apatite and zircon crystals supports the theory that the source material was volcanic in origin. The wide geographic extent of the beds and the nature of the associated rocks indicates that the volcanic detritus was probably in the form of fine glass fragments laid down in shallow seas in which large amounts of limestone were being deposited. The lack of quartz phenocrysts and the fairly high index of refraction of 1.55 of unaltered glass fragments (characteristic of a glass low in silica) plus the presence of the minerals mentioned previously, indicate that the ash probably had the composition of a trachyte or possibly a latite.

TABLE 12

X-ray Data on Apatite from Sample OH-2

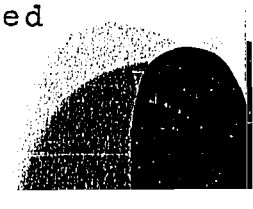
OH-2		Fluor-Apatite		Chlor-Apatite	
d	I	d	I	d	I
8.20 Å	ww				
4.51	ww				
4.10	ww	4.04	.1	3.92Å	.05
		3.87	.1		
3.45	m	3.44	.4	3.42	.2
3.34	ms				
3.11	ww	3.16	.1	3.08	.1
		3.05	.2		
2.82	s	2.78	1.0	2.85	.9
2.73	ms	2.69	.6	2.76	1.0
2.64	ww	2.61	.4	2.64	.2
2.54	ww	2.52	.1		
2.445	ww			2.55	.1
2.395	ww				
2.350	ww			2.31	.3
2.270	w	2.29	.1		
		2.24	.4		
2.151	ww	2.13	.1	2.16	.05
2.085	ww	2.06	.1	2.04	.05
1.949	ww	1.990	.1	1.952	.5
1.903	w	1.933	.4	1.905	.2
1.848	ww	1.869	.3	1.840	.5
1.809	ww	1.830	.5	1.808	.2
1.781	ww	1.791	.3		
1.758	ww	1.762	.3	1.766	.1
1.731	ww	1.740	.3		
1.724	ww	1.712	.3		
1.677	ww			1.691	.2
				1.610	.1

Presumably, this material was the source of the mixed layer clay mineral of which the beds are composed. The presence of chert in the outer edges of the beds and in the adjacent limestone indicates that the volcanic detritus was also the source of silica. The increase of chlorite from a low concentration in the limestone to a relatively high concentration at the outer edge of the K-bentonite beds suggests that this mineral also was formed by the alteration of the volcanic ash. On the other hand the non-expanded dioctahedral 2:1 clay, which is most abundant in the limestone and diminishes with increasing chlorite and mixed layer clay, is probably detrital in origin and unrelated to the volcanic activity.

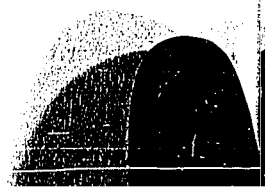
With these relationships in mind, the origin of the K-bentonites and the associated minerals can be explained by the following line of reasoning.

Assuming that the relatively stable Al_2O_3 was not taken into solution, much of the silica, iron, and alkalies of the volcanic ash was removed to the extent that about one and one-half parts of glass were required to produce one part of clay. Some of the silica was precipitated to form the chert commonly found in the upper and lower portion of the bentonite beds.

After removal of sufficient amounts of the various ions, an impure pyrophyllite lattice was probably formed with a composition similar to that of the Cretaceous and Tertiary expanded dioctahedral 2:1 clays. This is suggested



by the high temperature hydroxyl-endothermal reaction of the randomly interstratified clay mineral and is further verified by chemical analyses which, when presented in the form of structural formulas, are similar to many of those listed by Ross and Hendricks (1945) for the montmorillonite-beidellite series. Many of the Cretaceous and Tertiary clays, which were derived from glass similar in composition to the Ordovician ash, were formed in saline lakes and seas. However, any potassium in the glass was removed and the resulting clays attracted calcium as the most abundant external base. A similar situation probably prevailed in the calcium-saturated Ordovician sea suggesting that the K-bentonite, in its original form, probably had this ion as the predominant external base and consequently consisted of an expanded dioctahedral 2:1 clay. As the Ordovician period was relatively quiescent as compared to the Cretaceous and Tertiary, it is likely that the Ordovician volcanic ash was in contact with sea water for a much longer period of time than were the more recent ash falls. Therefore, it is believed that due to the availability of potassium in the sea water, a cumulative retention occurred, extending over such a period of time, that the calcium in the Ordovician K-bentonite was replaced in 80% of the layers resulting in this proportion of non-expanded clay minerals.



ORDOVICIAN LIMESTONE

INTRODUCTION

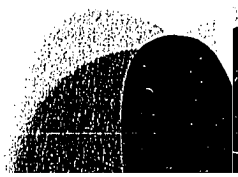
In an attempt to obtain some idea of the duration of volcanic activity during Ordovician time, samples of limestone above and below several of the K-bentonite layers were collected at Oak Hall Quarry three miles east of State College. The clay minerals and the varietal minerals in the limestone were compared to those in the K-bentonites.

From the north wall of the quarry 26 samples were collected within a vertical range of 58 feet from three vertical sections (A, B and C) 25 feet apart. Within this range occur three beds of K-bentonite from which samples OH-2, OH-1, and OH-0 were obtained (Figure 25). The limestone is a hard, dense, fine grained, light gray to black rock which in most cases is massive and has a semi-conchoidal fracture, but immediately above and below the K-bentonite beds has a shaly appearance.

MINERALOGY

Carbonate Minerals

X-ray spectrometer patterns of six selected bulk samples (2A, 6A, 10A, 8B, 4C), of the limestone itself, contained strong calcite peaks and no dolomite peaks, indicating a fairly uniform $CaCO_3$ limestone throughout the section.



The calcite occurs as fine grained xenomorphic crystals without noticeable orientation. The thin sections commonly show a grumelense or nodular structure with the individual nodules 0.05 to 0.10 mm. in diameter. These subspherical granules consist of very fine grained calcite particles averaging 0.007 mm. in diameter, and are much darker than the matrix limestone which is quite clear. This dark color is apparently caused by clay which is concentrated in the nodules. Grains of the matrix calcite range from .015 to 0.50 mm. in diameter with the average tending towards the small size. Occasionally a few idiomorphic rhombs of dolomite are found.

Insoluble Residue

Description

The limestone samples were crushed to pieces 1/4 to 1/2 inches in diameter and placed in a 25% solution of HCl until all the calcite was dissolved. In Figure 25 is listed the percent of insoluble residue for each sample. Horizontally, within beds, there is little variation; vertically the percentage varies from 4.2% 9 feet below K-bentonite bed OH-1 to 70% immediately below bed OH-2. There appears to be an increase in the amount of insoluble residue in the limestone as the K-bentonite beds are approached either from below or above. This would indicate that much of the residue was formed from volcanic detritus, the volcanic deposition beginning slowly, building up to a maxi-

Location of Oak Hall Samples

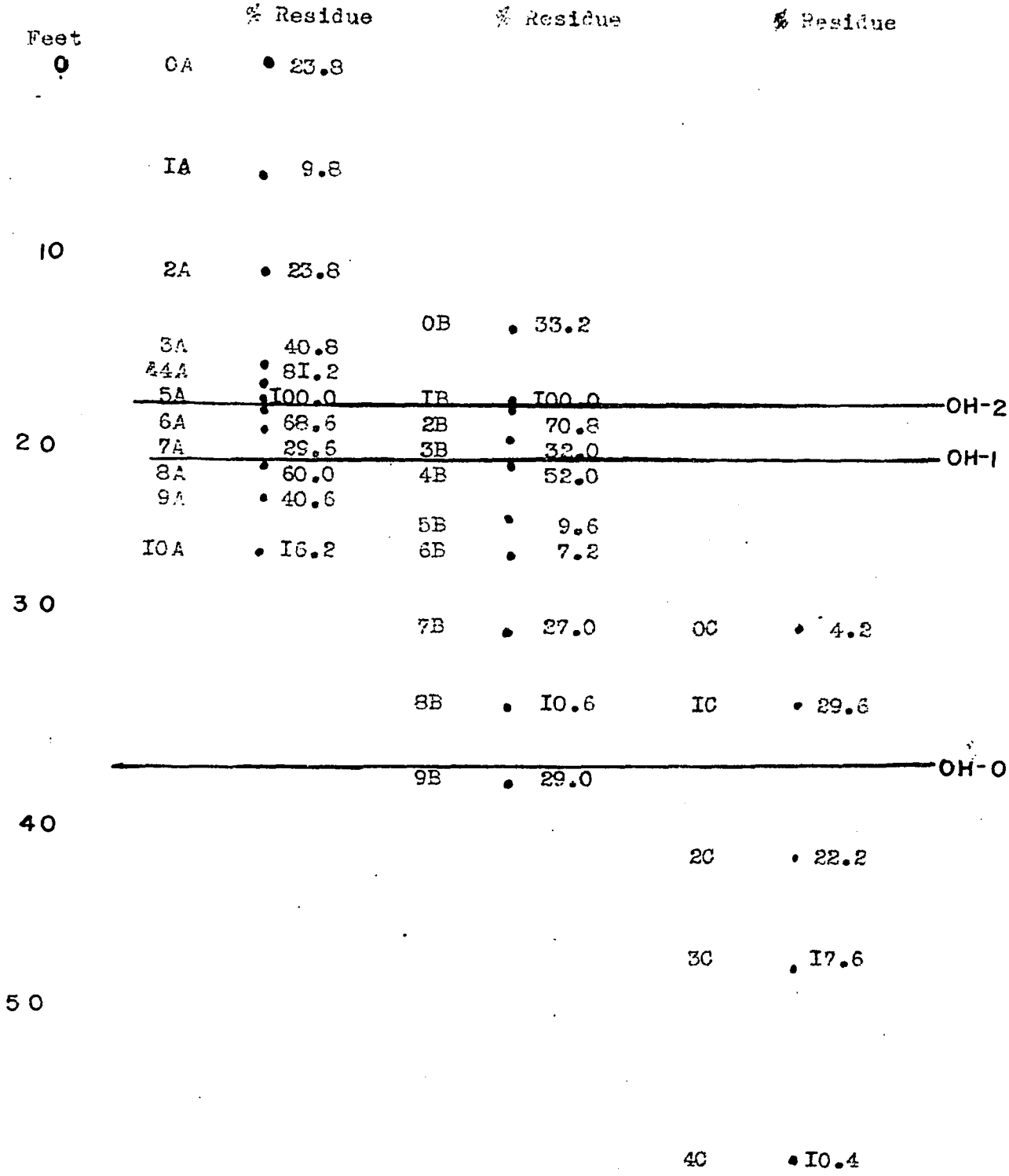


Figure 25

mum when the K-bentonite beds were deposited, and then gradually falling off to a minimum before increasing again. In order to see if this was the actual situation the residues were examined with the intent of determining their source.

X-ray spectrometer patterns of the residues, using the data from seven samples were selected and film-type x-ray diffraction patterns run. Further detailed studies were made on the less than one micron fraction of three representative samples. Loose grains of each residue were examined under the binocular and petrographic microscope and in three samples (2A, 1B and 4C) the heavy minerals were separated and examined. Several thin sections were examined under the microscope.

All of the residues are dark black and contain considerable organic material. Table 13 lists the intensities of the peaks in the x-ray spectrometer patterns of the bulk, uncleaned residues. All samples show a prominent peak at approximately 10 Å, in most cases due to a non-expanded, dioctahedral 2:1 clay. In addition many of the samples give patterns with peaks at 14 Å and 7 Å indicating possibly chlorite or an expanded dioctahedral 2:1 clay. The clay fraction will be discussed in detail later.

Light Minerals

Quartz: All x-ray patterns show a strong reflection. The quartz occurs in three forms:

(1) Detrital quartz. - A few sub-rounded, fine (0.05 mm) grains of detrital quartz are present.

(2) Authigenic quartz. - Idiomorphic quartz crystals, ranging in length from 0.15 to 0.30 mm. are found in nearly all the limestone samples. The crystals have prism and rhombohedron faces. The edges in all cases have a rough, irregular contact with the calcite. Calcite inclusions are abundant, frequently making up half the quartz crystal.

(3) Chert. - Chert commonly occurs in irregular fragments averaging about 0.05 mm. in size. The individual microcrystals are a few microns in diameter. The irregularly shaped angular grains suggest that the chert is authigenic.

A semi-quantitative examination of the x-ray spectrometer patterns indicates that there is a concentration of quartz near the bentonite beds.

Albite: Authigenic albite is found in every limestone residue. It is extremely uniform in morphology throughout the three sections. Approximately 50% of the grains are idiomorphic and the majority of the others are hypidiomorphic. Twinning is not common. The majority of the grains are clear containing no inclusions and showing no alteration. However, many of the grains have carbonate inclusions covering from one to 25% of the surface of the crystal. (Figure 26)

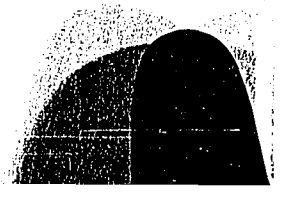


TABLE 13

X-ray Spectrometer Data on Bulk Limestone Residues

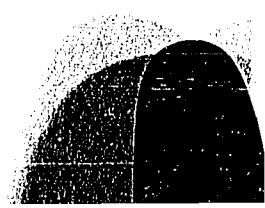
	Quartz	Albite	10 Å Illite	14 Å Chlorite	Percent Residue
0A	m	m	m*		24
1A	m	m	m*		10
2A	m	w	m		24
3A	s	w	w		41
4A	s	w	s	w	81
5A	s	ww	s	w	100
6A	s	ww			69
7A	ss	s	w		30
8A	s	m	ms		60
9A	s	w	ws	w	41
10A	s	m	m		16
0B	s	w	m	m	33
1B	ss	w	s	m	100
2B	ss		m	m	71
3B	s	w	w*		32
4B	s	m	m		52
5B	s	ss	m	w	10
6B	s	ss	m*		7
7B	m	w	m	w	27
8B	s	m	m*		11
9B	m	w	m	w	29

*No (001) peak

TABLE 13 (cont.)

X-ray Spectrometer Data on Bulk Limestone Residues

	Quartz	Albite	10 Å Illite	14 Å Chlorite	Percent Residue
0C	s	ss	m	w	4
1C	s	w	m	w	30
2C	m	w	m	w	22
3C	s	m	m	ww	18
4C	s	s	s	w	10



The majority of the crystals fall in the 0.01 to 0.04 mm. range although occasionally grains are as large as 0.08 mm. These larger grains are xenormophic and angular with a rough, "pot hole" surface, and resemble the large crystals in the K-bentonite (OH-2).

Table 13 shows the relative strength of the albite peaks in the x-ray spectrometer patterns in each residue. There is a marked tendency for the smaller percentage of residue to have the greater concentration of albite. Albite ranges from a trace (ww) in samples 5A and 6A up 60 to 70% (ss) of the residue in samples OC, 5B and 6B. Indications are that the absolute amount of albite remains constant while the clay and quartz content of the residue varies. This would indicate that the formation of the albite is independent of the amount of volcanic detritus present.

Tuttle and Bowen (1950) have shown that there is a difference between the x-ray patterns of high and low temperature albite. A study was made of the albite from the K-bentonite (OH-2) and from the limestone (OH-4C) in an effort to discover any difference between the two (the albite from the K-bentonite possibly being the high temperature type and the definitely authigenic variety from the limestone the low temperature type).

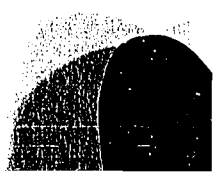


Fig. 26 - (OH-4C) Idiomorphic, authigenic albite crystals from an Ordovician limestone sample. X 400

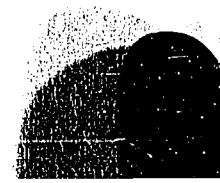
The albite was concentrated by placing the sample in a mixture of acetone and bromoform and centrifuging at 10,000 rpm. The material which sank and that which floated was examined after each centrifuging and more acetone or bromoform was added accordingly and the process repeated. In this manner a concentration of approximately 95% albite was obtained.

X-ray spectrometer and film type patterns show appreciable difference between the two samples of albite. The d values check closely with those listed by Tuttle and Bowen for the low temperature Amelia albite (Table 14). This evidence plus the presence of carbonate inclusions in the albite indicates that it is authigenic in both samples. Possibly the large size attained by the albite in the K-bentonite (on the average four times as large as that in the limestone), and rapid growth, as indicated by the highly irregular surfaces, prevented the albite from developing an idiomorphic form.

Heavy Minerals

A study of the heavy separates from three samples gave the following results:

1. OH-1B - This sample lies immediately above K-bentonite OH-2. The non-opaque minerals consist of about 98 percent apatite, identical in character with the two types found in the K-bentonites. The other



two percent consists of idiomorphic zircons. The average grain size of these two minerals appears to be slightly smaller in this sample than in the bentonite. The heavies contain about 30 percent of pyrite which is usually in a cubic form.

2. OH-2A - This limestone sample seven feet above OH-2 contains four major non-opaque minerals and one opaque mineral.

Biotite: Light pinkish-brown biotite forms 60 percent of the non-opaques. The grains are occasionally hypidiomorphic though usually xenomorphic; they vary from angular to sub-round, and average 0.15 to 0.20 mm. in size. They frequently contain irregular brown inclusions and are characterized by the presence of rod shaped inclusions which commonly form angles of 60° with one another. These inclusions cover from 1 to 20 percent of the surface area of the flakes. This biotite is similar to that in the K-bentonites and is presumably characteristic of the volcanic ash.

Zircon: Colorless zircons form 30 percent of the non-opaques. Idiomorphic and hypidiomorphic grains averaging 0.05 mm. and ranging up to 0.115 mm. comprise about 90 percent of the total. The remaining 10 percent of zircons are rounded and average about 0.03 mm. These and probably some of the smaller, idiomorphic zircons are apparently detrital, but the majority of the idiomorphic and hypidiomorphic grains

TABLE 14

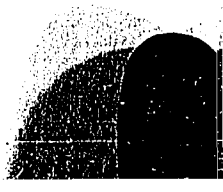
Spacings and Intensities for Albite

Amelia Albite	I	OH-2 and OH-4C	I
6.38	1	6.4	ww
4.02	3	4.03	w
3.83	2	3.84	ww
3.79	2	3.77	w
3.67	3	3.67	w
3.51	1	3.52	ww
3.38	1	3.38	w
3.20	10	3.21	s
2.96	2	2.96	w
2.93	3	2.93	w
2.86	1	2.86	ww
2.64	1	2.64	ww
2.562	1	2.56	w
2.448	1	2.450	ww
2.412	1		
2.325	1		
2.280	1		
2.190	1		
2.126	1		
2.081	1		
1.893	1	1.890	ww
1.832	1	1.830	ww
1.808	1	1.802	w
1.790	1	1.791	w

TABLE 14

Spacings and Intensities for Albite (cont.)

Amelia Albite	I	OH-2 and OH-4C	I
1.755	1		
1.723	1	1.727	w
1.676	1		
1.576	1		
1.564	1	1.562	ww
1.535	1	1.529	ww
1.507	1		
1.468	1	1.463	ww
1.437	1	1.431	ww



presumably have a volcanic source.

Tourmaline: About 10 percent of the non-opaques consist of tourmaline grains. These average 0.04 to 0.05 mm. in size and vary from round to sub-round. They are pleochroic from light to dark gray and from light olive to colorless. The distinct rounding of the grains, plus the fact that none are found in the K-bentonites examined nor are reported in similar bentonites (Bonine and Honess 1929), indicates a detrital origin.

Muscovite: A few colorless, clear, sub-round flakes of this mineral can be found.

Pyrite: About 50 percent of the total heavy separate consists of pyrite cubes, usually in aggregates.

3. OH-4C - The heavy separate of this sample 21 feet below OH-0, contains about 95 percent pyrite in the form of cubes and octahedrons joined together in irregular aggregates.

Zircon: Colorless zircons comprise 90 percent of the non-opaques. There are very few zircons in this separate but the majority of those present were rounded to some extent. The average grain size is 0.04 mm.

Tourmaline: Approximately 10 percent of the non-opaques are sub-round to angular, prismatic tourmalines which are pleochroic from light green to

colorless and average 0.04 mm. in grain size.

A few grains of chlorite and rutile were found.

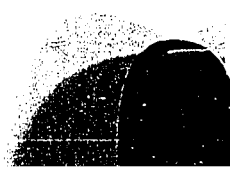
Significance of Heavy Minerals

Assuming that the tourmalines and the rounded zircons are non-volcanic, and that the biotite, idiomorphic zircon, and apatite are volcanic, a rough estimate can be made of the source of the insoluble material in the limestone. (The pyrite is undoubtedly authigenic).

The idiomorphic apatite and zircon assemblage in the K-bentonites and in the rock approximately six inches on either side indicates that most of the material was deposited as volcanic ash possibly directly from the air. Though no direct correlation can be found between the amount of heavy minerals and the total amount of volcanic material, comparison between samples can be made on a relative basis.

OH-2A, seven feet above the nearest K-bentonite contains approximately 15 percent of water transported non-opaque heavy minerals with a non-volcanic source and 85 percent which have a volcanic source. OH-4C, 21 feet below the nearest clay bed contains a much higher percentage of water transported non-volcanic heavies.

The prismatic shape of most of the tourmalines indicate that they were probably not derived from older sediments but from igneous or metamorphic rocks. The olive, green, gray and brown colors suggest that the source may have been granitic (Krynine 1946).



Clay Minerals

X-ray spectrometer patterns of the limestone residues showed that all the samples but one contain considerable clay. Table 13 gives the relative intensities of the x-ray reflections from the (001) planes of the clay mineral. All of the samples but one give a fairly strong peak equivalent to a non-expanded Al 2:1 clay mineral with an (001) spacing of about 10 Å. In many of the residues the organic material present prevented good orientation on the x-ray slide and the (001) reflection was very weak. However, in these cases the 4.47 Å d value was assumed to be due to the (110) reflection of the 10 Å clay. Additional reflections at 14 Å and 7 Å were obtained from about half the residues indicating a mineral of the chlorite or montmorillonite type. These weak reflections were probably present in all patterns but not detected in some.

Seven representative residues were selected and x-ray diffraction patterns were run of the bulk residue prepared as follows: untreated, cleaned of organic matter, saturated in NH_4OH, ethylene glycol, and heated to 600° C for 24 hours. Table 15 lists some of the important (001) values of these patterns. The less than one micron fraction was separated from samples 2A, 1B, and 4C. These three samples were also subjected to a variety of treatments and x-ray diffraction patterns were run, Table 16.

The uncleaned bulk residue of sample 1B gives an x-ray diffraction pattern with moderately strong line at 14.2 Å. A moderate line at 7.0 Å and a weak line at 3.50 Å indicate the reflections are probably due to chlorite (the 7.0 Å (002) reflection does not commonly occur in montmorillonite patterns). In addition a moderately strong band is found which extended from 8.8 to 11.0 Å. Such a wide band indicates an interlayering of 10 Å layers and wider layers.

When this bulk residue was heated to 600° C for 24 hours there was a slight shrinkage of the larger spacing from 14.2 to 14.0 Å. The 14.0 Å line became darker while the 7.0, 4.70 and 3.50 lines became weaker.

The less than one micron fraction of this sample gave a sharp 14 Å reflection with the corresponding (001) series. The identification of the mineral responsible for this series was described in the K-bentonite section. It was found to be chlorite.

When the less than one micron fraction of this residue was x-rayed it gave a fairly sharp line at 10.3 Å as compared to the broad band in the x-ray patterns of the bulk material. This fine fraction was saturated with NH_4OH, $CaCl_2$ and ethylene glycol and x-rayed in each case. Table 16 gives the d values of the three characteristic x-ray lines for the variously treated clays. If these values are compared with the mixed layer data listed in progress report six it can be seen that the values check very closely with the values for samples OH-N_1 and OH-2. It can there-

TABLE 15

X-ray Data on Treated Bulk Samples of Limestone Residues

	(001)	(001)	(002)	(003)	(004)
2A-uncleaned	14.0ww	10.1wm	7.0w	4.70w	3.47ww
600°C-24 hrs.	14.0m	9.9m	7.1m	4.70ww	3.50w
NH_4OH	14.1w	10.0wm	7.0wm	4.70w	3.50w
E. glycol	14.0m	10.0ms	7.0s	4.70w	3.50w
9A-cleaned	14.0wm	10.0wm	7.2wm	4.70w	3.48ww
1B-uncleaned	14.2m	8.8-11.0m	7.0m	4.70m	3.50w
600°C-24 hrs.	14.0s	10.1mw	7.0w	4.70w	3.50ww
2B-uncleaned	13.9m	8.6-10.8m	6.9s	4.67w	3.50w
600°C-24 hrs.	14.0s	8.9-11.2wm	7.1m	?	A
9B-cleaned	14.2ww	10.0m	7.1w	4.67w	3.50w
0C-uncleaned	14.0m	10.1wm	7.0m	4.70m	3.48
600°C-24 hrs.	13.8wm	9.9ww	7.0w	?	?
4C-cleaned	14.1ww	10.0m	7.0wm	4.70w	3.48w
600°C-24 hrs.	14.0wm	10.0m	7.0ww	4.70ww	3.48wm

TABLE 16

X-ray Data on the Less Than One Micron Fractions of the Limestone Residues

	OH-1B		OH-2A		OH-4C	
Uncleaned	14.1m	10.3w				
Cleaned	14.0m	10.45s	14.0ww	10.0s	14.0ww	10.0s
NH_4OH	13.9w	10.3ss				
$CaCl_2$	14.2m	10.7-9s				
E. glycol	14.2m	11.4-9.33m				
600°C D.T.A.	13.8s	9.9m				
600°C-24 hrs.	13.6s	10.0m			13.2ww	10.0s

Mixed Layers Lines - OH-1B

Cleaned	10.45m	5.2w	3.25w
$CaCl_2$	10.9s	4.92m	3.33w
NH_4OH	10.3s	5.2ww	3.28w
E. glycol	11.4-9.3m	5.2b	---

fore be concluded that sample 1B contains a randomly interstratified clay containing approximately 20 percent of expanded and 80 percent of non-expanded Al 2:1 layers. However, this sample contains a larger proportion of chlorite than sample OH-2.

Sample 2B is quite similar to 1B. X-ray diffraction patterns of the bulk residue show moderately strong chlorite reflections and moderately strong reflections from an interstratified clay which appear to have approximately the same proportion of expanded and non-expanded layers as 1B.

X-ray diffraction patterns of the bulk residue of samples 9A, 9B, and OC are similar to one another. The patterns for the three samples contain weak to moderate 14 Å reflections. The presence of the (002), 7 Å reflection and the characteristic change in intensity of several of the lines when the residue is heated to 600° C for 24 hrs. indicates that the reflections are caused by chlorite. In addition, a weak to moderate 10 Å reflection is found for all three samples. The other lines associated with the 10 Å reflection indicate that the clay is a pure non-expanded Al 2:1 clay mineral, in contrast to the interstratified clays in the samples described previously.

The x-ray diffraction pattern of the bulk residue of sample 2A contains a very weak 14 Å line and weak 7.0, 4.70 and 3.47 lines. This sample was saturated with NH_4OH and ethylene glycol to see if the clay was an expanded Al or Mg 2:1 mineral. No change occurred in the 14 Å series.

This data plus the characteristic change in intensity of the x-ray reflections when the clay is heated indicates the material is chlorite. In addition to the chlorite pattern a sharp weak to moderate intensity non-expanded Al 2:1 clay mineral pattern is found. The x-ray pattern of the less than one micron fraction of sample 2A also shows lines of chlorite and a non-expanded Al 2:1 clay. However, here the chlorites line are weaker and the 2:1 lines are stronger than in the patterns of the bulk sample, indicating that the chlorite is probably coarser grained than the 2:1 clay.

Sample 4C, in both the bulk and the less than one micron fraction, gives x-ray patterns nearly identical with sample 2A. The non-expanded Al 2:1 reflections for 4C are slightly stronger than those for 2A. When the less than one micron fraction was heated at 600° C for 24 hours the chlorite line shifted to 13.2A.

Figure 27 shows differential thermal analysis curves of the less than one micron fraction of residues 2A and 4C with the organic matter partially removed. (Sample 4C was run after first being heated to 200° C and as a result the low temperature endothermal peak is small). The exothermal reactions between 300° and 450° C are due to organic matter. The large hydroxyl endothermal reaction extending from 450 to 700° C with a maximum at 600° C is typical though slightly higher than that of the Carboniferous illites. The relatively sharp chlorite peak which occurs

at 600° C in sample 1B is apparently masked by the broad non-expanded clay peak in these two samples. The high temperature endothermal and exothermal reactions are similar to those of other non-expanded clays.

Electron micrographs of sample 1B show thin, clear, angular flakes similar to those in OH-2. The electron micrographs of 2A are similar to 1B but the flakes are less angular and many are slightly rounded (Figures 28 and 29).

ORIGIN

The K-bentonite OH-2 is composed largely of randomly interstratified layers of expanded and non-expanded Al tetoctrite in the proportion of 1:4. In addition the clay contains one or two percent of chlorite. Samples OH-1B and 2B immediately above and below the K-bentonite bed are composed largely of an interstratified clay identical with that in the K-bentonite. However, these two samples contain considerably more chlorite than the K-bentonite.

All other samples examined (2A, 9A, OC, and 4C) have a non-expanded Al 2:1 clay as their most abundant mineral. In addition they all contain varying amounts of chlorite but less than samples 1B and 2B. Samples 2A and 4C which are farther away from K-bentonite beds than any of the other samples contain less chlorite than any other sample except the K-bentonite itself. (Most of the Lower and Upper Ordovician rocks contain a detrital non-expanded

DIFFERENTIAL THERMAL CURVES

Figure 27

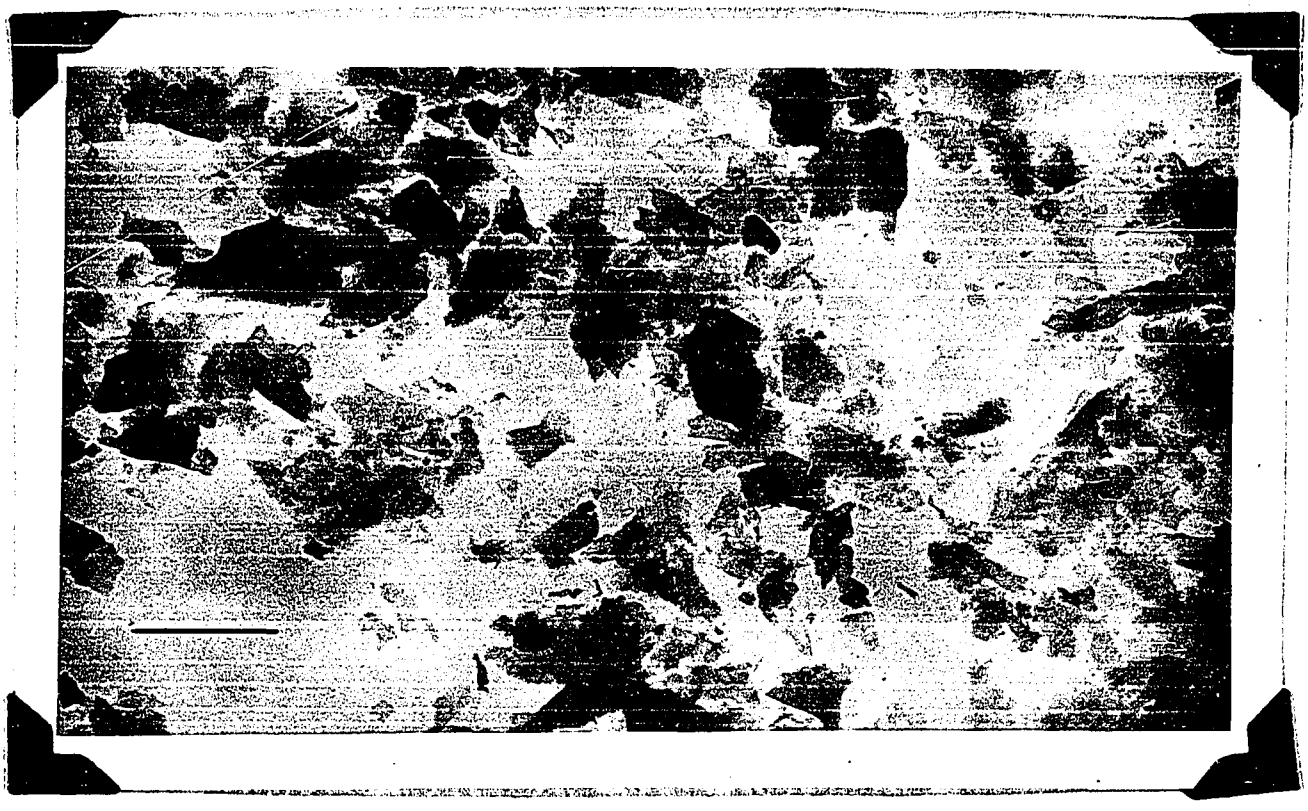


Fig. 28 - (OH-1B) The less than one micron fraction of a cherty K-bentonite. X 18,000

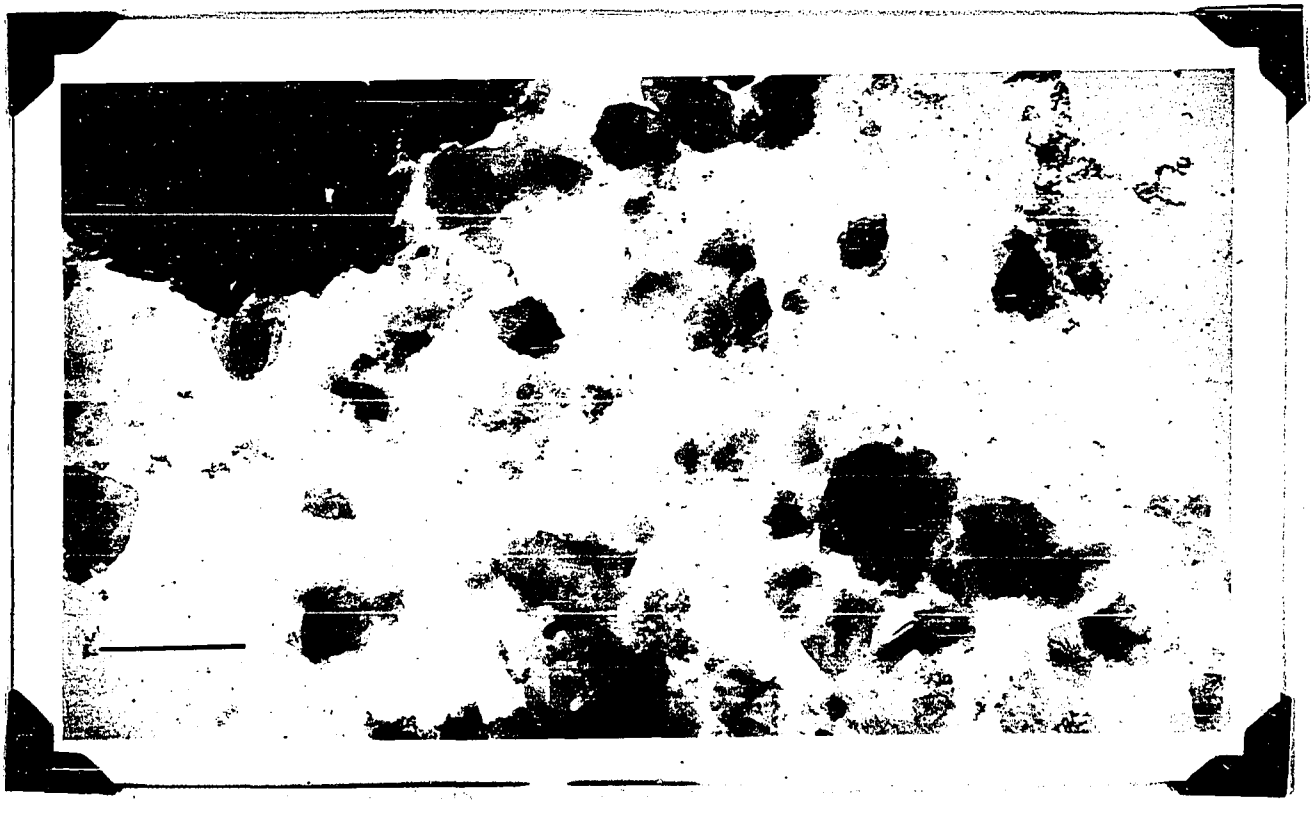


Fig. 29 - (OH-2A) The less than one micron fraction of the insoluble residue of an Ordovician limestone sample. X 18,000

Al 2:1 clay as the predominant clay mineral).

In summary the chlorite is rare to absent in the middle of the K-bentonite bed, increases to a maximum concentration at the outer edges of the beds, and gradually decreases in amount in the limestone as the distance from the clay bed increases.

The petrographic examination showed that the K-bentonite beds and the shaly layers on either side contain only volcanic heavy minerals. The limestones contain both volcanic and non-volcanic heavy minerals with the volcanic minerals decreasing with increasing distance from the K-bentonite beds.

On the basis of the data collected a reasonable theory can be developed to explain the origin of the clay minerals and the extent, in time, of the volcanic activity.

The majority of the latites and trachytes do not contain as much MgO as is found in the present K-bentonites. Ross and Hendricks (1945) concluded that most of the MgO in bentonites resulting from the weathering of volcanic ash was derived from the surrounding sea water.

The distribution of the chlorite suggests that the formation of chlorite depended upon the availability of magnesium. This availability is probably enhanced by the presence of calcite ooze. Whereas a plentiful supply of available Mg changed much of the ash in the outer portion of the clay beds and all of the ash in the limestone to chlorite, more restricted circulation of sea water

and the absence of calcite inhibited the same sort of alteration within the K-bentonite beds. Here the octahedral layers of the clay mineral retained the high percentage of aluminum available from the ash and the sea water supplied sufficient calcium for the base exchange positions. In time 80 percent of the calcium was replaced by potassium to give the randomly interstratified 20 percent expanded 80 percent non-expanded layers comprising the clay mineral now found in the K-bentonite beds.

The distribution of clay minerals and heavy minerals indicates that the lime ooze farthest from an ash bed received a small supply of ash which was entirely changed to chlorite. At the same time considerable non-expanded Al 2:1 clay was carried into the ooze from the surrounding shore. This resulted in a limestone with a residue composed largely of a non-expanded Al 2:1 clay and a lesser amount of chlorite with both volcanic and non-volcanic detrital heavy minerals (4C).

As volcanic activity increased more ash was deposited along with the non-expanded clay and the relative amount of chlorite increased accordingly (9B, 0C, 9A).

The volcanic activity reached a sudden peak and deposited an immense amount of ash in a short period of time. The amount of non-expanded clay deposited during this time was negligable. This large amount of ash altered as described previously (0H-2, 1B and 2B).

After reaching this peak the volcanic activity

tapered off and the detrital non-expanded Al 2:1 clay again became predominant over the chlorite (2A).

ORDOVICIAN BEDDING CLAY

INTRODUCTION

K-bentonite bed OH-N_1 occurs approximately 70 feet below OH-O and 15 feet below this is OH-N_2. Four samples were collected below the latter.

OH-1x - 6 feet below OH-N_2
OH-2x - 38 " " "
OH-3x - 52 " " "
OH-4x - 64 " " "

Each of these four samples were obtained from thin bands of clay, 1/32 to 1/8 of an inch wide between the bedding planes of the massive limestone. In the freshly quarried areas of the quarry it can be seen that the bedding between the massive (1 to 10 foot) layers of limestone is marked in all cases by the presence of these thin black layers of clay.

MINERALOGY

Light Minerals

Table 17 lists the relative intensities of the peaks in x-ray spectrometer patterns of the bulk samples of the bedding clays. Whereas the limestone described

previously contained only calcite, the limestone on either side of the clays contain some dolomite associated with the calcite. All four samples produce very weak albite peaks and two give quartz peaks.

TABLE 17

X-ray Spectrometer Data on Bedding Clays

	Quartz	Calcite	Dolomite	Albite	Illite	Montmorillonite
OH-1x	ww	s	m	ww	m	a
OH-2x	a	ww	ww	ww	s	m
OH-3x	ww	s	ms	ww	m	a
OH-4x	a	ww	m	ww	s	w

Under the microscope the quartz can be seen to occur as rounded detrital grains and the albite as angular, xenomorphic to idiomorphic grains with carbonate inclusions. The albite is apparently authigenic.

Heavy Minerals

The heavy minerals of samples 1x and 2x were separated and examined.

1. OH-1x - This sample of clay is from the bedding plane of the limestone approximately 90 feet below OH-0. About 95 percent of the heavy separates are aggregates of pyrite cubes.

Apatite: About 80 percent of the non-opaque minerals are apatite grains which average 0.01 to 0.02 mm. in length. They are similar to those found in the K-bentonites.

Zircon: Twenty percent of the non-opaques consist of rounded zircons, averaging 0.015 to 0.01 mm. in size.

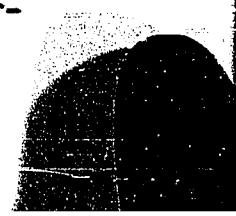
Tourmaline: A few grains of subangular, pleochroic olive to colorless tourmaline are found.

2. OH-2x - This clay is found in the bedding plane of the limestone 125 feet below OH-0. About 90 percent of the heavy separates consists of aggregates of pyrite crystals.

Zircon: About 60 percent of the non-opaques consists of colorless zircons averaging 0.02 to 0.03 mm. in size. About 90 percent of the zircons vary from hypidiomorphic to idiomorphic. Ten percent are rounded.

Biotite: 40 percent of the non-opaques are made up of light pinkish tan, sub-round to angular, rod-containing biotite which has been described previously. The average grain size is 0.08 mm., ranging up to 0.15 mm. (Figure 30).

Tourmaline: Five percent of the non-opaques consists of round, prismatic tourmalines ranging from 0.02 to 0.07 mm. in size. The crystals are pleochroic from brown to colorless and from light olive to colorless.



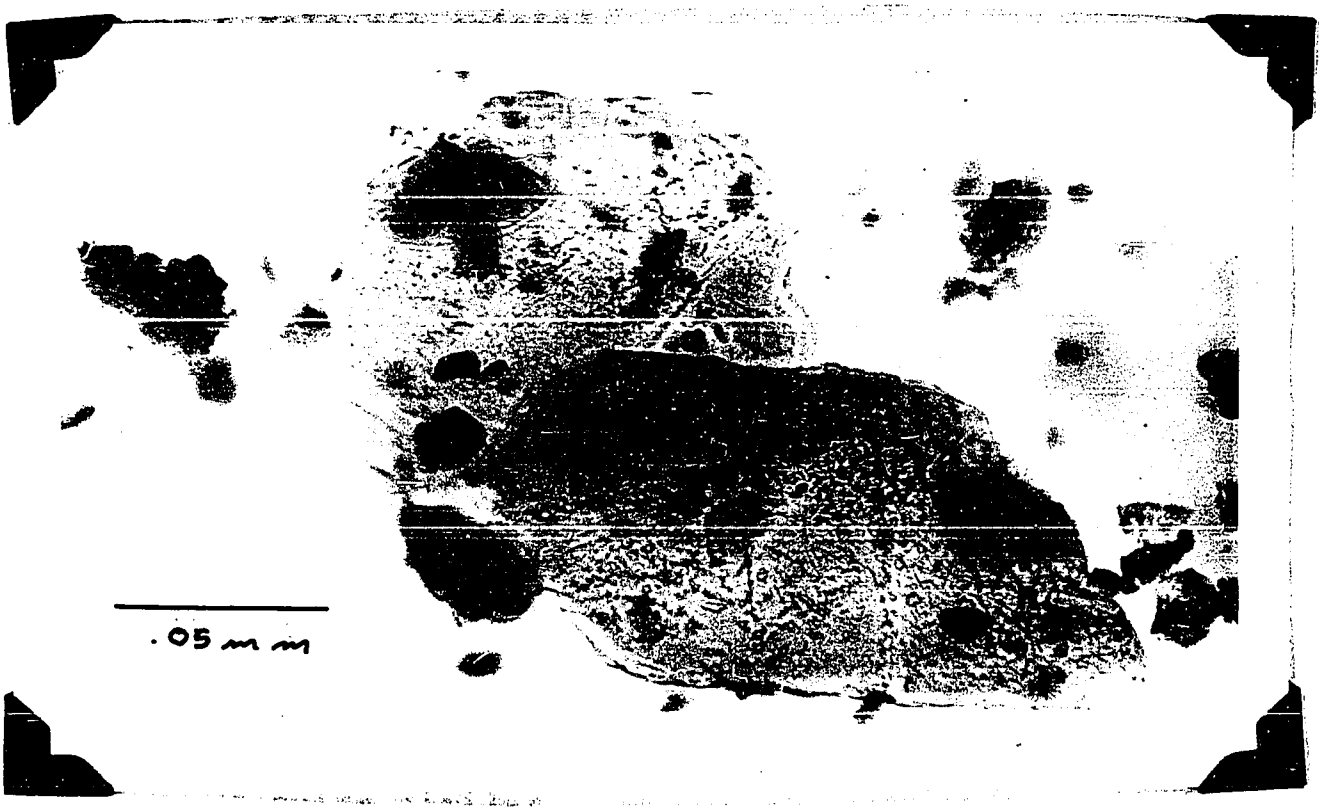


Fig. 30 - (OH-2x) Biotite flakes in heavy concentrate from a bedding clay sample. X 500

Chlorite: A few, angular, light green grains showing irregular extinction are present.

Muscovite: Several, clear, rounded flakes were found.

These two samples, six and thirty-eight feet respectively below the nearest K-bentonite bed contain approximately 10 to 20 percent of non-volcanic, water transported, non-opaque heavy minerals (assuming that the apatite has a volcanic origin).

Clay Minerals

The spectrometer patterns indicate that all samples contain a considerable amount of a non-expanded Al 2:1 clay. In addition samples 2x and 4x contain a 15 Å expanded Al 2:1 clay (the 7 Å peak is weak or missing and the 4.70 Å peak is missing).

X-ray diffraction patterns were made of the bulk clays and the less than one micron fractions after a variety of treatments, Table 18. Samples 1x and 3x, 2x and 4x were quite similar.

The bulk material of samples 1x and 3x gave x-ray diffraction patterns which contain weak to moderate lines of a non-expanded Al 2:1 clay mineral. In addition, sample 1x gave a moderate line at 14.2 Å. When this sample was heated at 600° C for 24 hours the 10 Å line was strengthened, the 14.2 Å line increased slightly in intensity and the 7.0

and 4.68 Å lines disappeared. This indicates that the clay contains minor amounts of an expanded Al 2:1 clay and chlorite.

The x-ray patterns of the less than one micron fraction indicate that it is composed largely of 10 Å illite. A very weak line occurs at 14.0 Å and is probably caused by a small amount of chlorite. The differential thermal curve of the less than one micron fraction, Figure 31 is a typical curve for a non-expanded Al 2:1 clay mineral and is similar to the curves of the non-expanded clay from the limestone residues. The broad hydroxyl-endothermal peak reaches a maximum at 600° C.

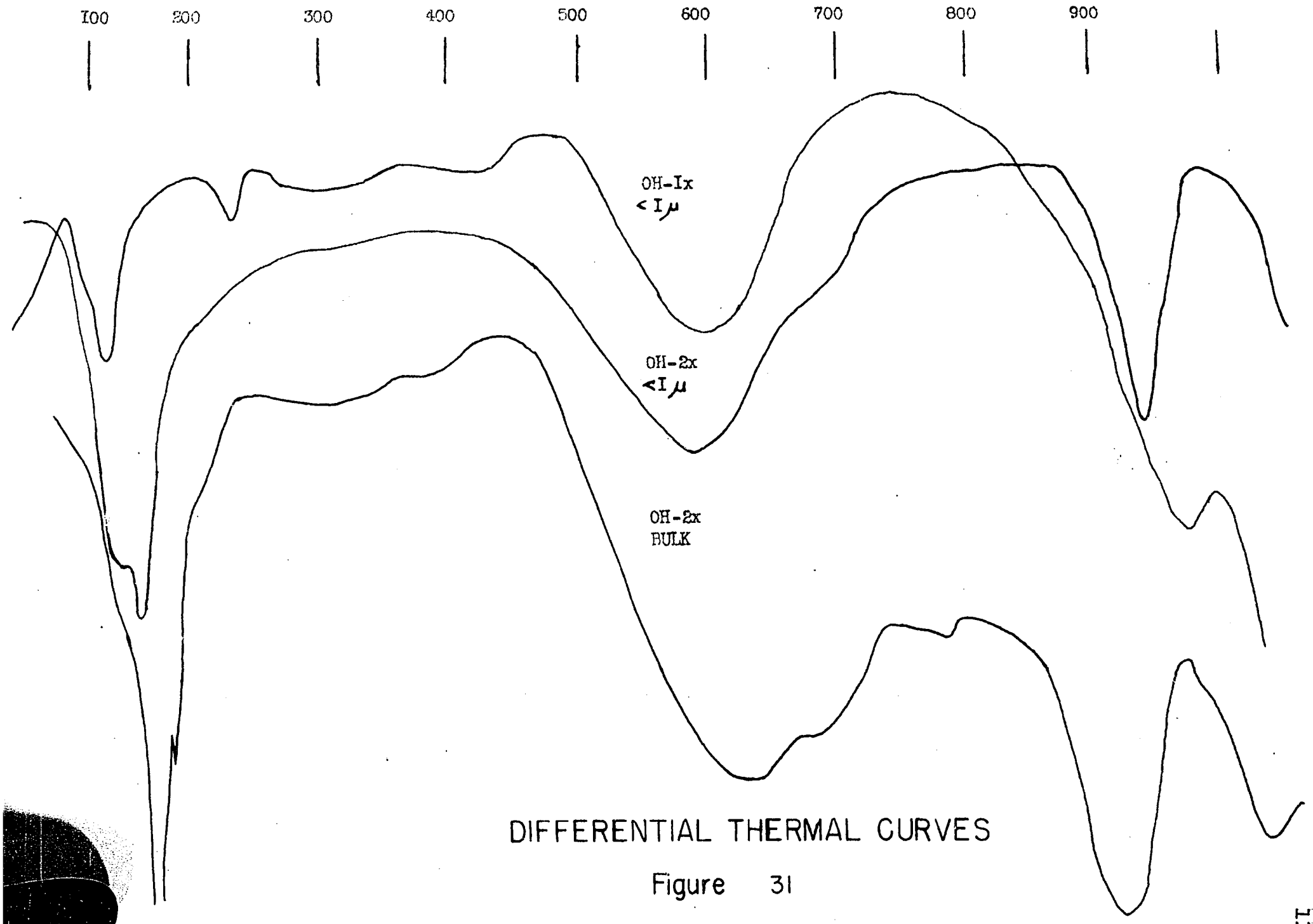
The bulk material of sample 3x apparently contains only a non-expanded Al 2:1 clay, though the pattern is quite diffuse and lines with larger d spacings are probably present.

Samples 2x and 4x contain similar clays. Both have moderate to strong x-ray patterns of a non-expanded Al 2:1 clay. The bulk material gives, in addition, a weak line at 15.1 Å which expands to 16.8 Å when treated with ethylene glycol and which almost disappears when heated to 600° C for 24 hours (the 10 Å line becomes stronger). The very weak line found at 14.8 Å after the sample was heated presumably is the result of some reabsorption by the expanded Al 2:1 clay. The less than one micron fraction produces a strong 10 Å non-expanded clay found in the bulk material.

TABLE 18

X-ray Diffraction Data on Treated Bedding Clays

OH-1x		
Bulk	14.2ww	10.0w
" 600°C-24 hrs.	14.2w	10.0m
<1μ	14.0ww	10.0s
OH-2x		
Bulk	15.1mw	10.0m
" 600°C-24 hrs.	14.8ww	10.0s
" E. glycol	16.8m	9.9m
<1μ	14.ww	10.1s
OH-3x		
Bulk		10.0m
OH-4x		
Bulk	15.1ww	10.0m



DIFFERENTIAL THERMAL CURVES

Figure 31

The differential thermal analysis curves, Figure 31, of the bulk and the less than one micron fraction of OH-2x show the typical broad non-expanded Al 2:1 clay hydroxyl-endothermal peak with a maximum at 600° C. However, in this sample, the broad peak has a second down warping at 700° C which is more pronounced in the curve of the bulk material than in that of the less than one micron fraction. This 700° C inflection is possibly caused by the expanded clay present.

ORIGIN

The smooth flat bedding plane on which this clay is found indicates that the change in deposition occurred while the limestone was still covered by water. The heavy and light minerals indicate that the clay had both a volcanic and a non-volcanic source. The non-expanded Al 2:1 clay probably had a detrital source and was derived from the surrounding rocks. The expanded Al 2:1 clay is probably authigenic and derived from volcanic ash. The 700° C hydroxyl-endothermal peak of the expanded clay is similar to the peaks for the interstratified K-bentonites and indicates a similar composition for the octahedral layers and probably for the tetrahedral layers in the mineral. There are two possible explanations for the origin of the expanded clay: (1) for some reason the ash in the bedding planes was not in contact with sufficient potassium and therefore did

not form an interstratified clay; Or (2), more likely, the ash originally formed an interstratified clay or possibly a chlorite which was later altered to an expanded clay by solutions traveling along the bedding planes.

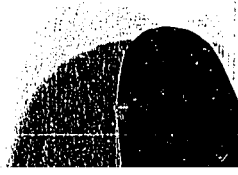
There are four possible ways in which the bedding clay could have been deposited:

1) If there was a temporary interruption of the deposition of limestone the clay and other minerals could have been deposited as water transported detritus.

2) The deposition of the limestone was interrupted but the deposition of the water transported illite and coarser minerals continued and at the same time volcanic ash was deposited from the air.

3) Deposition of the limestone was not stopped. All of the detritus could have been blown into the sea from the shore by strong windstorms in a relatively short time. Folk (1951) has shown that in the lower Ordovician a considerable portion of the detritus in the limestone was wind transported.

4) It has also been suggested that the current was sufficiently large to winnow the clay from the limestone ooze and keep it in suspension. The current, carrying a concentration of clay, eventually reached an area where it was slackened or where the pH changed and the clay deposited as a relatively pure layer.



OSWEGO AND JUNIATA GRAYWACKES

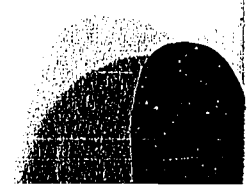
INTRODUCTION

Near State College, the Upper Ordovician contains about 800 feet of a thick-bedded, greenish-gray sandstone known as the Oswego graywacke. In the Oswego outcrop at Skytop (3 miles northwest of State College) six thin beds of pure clay were found in the coarse grained graywacke. These beds are similar in appearance to the K-bentonite beds in the middle Ordovician limestone and an investigation of several of the clays was made to determine their mineralogy and origin.

Below are listed the clay beds found at the Skytop outcrop:

Sample No.	Feet Below Juniata Shale	Thickness	Color
OS-1	200	6"	gray
2	212	1"	gray
3	227	1"	gray & yellow
4	280	2"	gray
5	296	2"	gray
6	304	6"	gray

A sample of shale (OS-7) was collected from a section of the formation approximately 370 feet below the Juniata shale. A sample of weathered, friable, fine grained sandstone (OS-8) was collected 203 feet below the Juniata. A sample of the Juniata red shale (Ju-1) was collected 100 feet above the Oswego contact.



Immediately below sample OS-5 is six inches of graywacke which contains gray, lens shaped, clay gulls one half to two inches in diameter. They comprise about five percent of the rock. These gulls are nearly pure clay which is identical in appearance with the clay in the beds.

In a fresh road cut through the Oswego near Williamsport, Pennsylvania, 60 miles northeast of State College several one to six inch beds of clay were found and samples collected. In addition it was noticed that the parallel breaks (commonly called bedding) in the coarse sandstone contain thin, one sixteenth to one quarter inch, layers of clay similar to that in the larger beds. This same thing was noticed in the Ordovician limestone. Apparently, thin clay layers deposited at irregular intervals quite commonly produce the temporary changes in lithology that result in bedding in a rock of otherwise uniform lithology.

MINERALOGY

Tuttle's (1940) study of the Oswego and Juniata graywacke showed that the average composition of the Oswego is 40 percent rock fragments (slates, phyllites, argillites, schists, etc.), 50 percent quartz grains, 10 percent clay, and from less than one to fifteen percent feldspar (albite, andesine, microcline). The Juniata is similar except for the presence of considerable iron oxide.

He found that the non-opaque heavy minerals are predominately zircon and tourmaline which vary in shape from round to angular with apatite and chlorite being fairly abundant. Leucoxene, anatase, and iron oxides are the most common opaque heavy minerals.

Heavy Minerals

The heavy minerals were separated from a sample of the clay (OS-1), the shale (OS-7), and the fine sandstone (OS-8). The heavy minerals are quite similar to those described by Tuttle. The non-opaques form 5 to 10 percent of the total heavy separate in each sample.

Zircon: The majority of the zircons are sub-round to round, colorless, and contain a few bubble inclusions. A few yellow zircons were found (Tuttle reported a few yellow grains). A few grains are hypidiomorphic.

Sample	Percent of Zircon in non-opaques
OS-1	25
OS-7	30
OS-8	85

Tourmaline: The tourmalines vary from sub-round to angular. Hypidiomorphic grains are fairly common. The majority of grains contain a few bubble inclusions. The olive and brown varieties are by far

the most abundant. Occasional, blue, gray, colorless and multicolored grains are found.

Sample	Percent of tourmaline in non-opaques
OS-1	75
OS-7	70
OS-8	15

Rutile: A few grains of yellow rutile occur in each thin section. Though the grains are usually irregular in shape a few occur as slender rods.

Muscovite: Sub-round to round flakes of muscovite are common in all samples. The flakes usually show irregular extinction.

Pyrite: Irregular pyrite aggregates form about half of the opaque minerals in samples OS-1 and OS-7.

Leucoxene: Leucoxene occurs as dull white irregular aggregates. It forms half the opaques in OS-1 and OS-7. X-ray patterns of the leucoxene yield anatase lines.

Anatase: A few idiomorphic grains of anatase occur in OS-1 and OS-7. In OS-8 it is nearly the only opaque mineral present and forms 90 percent of the total heavies. It most frequently occurs as aggregates of pale yellow, tabular, also rectangular grains. Rectangular and square grains less than one quarter of a micron in diameter can also be seen under the electron

microscope. The anatase is undoubtedly authigenic.

The light fraction of OS-1 contains a good deal of round to sub-angular muscovite. Sub-round quartz and rock fragments are abundant. Albite and microcline are common. OS-7 is similar but contains considerably more muscovite. OS-8 is composed largely of sub-round quartz and rock fragments.

Clay Minerals

X-ray spectrometer and differential thermal analysis patterns were made of the bulk clay samples. The less than one micron fraction was decanted from samples OS-1, 4, 7 and 8. Film-type x-ray diffraction, oriented x-ray spectrometer, and differential thermal analysis patterns were made of each sample. Electron micrographs were taken of both the bulk and fine fractions.

The morphology of these clays as seen in the electron micrographs is the most interesting feature noted in this study. Though a few fairly equant flakes are present in sample OS-8 most of the clay particles consist of thin laths. The majority of the laths are 0.07 of a micron wide and from 0.2 to six microns in length. Individual laths are the most common but frequently the laths are joined in a parallel arrangement to form large equant or rectangular flakes (Figure 32 and 33).

Samples OS-1 and 4 contain a few laths but are composed largely of thin, angular, sub-equant flakes (Figures 34 and 35). Sample OS-7 has a predominance of thin, sub-

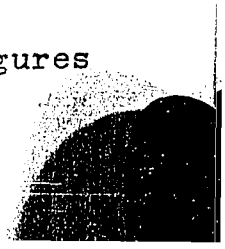


Fig. 32 - (OS-8) Lath shaped particles of a non-expanded Al 2:1 clay mineral occurring in the less than one micron fraction of a fine grained Oswego sandstone sample. X 24,000

Fig. 33 - (OS-8) Lath shaped particles of a non-expanded Al 2:1 clay mineral occurring in the less than one micron fraction of a fine grained Oswego sandstone sample. X 24,000

Fig. 34 - (OS-1) The less than one micron fraction from an Oswego clay bed. X 18,000

Fig. 35 - (OS-4) The less than one micron fraction from an Oswego clay bed. X 18,000

Fig. 36 - (OS-7) The less than one micron fraction of an Oswego shale sample. This picture shows flakes of a non-expanded Al 2:1 clay mineral and tubes of halloysite. X 38,000

equant flakes but it also has many lath shaped particles. Here the laths are not as thin as in OS-8 and the length to width ratio is only about 4:1 (Figure 36). In addition electron micrographs of OS-7 show numerous halloysite tubes. These tubes are well developed and evidence of the hollow center can be observed. The tube in tube arrangement and partially unrolled tybes can also be seen (Bates, Hildebrand and Swineford, 1950).

Sample Ju-1 is composed of thin, angular, sub-equant flakes. Neither laths nor tubes were seen (Figure 37).

The d spacings of the less than one micron fraction of all five clays are nearly identical to those listed by Grim, Bray and Bradley (1937) for illite. Table 19 lists the d values for the lath shaped clay in sample OS-8. The values obtained from the other four clays are the same except that they contain weak lines at 3.2 Å and at 2.97 Å. The similarity of the d values and intensities of the x-ray reflections of the lath shaped clay to those of the non-expanded Al 2:1 clay suggest that the clay has a non-expanded 2:1 structure. X-ray spectrometer patterns of oriented slides of OS-8 show the same (001) periodicity and intensity as in the non-expanded Al 2:1 clays and thus indicate that the "c" axis is perpendicular or nearly perpendicular to the planes of the laths. The oriented patterns also contain a broad, very weak peak at approximately 7.2 Å which is probably caused by a small amount of kaolinite. As no halloysite tubes were seen in the electron micrographs it is likely that the sub-equant flakes are kaolinite.

The less than one micron fraction of Ju-1 gives a strong non-expanded Al 2:1 clay x-ray pattern identical with those of the Oswego clays. In addition, there is a very weak line with a spacing of about 14 Å. The x-ray diffraction pattern of the bulk sample Ju-1, in addition to the non-expanded clay lines, has a moderately strong series of lines, 14.0, 7.0, 4.68, 3.50, which indicates the presence of considerable chlorite in the coarser fraction.

Differential thermal analysis curves of the less than one micron fraction of samples OS-1, 4, 7, and 8 are shown on Figure 38. Samples OS-1 and 4 give typical non-expanded Al 2:1 clay curves with a weak endothermal peak at 125° C, a broad endothermal peak with a maximum at 630-650° C - a little higher than most non-expanded Al 2:1 clays - and a final endothermal peak at 970° C followed by a weak exothermal peak at 1000° C.

The curve of OS-7 has no 125° C endothermal peak as the low temperature water was driven off before the pattern was run. However, it has the broad 630-650° C, endothermal peak found in OS-1 and 4, but in this pattern an additional sharp peak is found at 580° C extending below the broad peak. This 580° C peak is probably caused by the small amount of halloysite in the sample.

Sample OS-8, which is composed largely of laths, gives a differential thermal curve similar to those for the non-expanded Al 2:1 clays in many respects. It has a very

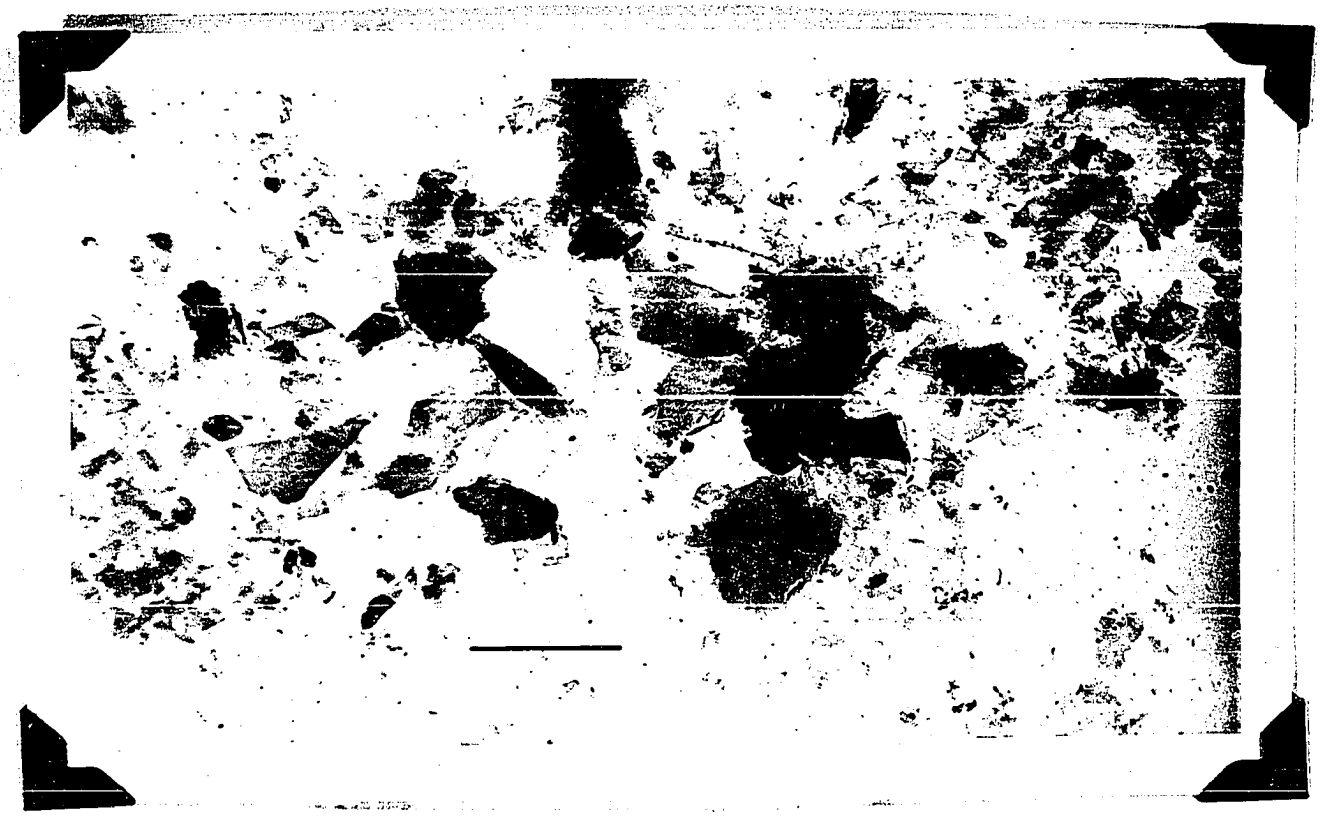


Fig. 37 - (Ju-1) The less than one micron fraction of a sample of Juniata shale. X 18,000

TABLE 19

X-ray Data on OS-8

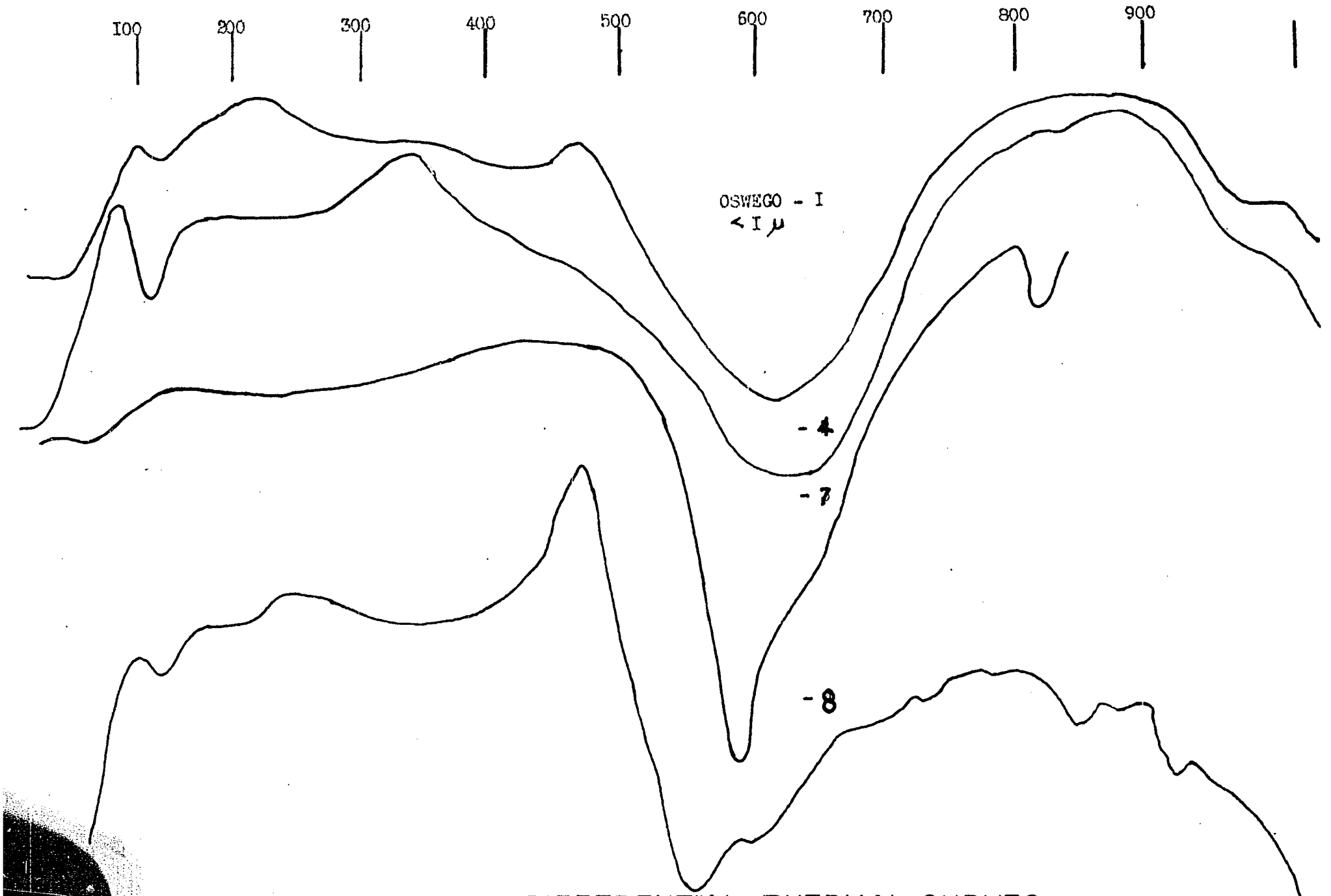
d in Å	I
10.0	s
4.9	w
4.45	s
4.29	ww
3.7	ww
3.5	ww
3.32	m
3.05	w
2.82	w
2.56	s
2.44	w
2.37	m
2.24	m
2.19	w
2.13	w
1.98	s
1.94	ww
1.65	m
1.66-1.62	w
1.49	s
1.33-1.34	w
1.294	m
1.240	w

weak endothermal peak at 120° C. A moderate exothermal peak which occurs at 470° C is probably caused by either pyrite or organic material. Following this peak is a broad double endothermal peak extending from 500° C to 700° C with maximums at 550° C and 600° C. The 550° C peak is probably caused by the small amount of kaolinite which was detected in the x-ray patterns. At 600° C is the apex of the broad non-expanded clay hydroxyl-endothermal peak. The high temperature endothermal and exothermal peaks are not pronounced but there is evidence of a slight endothermal reaction at 920° C.

The curve of sample OS-8 is strikingly similar to that for celadonite (Grim and Rowland (1942)). In both cases the low temperature side of the 600° C hydroxyl-endothermal peak is much steeper than the high temperature side. Both have weak 120° C and 920° C endothermal peaks.

The differential thermal curve for the less than one micron fraction of Ju-1, Figure 39, is nearly identical with those for OS-1 and 4. In Ju-1 the hydroxyl-endothermal peak is slightly lower, occurring at 600° C. The lower temperature of the apex of this peak may be caused by the small amount of chlorite in the sample.

The Oswego clay from Williamsport gives a good non-expanded Al 2:1 clay x-ray spectrometer pattern and differential thermal curves, Figure 39, similar to those for OS-1 and 4. The slight inflection at 590° C is probably caused by the presence of a small amount of kaolinite or halloysite.



DIFFERENTIAL THERMAL CURVES

Figure 38

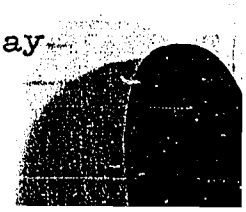
The reason that the Oswego non-expanded Al 2:1 clay develops in the form of laths is not known at present. Some chemical data will be needed before the reason for the lath structure can be discovered.

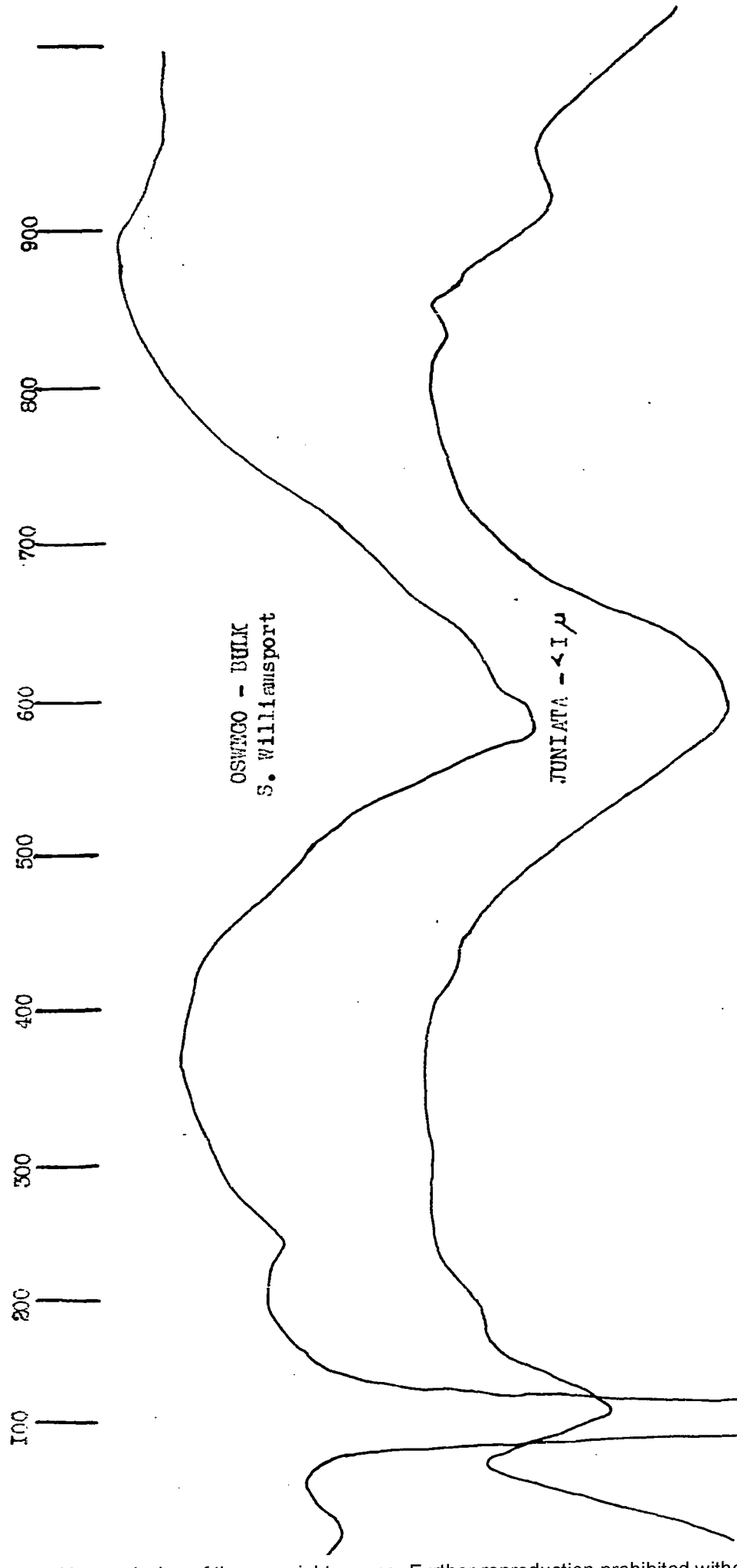
The predominant growth along one axis is most likely caused by a directional strain in the mineral lattice caused by the inequality in size between the octahedral layer and the two tetrahedral layers. Whereas a similar misfit in the 1:1 lattice causes curved plates and in many cases tubes, here the misfit layer is sandwiched on both sides by layers of equal size which prevent curling of the lattice but does not relieve the strain.

ORIGIN

The examination of the heavy and light minerals revealed no trace of the common volcanic minerals. The heavy minerals are similar to those of the coarser grained Oswego and Juniata graywacke. It is concluded therefore that the clay had the same source area as the coarser material and is detrital in origin.

The concentration of the clay into relatively pure layers one to six inches thick is possibly caused by a winnowing of the clay from the coarser sand by wave action. Ocean currents would carry the clay away in suspension until calmer water were reached and it would then be deposited for varying lengths of time until the current became strong enough to include silt and sand grains in its load. The thin clay-





DIFFERENTIAL THERMAL CURVES

Figure 39

layers between the bedding planes were probably deposited by a similar process during a much shorter period of time.

DEVONIAN CLAYS

INTRODUCTION

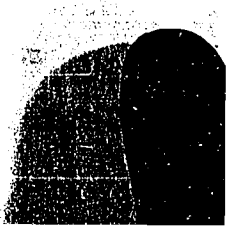
Ebright, Fettke and Ingham (1949) have described a clay bed overlying the middle Devonian Onondaga limestone which Fettke has called the Tioga bentonite. This clay has not been found as an outcrop but is commonly found in oil and gas drill holes throughout western and central Pennsylvania. The particular sample used in this study was obtained from Dr. R. E. Bayles of the Peoples Natural Gas Company of Pittsburgh. The sample is from the New York State Natural Gas Corporation's Well No. N-188 on the R. P. Daugherty farm, Leidy Township, Clinton County, Pennsylvania. The sample was collected at a depth of 6074 - 6077 feet.

An Upper Devonian sample was collected from a two inch bed of pure clay in the Chemung formation. This bed was found in the shaft of an abandoned silver mine about five miles northeast of Jersey Shore, Pennsylvania.

MINERALOGY

Heavy Minerals

The heavy minerals of the Daugherty sample con-



sist of about 94 percent of pyrite mostly in the form of aggregates of cubes and octahedrons. Striations are common. The non-opaques contain approximately 50 percent apatite. About half of the apatite is idiomorphic, some of it with slight irregularies caused by incipient rounding. A quarter of the apatite consists of large idiomorphic to hypidiomorphic grains.

35 percent of the non-opaques are zircons which vary from idiomorphic to hypidiomorphic. Five percent consists of biotite flakes. The flakes vary from xenomorphic, sub-angular to idiomorphic. The biotite is a light pinkish brown and contains abundant rod-shaped inclusions. The idiomorphism, color and inclusions are the same as those of volcanic biotite from the Ordovician.

Approximately 10 to 15 percent of the non-opaques consists of hypidiomorphic to xenomorphic grains of clinozoisite (colorless, index approximately 1.7, biaxial positive, interference colors anomalous middle first order, parallel extinction).

90 percent of the non-opaque heavy minerals from the Jersey Shore clay are hypidiomorphic to idiomorphic apatite grains averaging 0.04 mm. in length. The remaining 10 percent consists of sub-angular zircon, light tan biotite flakes and a few grains of colorless to olive tourmaline. Six inches above this bed of clay is a thin, one quarter of an inch, mica bed consisting of 85 percent light pinkish brown, rod-containing biotite, 10 percent of clear muscovite, and 5 percent of a grass-green chlorite. The flakes average from 0.2-0.3 mm. in diameter and vary from sub-round to sub-angular

In many cases the biotite flakes contain large, light green patches, particularly around the edges, which may indicate some leaching of the iron from the biotite.

Clay Minerals

Table 20 lists the (001) x-ray diffraction values of the bulk Daugherty clay after various treatments. The untreated material gives a fairly wide, strong line at 10.2 Å and a very weak line at 10.0 Å. When the material is treated with $CaCl_2$ three lines are obtained: 11.0 Å strong, 10.0 Å strong, and 10.0 Å very weak. The 11.0 Å line is apparently due to interstratified material similar to that of the Ordovician K-bentonites where a value of 10.8-10.9 Å was obtained. The 10.0 Å line is due to a non-expanded Al 2:1 clay. (The second order reflections also indicate two clay types). A value of 5.05 Å $(\frac{002}{003})$ was obtained for the interstratified clay and 4.94 Å (002) for the non-expanded Al 2:1 clay. When the material is heated to 600° C for 24 hours the very weak 14.0 Å, (001) line shifts to 13.4 Å and becomes stronger. The (002) and (003) lines become much weaker. This indicates that the 14.0 Å clay is chlorite.

The Jersey Shore bulk clay, Table 20, gives a strong x-ray diffraction pattern of a non-expanded Al 2:1 clay and a weak pattern of chlorite. The typical change in the chlorite pattern was obtained when the material was heated at 600° C for 24 hours. When the material was treated with $CaCl_2$ no change in 001 spacing was observed.

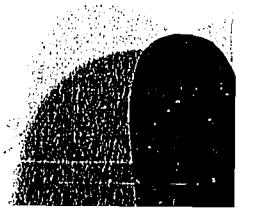


TABLE 20

X-ray Data on Devonian Clays

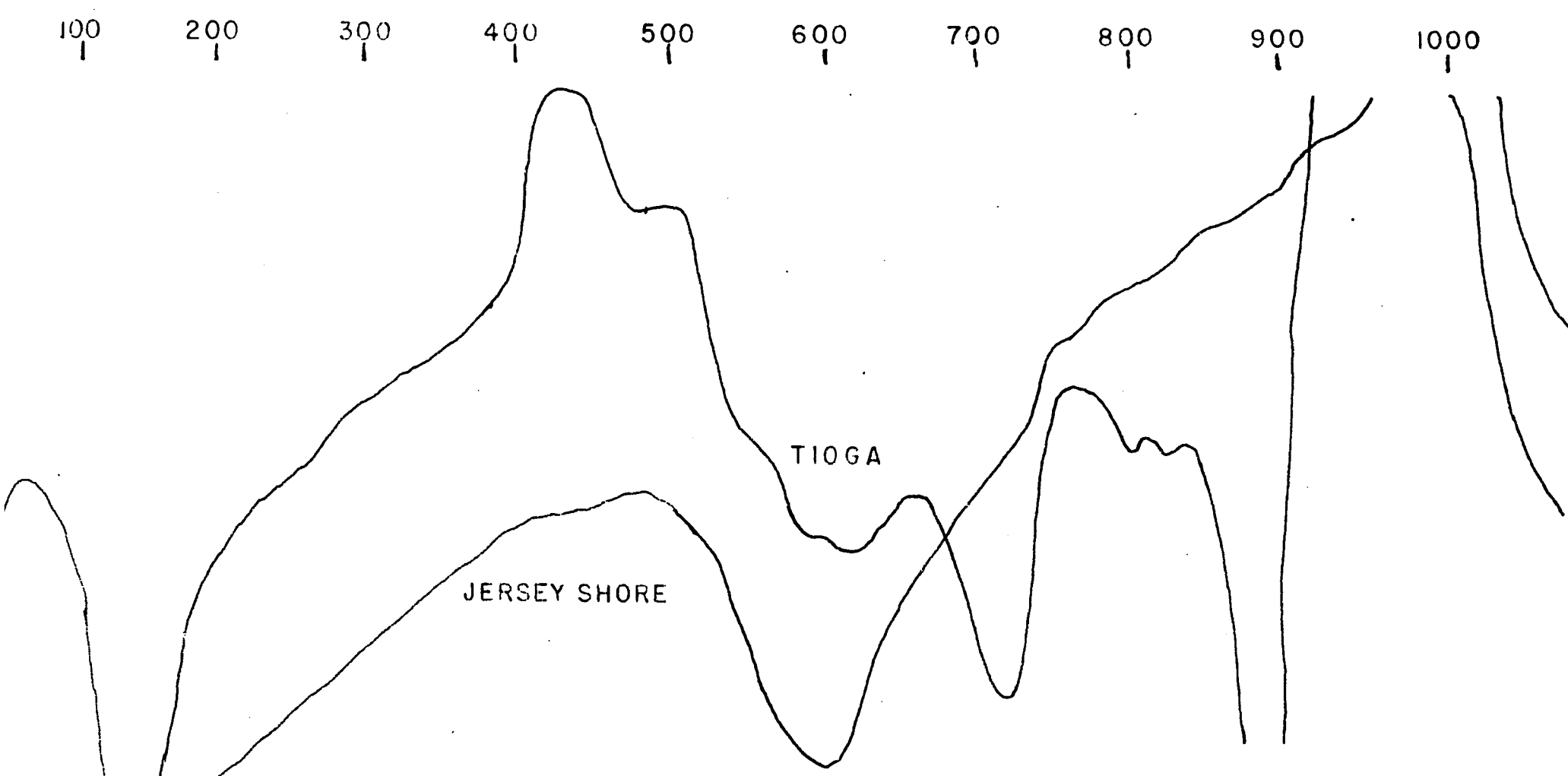
	Daugherty (Tioga Bentonite)			
	d in Å	I	d in Å	I
Bulk	10.2	s		
Untreated	10.2	s	14.0	ww
Cleaned	10.3	s	14.0	ww
$CaCl_2$	11.0	s	14.0	ww
600° C-24 hrs.	10.0	s	13.4	w
	Jersey Shore			
Untreated	10.0		14.0	w
$CaCl_2$	10.0		13.8	wm
600° C-24 hrs.	10.0		14.0	w

Figure 40 shows the differential thermal analysis curves of the two clays. The Daugherty clay has an exothermal peak at 425-525°C probably due to organic matter and pyrite and a strong exothermal peak at 900°C due to calcite. The curve contains the double hydroxyl-endothermal peaks which were found in many of the Ordovician K-bentonites. The 600°C peak, which was assigned to chlorite in the K-bentonites, is considerably broader than the pure chlorite peak. This is due to the presence of appreciable non-expanded Al 2:1 clay in the sample. The 730°C peak is typical of those obtained in the K-bentonites for the interstratified expanded and non-expanded Al tetoctrite. The Jersey Shore clay has a 600°C hydroxyl-endothermal peak which is typical of non-expanded Al 2:1 clays in this study. The chlorite peak apparently overlaps this peak.

Electron micrographs of the Tioga bentonite contain discrete flakes similar to the Ordovician K-bentonite (Fig. 41).

ORIGIN

On the basis of the heavy minerals it is possible that the Tioga K-bentonite was derived from volcanic ash. The idiomorphic apatite and probably the larger grains of apatite are suggestive of volcanic phenocrysts as are the idiomorphic zircon grains and biotite flakes. The origin of the round apatite, zircon and clinozoisite is in doubt but they probably came from the surrounding sediments and did not have a volcanic source. The mineralogy of the clay minerals i.e. chlorite and interstratified expanded and non-expanded Al 2:1 layers, indicates a close similarity in composition and



DIFFERENTIAL THERMAL CURVES

Figure 40

Fig. 41 Unfractionated sample of Tioga K-bentonite.

X 24,000

structure to that of the clay minerals of the K-bentonites of the Ordovician and suggests that the original ash may have been of a similar composition. It is believed that the non-expanded Al 2:1 clay in this material had a non-volcanic, detrital source and came from chips of the surrounding limestone and shale which contaminated the sample. However, it is possible that this material fixed more potassium than did the Ordovician K-bentonites and formed large packets of non-expanded layers.

The presence of apatite and biotite in the Jersey Shore clay suggests that at least part of the material is volcanic. It is likely that the chlorite was derived from the volcanic ash and the predominant non-expanded Al 2:1 clay, together with the zircons and tourmalines, had a non-volcanic detrital source.

The clay bed and the thin mica bed were probably concentrated by a winnowing of the associated graywackes.

This material may be related to the bentonite found by Hass (1948) in Upper Devonian Chattanooga shale of Tennessee. This bentonite contains 30 percent of biotite and the clay was considered by the above mentioned author to be similar to that in the Ordovician K-bentonite.

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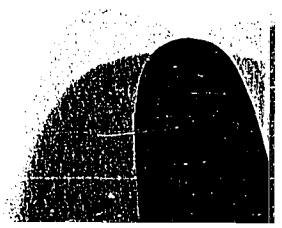

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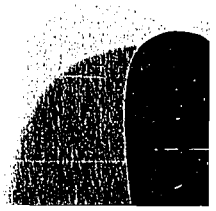

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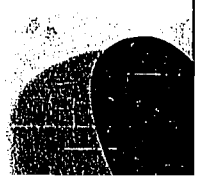

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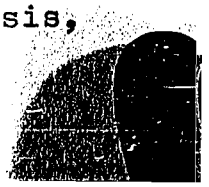

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