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CLAY MINERALOGY OF PRE-COLDWATER
(MISSISSIPPIAN) ARGILLACEOUS SEDIMENTS
IN THE STATE-FOSTER NUMBER 1 WELL,
OGEMAW COUNTY, MICHIGAN

presented by

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CLAY MINERALOGY OF PRE-COLDWATER (MISSISSIPPIAN) ARGILLACEOUS SEDIMENTS IN THE STATE-FOSTER NUMBER 1 WELL, OGEMAW COUNTY, MICHIGAN

By

Ronald P. Nowak

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ABSTRACT

CLAY MINERALOGY OF PRE-COLDWATER (MISSISSIPPIAN) ARGILLACEOUS SEDIMENTS IN THE STATE-FOSTER NUMBER 1 WELL, OGEMAW COUNTY, MICHIGAN

By

Ronald P. Nowak

A study of the clay mineralogy and alterations from shale horizons was undertaken from the State-Foster Well in the Michigan Basin. The Foster Well with shale units occurring at intervals from 6,000 to 10,000 feet, was chosen based upon criteria from previous work in the Gulf Coast, which showed alterations occurring at these depths.

The clay mineralogy was determined from shales representing the Antrim, Bell, Salina Group, Utica, Glenwood and Upper Cambrian which showed a lack of discrete montmorillonite in all samples. Only traces of other "expanding clays" occurred in all but one sample. Higher feldspar content was present in Upper Cambrian samples. Comparisons between the predominant clay minerals, illite, chlorite and kaolinite showed suggestive evidence of both diagenetic and detrital origin. Detrital origin may be detected by a similar clay mineralogy in the Antrim, Bell, Utica and Glenwood which also corresponds to orogenic activity in the Appalachian region.

ACKNOWLEDGMENTS

The author would like to thank and express his sincere gratitude to Dr. Chilton E. Prouty for his many hours of assistance and professional guidance in completing this problem. Many thanks are extended to Dr. A.T. Cross and Dr. M.M. Mortland for their suggestions and constructive criticism in preparation of the manuscript.

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INTRODUCTION

Purpose and Scope

In previous years, a number of studies have been made to explain the alteration of clay minerals in relation to various conditions and environments. Until recently little attention has been applied to alterations resulting from deep burial, especially as to the role of compaction. From previous studies, explanations for alterations include geologic age, geothermal gradient, chemistry of pore solutions, overburden pressures as well as source material. The role of temperature has been discussed as a primary factor in recent literature (Price, 1976; Burst, 1969).

The primary purpose of this study is to analyze the shale units that occur in one well in the Michigan Basin. The clay mineralogy of each unit is to be determined in hopes of detecting any vertical alterations that may occur. With much of the study of deep-burial alterations having been made in the Gulf Coast area, a comparison of the Michigan Basin data to these models may indicate interesting comparisons, or contrasts, in the sedimentary columns of the two areas.

Shales of the Antrim, Traverse (Bell), shale interbeds in the Salina, Richmond (Utica), Glenwood, and shale partings from Upper Cambrian (Figure 3) were representative units sampled from the Paleozoic Section in the Michigan Basin.

The State-Foster No. 1 Well was chosen to be used in the study based upon criteria from previous studies. Powers (1967) and Burst (1969) indicated that clay mineral alteration begins at depths of 6,000 feet and continues to depths of around 10,000 feet. The State-Foster Well is the only available well in the Michigan Basin which has shale occurring at these depths.

Location of Well

The State-Foster No. 1 Well, a dry hole, was drilled in the SW¼, SE¼, SE¼, Section 28 - T24N - R2E, Ogemaw County. It is located 330 feet from the south line and 990 feet from the east line of the quarter section (Figure 1).

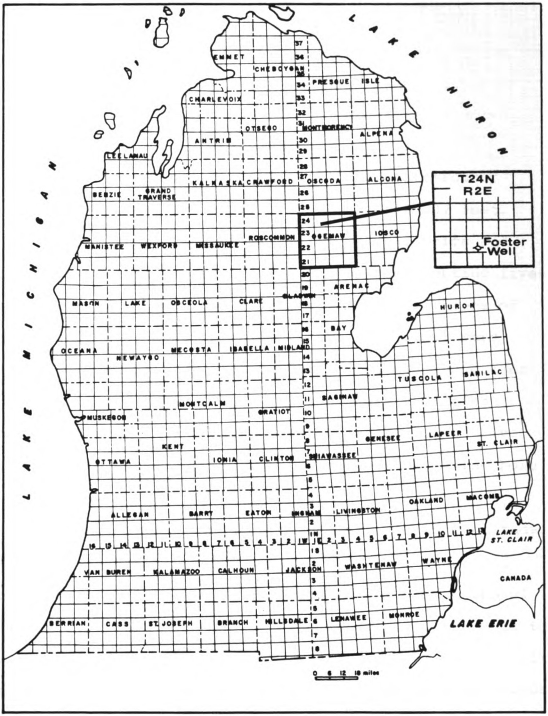


Figure 1. Location of State-Foster No. 1 Well

METHOD OF INVESTIGATION

Sampling Method

The total sampling interval in the State-Foster No. 1 Well represented a depth of 1790 to 12,707 feet. Forty-two samples from Antrim, Bell, Salina, Utica and Glenwood were taken from drilling chips representing five-foot intervals. The top, middle and bottom portions of each continuous shale unit (Antrim, Bell, Utica) were sampled. The shales of the Salina and Glenwood occur as interbeds and were sampled at points where sufficient amounts of shale are present in drilling samples. Five samples were extracted from the cored portion of the hole which represents the Upper Cambrian (Table 1).

The Antrim shale was the youngest unit in the study. All Michigan Basin Paleozoic sediments older than, and including, the Antrim were deposited under conditions of similar structural form, with depocenters (Figure 2) in the same general area, Saginaw Bay (Prouty, 1971). The results of this study could be compared to the results of previous work on the clay mineral suite of the Antrim shale (Asseez, 1967). The total depth of the State-Foster Well was 12,989 feet which is probably within the Mount Simon Formation (Kashfi, 1967). This is the oldest rock unit included in

Table 1. Sample Horizons from the State-Foster No. 1 Well

GEOLOGIC AGE	TYPE SAMPLE	Sample Horizon	Sample Number and Average Depth In Hole From Surface		Lithologic Identification
DEVONIAN	SAMPLES FROM DRILLING CHIPS	Antrim Shale	At-1 At-2 At-3	1790'	Shale, dark gray to gray, slightly pyritic, micaceous
			Am-4 Am-5 Am-6	1980'	Shale, dark gray to gray, some greenish gray, slightly pyritic
			Ab-7 Ab-8 Ab-9	2165'	Shale, dark gray to gray, some pyrite; some brownish-gray limestone
		Bell Shale	Bt-1 Bt-2 Bt-3	2880'	Shale, gray to greenish gray, interbedded with buff to brown limestone, fossiliferous
			Bm-4 Bm-5 Bm-6	2920'	Shale, gray to greenish gray, interbedded with buff to brown medium-crystalline limestone, fossiliferous
			Bb-7 Bb-8 Bb-9	2960'	Shale, gray, finely micaceous with buff limestone
SILURIAN		Salina	S-1 S-2 S-3 S-4	5860'	Dolomite, buff, microcrystalline; some anhydrite, brownish-gray; shale, red with some green
			S-5 S-6 S-7 S-8	7030' ---- 7065'	Shale, gray to green, some dolomite; salt, clear (contamination?)
ORDOVICIAN		Utica Shale	Ut-1 Ut-2 Ut-3 Ut-4	9440'	Shale, gray to greenish gray, calcareous; limestone, buff
			Um-5 Um-6 Um-7 Um-8	9600'	Shale, gray, slightly calcareous; interbedded with buff-brown; limestone, fossiliferous
			Ub-9 Ub-10 Ub-11 Ub-12	9765'	Shale, gray, slightly calcareous; some limestone, buff to brown, medium crystalline
		Glenwood	G-1 G-2 G-3 G-4	10,430'	Dolomite, gray to black, interbedded with black shale, carbonaceous; slight trace of quartz, subangular
	SAMPLES FROM CORE	Upper Cambrian	C-1	11,643'	Shale, black to gray, dolomite pyritic
CAMBRIAN			C-2	11,823'	Shale, black, micaceous, dolomite
			C-3	12,114'	Shale, black, micaceous, some dolomite, black
			C-4	12,553'	Shale, gray to dark gray, micaceous in part
			C-5	12,707'	Shale, gray to dark gray, micaceous, pyritic

this study.

Preparation of Samples for Analysis

After collection of samples, a series of pretreatments were completed to prepare the samples for x-ray analysis. A method was utilized after Dr. Max Mortland (Department of Soil Science and Department of Geology, Michigan State University). The process makes possible the removal of soluble salts and carbonates, organic matter and free iron oxides with little risk of altering or destroying the clay structures. After completion of pretreatment, the clay fraction of each sample was removed by fractionation.

Removal of carbonates and salts: The removal of carbonates and salts deterred flocculation by any of the physical and chemical properties present. The presence of carbonate cements could cause sample loss during fractionation.

To remove the salts and carbonates, the samples were treated with 1N sodium acetate, buffered to a slightly acidic solution (pH 5). With additional heat application, the digestion of the carbonates and salts occurred.

Removal of organics: The removal of organics was necessary to aid in complete dispersion of clays in the fractionation procedure. Also, the presence of organics on clay particles may cause a "masking effect" which reduces the intensity of the x-ray peak.

Treatment with thirty percent hydrogen peroxide and heat digested the organics present. The process also dissolved any pyrolusite (MnO_2) that was present.

Removal of iron oxides: The removal of iron oxides was critical because they act as cementing agents. They also may decrease the sensitivity of x-ray analysis.

Two steps were utilized for treatment of iron oxides. First, .3N sodium citrate and 1N sodium bicarbonate were added to keep iron in solution and prevent precipitation of FeS. The bicarbonate was used to maintain neutrality in the reaction and prevent removal of structural iron. Secondly, after heating to 80°C, sodium hydrosulfite was added which reduced all iron to Fe^{2+}.

Fractionation: The separation of the clay fraction from the sample was accomplished by gravity sedimentation. With the removal of all carbonates, salts, and iron oxides, the samples were placed in a sedimentation cylinder and filled with distilled water. The samples were stirred vigorously for a recorded length of time and allowed to settle. The size fraction of <2μ was collected by siphoning off the top 10 centimeters of material. This was repeated three times for each sample

Slide preparation for x-ray: A portion of the clay suspension material was removed and excess salts removed by washing with water and alcohol. The clay suspension was oriented on a porous plate by placing the plate in a holder on top of a vacuum flask. The clay suspension was poured into the holder and the liquid removed through the porous plate by the vacuum. This resulted in an oriented Z-direction sample which could be further treated for mineral identification. (Refer to Appendix II for detailed sample preparation guide.)

X-ray analysis: All samples were x-rayed to determine the clay mineral species present. A General Electric X-ray Diffractometer with iron tube from Michigan State University Geology Department was utilized until a mechanical breakdown occurred. Work was finished on a Phillip Norelco unit with copper tube from Central Michigan University Geology Department. According to Mortland (1978), it was considered the discrepancy would not be critical as results of the clay minerals present were in relative proportions of their (001) peaks.

TECTONIC FRAMEWORK OF THE MICHIGAN BASIN

Regional Setting of the Michigan Basin

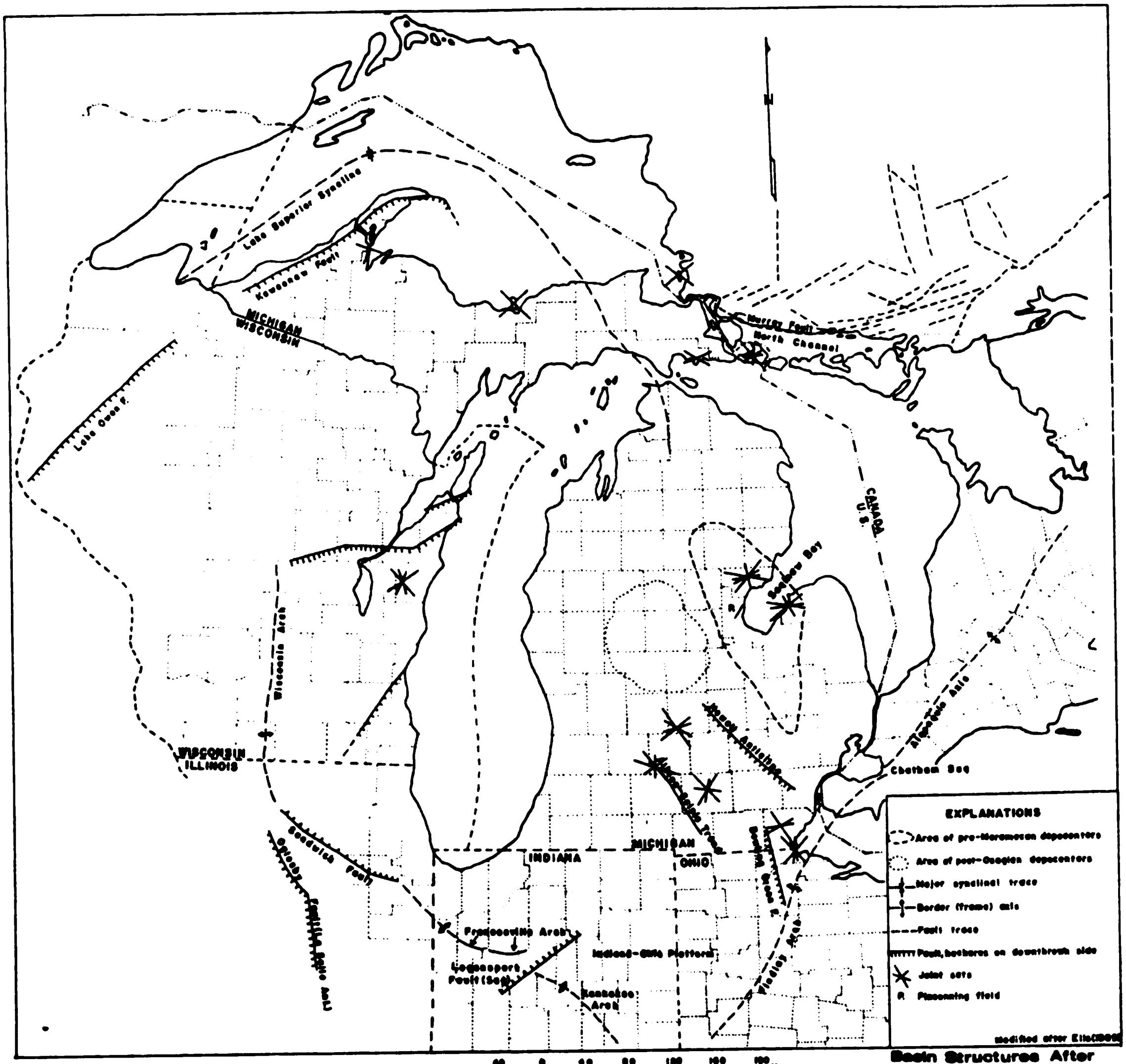
The Michigan Basin is a roughly circular structural depression referred to as an autogeosyncline (Kay, 1951) or an intracratonic basin. It encompasses the Southern Peninsula of Michigan, part of the Northern Peninsula, eastern Wisconsin, northern Illinois, northern Indiana and northwestern Ohio. Its present center is located near the center of southern Michigan.

The Canadian Shield, which extends through northern Ontario, forms the northern boundary of the Basin. Large arches surround the Basin elsewhere with the Wisconsin Arch to the west, Algonquin Arch to the east and southeast, Findlay Arch to the southeast and the Kankakee Arch to the southwest. The Kankakee and Findlay Arches are considered to be western and eastern bifurcations of the Cincinnati Arch.

The Canadian Shield is of Precambrian origin. The Kankakee, Findlay and Wisconsin Arches are thought to be Upper Cambrian (Cohee, 1948). These structural features have been considered critical factors in the formation of the Michigan Basin.

The origin of the Basin has been a disputed subject for many years. Newcombe (1933) thought the northwest elongation of the Basin along with northwest trending anticlinal structures were related to forces from a northwest direction. Pirtle (1932) believed that the origin of the Basin was a response to sediment load and that fold trends were related to weaknesses in the basement rocks. Using regional gravity and magnetic data of Michigan, Hinze (1963) proposed the Basin originated from isostatic sinking in response to the added mass of Keweenawan basic rocks in the basement complex.

It has been recognized that intrabasinal structures display two major directional trends; one trending northwest-southeast (dominant) and the other northeast-southwest. The northwest-southeast trends are more pronounced and widespread in the eastern, southeastern and central portions of the Southern Peninsula. The northeast-southwest trends were noted in the southwest part of the State. Some north-south and east-west trends are recognized in the Basin. Prouty (Figure 2) shows a composite of structural axes in the Michigan Basin.



MAJOR STRUCTURAL TRENDS—MICHIGAN BASIN AND ENVIRONS

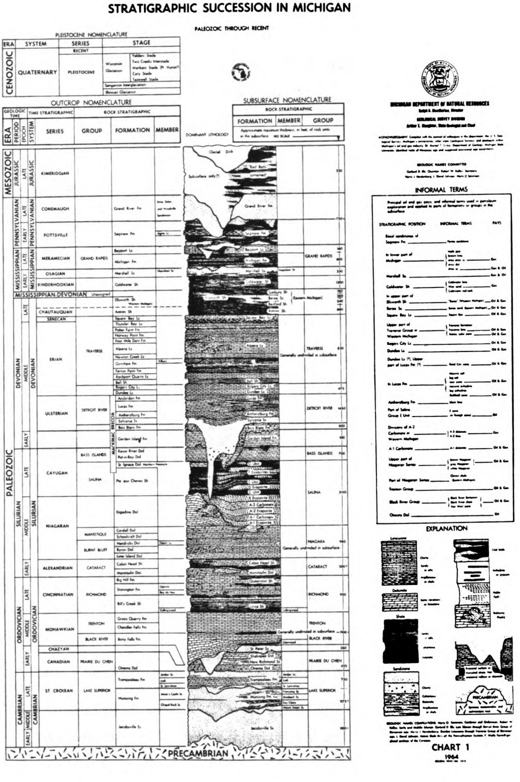
Basin Structures After Prouty (1971)

Figure 2

STRATIGRAPHY

In the Southern Peninsula of Michigan, a sequence of sediments up to 15,000 feet thick overlies Precambrian rocks. All the rocks above Precambrian are Paleozoic in age, excluding the Pleistocene glacial drift and the Late Jurassic "Red Beds." The Paleozoic rocks are considered to be mostly marine, except for the Pennsylvanian which is thought to be terrestrial-marine sequences (cyclothems).

The following stratigraphic description covers the general composition of the rocks of the Lower Paleozoic system in the Southern Peninsula of Michigan. Primary emphasis in this study is placed on the fine clastic sediments (mostly shales but some argillaceous carbonates). The general description is given here from the youngest to oldest, contrary to usual stratigraphic order of consideration, in order to conform to this study of the sequence of changes in clay mineralogy identifiable with increasing depth. The source direction and distance of transport of the sediments in the shale formations involved are of possible significance to the problem and will be mentioned in this regard as they are encountered. Reference to Figure 3, the general stratigraphic column for Michigan, may be helpful.



STRATIGRAPHIC SUCCESSION IN MICHIGAN

PALEOZOIC THROUGH RECENT

Figure 3.

Devonian-Mississippian Contact Zone

The Upper Devonian stratigraphic sequence in the Michigan Basin has been extensively discussed in the literature with much of the work focused on the position of the Devonian-Mississippian contact.

The undifferentiated Mississippian-Devonian sequence includes in descending order, the Sunbury shale, the Ellsworth formation and the Antrim shale in western Michigan; and Sunbury shale, Berea sandstone, Bedford shale and Antrim Shale in eastern Michigan. The Mississippian-Devonian boundary probably occurs at the top of the Bedford shale based on land plants (Cross and Hoskins, 1952) and the upper part of the Ellsworth shale.

The Antrim, the youngest unit sampled in the State-Foster Well, is a fissile carbonaceous shale sequence. It usually is black in color and displays some interbedding with shales dark gray to dark brown in color. The Antrim's dark color is attributed to its high organic content and is considered a portion of a widespread carbonaceous shale body throughout the central states. The most likely source for the shale is the Appalachian orogenic belt to the east. It is probably a westward extension and offshore facies of the Catskill Alluvial Plain.

The Bedford-Berea sequence is a clastic wedge (Asseez, 1967) composed of gray silty to sandy shale and fine-grained quartz sandstone, respectively. The sequence is generally restricted to the eastern portion of the Michigan Basin and is a part of a delta complex built by a stream system from the northeast, likely the northern Appalachian orogenic belt (Pepper, et al., 1954).

The Ellsworth shale, typically a grayish-green to greenish-gray argillaceous shale, is restricted to the west side of Michigan. It appears to be a time and facies equivalent of the Upper Antrim and Bedford-Berea sequence. The distribution of the Ellsworth, which thins from the west to its disappearance along a north/south line in central Michigan, indicates a source peripheral to the Michigan Basin on the west. It does not reach Ogemaw County and the Foster Well area.

The Sunbury shale which overlies the Bedford-Berea delta complex in eastern Michigan and rests directly on the similar carbonaceous shales of the Antrim beyond the reaches of the delta complex in central Michigan and western Ohio becomes a part of the widespread carbonaceous shale body elsewhere. The source of the Sunbury shale is also from the east and does occur in the Foster Well. It was not sampled, however, along with stratigraphically higher shale beds for reasons mentioned earlier.

Devonian

In late Devonian, a thick carbonate sequence composed of Traverse, Dundee-Roger City and Detroit River Groups underlies the Bedford and Antrim shales.

At the top of the Traverse Group, the Traverse

Formation (Fisher, 1969) has a relatively high shale content that distinguishes it from the purer Traverse "lime" beneath. Warthin and Cooper (1943) divided the Traverse into several stratigraphic divisions.

The lowest division of the Traverse Group, the Bell shale, is about 80 feet thick in the State-Foster Well and the most distinctive shale unit in the Traverse Group. It also appears to be the most distinctive shale unit down to the Upper Ordovician Utica shale. The Bell is predominantly a gray, calcareous shale with thin beds of limestone. The distribution in Michigan (Gardner, 1974) shows a southwestward thinning and ultimate disappearance in southwest Michigan, inferring a source from a general eastward direction. The Bell is considered of probable Erian age and likely represents the beginning of the Catskill Alluvial Plain in the Appalachian region. It would most likely represent a fine clastic westward extension of thicker shale and siltstone-facies farther east. Samples for x-ray analyses were obtained from well cuttings in the Foster Well.

Silurian

The Silurian in the Michigan Basin consists predominantly of carbonate rocks with some evaporites and only thin occasional shales. At the top, the Bass Islands Group is largely confined to the southern part of the State where the low structural position of the Chatham Sag occurs in the Findlay Arch. Mostly carbonates, but also some shale entered southeast Michigan through the Sag, apparently derived from the east.

The Salina Group consists of carbonates and evaporites and small amounts of shale, arranged cyclically. Fincham (1975) described the argillaceous units which range from shale to dolomitic shale. They are black, gray and reddish in color. Though shale is a minor constituent, a sufficient quantity was recovered to process and analyze. The argillaceous sediments are believed to have come from the east where they become a part of the Cayugan Series (Tonoloway Will Creek limestones and shales), which in turn grade farther east into the alluvial plain (deltaic) Bloomsburg red beds.

The biostromal and biohermal Niagaran carbonate occurs beneath the Salina units which drape over the petroleum-producing pinnacle reefs. The Niagaran of Michigan grades laterally, especially in the lower (Burnt Bluff Group) phase into the shaly and sandy Clinton Group of the Appalachian Basin. The Findlay-Algonquin Arch acting as an effective barrier along the east and southeast rim of the Michigan Basin allowed only small amounts of argillaceous sediments into the Basin, essentially none reaching the area of the Foster Well.

In the Alexandrian series, Cataract Group (Cabot Head formation), shale from the eastern clastic source mentioned above occurs with alternating carbonates over much of the Michigan Basin including small amounts in the Foster Well. The lower Cataract (Manitoulin) is predominantly limestone.

Ordovician

In Michigan, the Upper Ordovician Richmond Group is mostly limestone with some shales. The shales grade into thicker shales, silts and eventually coarse clastics of the Queenston-Juniata alluvial plain brought about by the Taconic Orogeny in the Appalachians. The Richmond Group becomes more shaly in the lower part (Utica shale) and in fact, other than the Antrim shale, represents the thickest shale unit in the Pre-Mississippian Paleozoic section of the Michigan Basin. Over 300 feet of Utica occurs in the Foster Well. This shale, dark gray to black with calcareous interbeds, is a westward extension of a widespread body throughout the Appalachian foreland and is generally attributed to the Vermontian Disturbance occurring in the Appalachian orogenic belt.

The Utica rests on the relatively pure Trenton-Black River limestones with a sharp contact relationship. The widespread late Middle Ordovician limestone represents one of the greatest marine transgressions of all time. The lowest portion of the Middle Ordovician (Chazyan) is represented by the medium to fine clastics of the Glenwood shale and/or St. Peter sandstone. The Glenwood is usually represented by greenish-gray shale and may have well rounded and frosted quartz sand grains which probably represents reworked St. Peter sandstone. Because of its physical characteristics, it has often been interpreted as an aeolian sand which could mean long exposure in dune phase and/or actual air transport. The clastic source, at least for the Glenwood, appears to be a part of the clastic sequence farther east which is attributed to the Blountian Disturbance (named from Blount County, Tennessee) in the Appalachians at the end of the Lower Ordovician. This orogeny, effective in the Appalachian orogenic belt was accompanied by a general regression and lowering of sea level, which created an erosional disconformity (Knox Disconformity) over most of the eastern half of the country. The St. Peter sandstone, may well have collected on this widespread erosional surface rendering it difficult to point to the ultimate source(s). The St. Peter distribution is erratic, presumably because of the topographic relief on the Knox Disconformity, with the quartz sand collecting in the "lows" along the erosional surface. There is some question as to the presence of the St. Peter in the Foster Well, but shales at this horizon (about 10,415 feet below the surface) have been interpreted as Glenwood by the writer, and sufficient shale was encountered to sample for analysis (Table 1).

The Lower Ordovician Prairie du Chien Group consists of several hundred feet (over 400 feet in the Foster Well) of dolomite with varying concentrations of quartz sand ranging from "floating" sand grains in the dolomite matrix to sandstone with dolomite cement. Where the formations can be differentiated in the subsurface they are in descending order, the Shakopee dolomite, New Richmond sandstone, and Oneota dolomite. The quartz sand concentration increases westwardly from the Appalachians indicating a general westward (cratonal) source, a point clearly verified by Syrjamaki (1977) in his regional study of the Prairie du Chien Group in Michigan.

Cambrian

The only definite Cambrian age rocks of the Michigan Basin are of Upper Cambrian (St. Croixian Series). The wells which reach and penetrate the Cambrian section are few and the identification of the standard section units of the St. Croxian outcrop in Wisconsin cannot be made with confidence in the Michigan Basin subsurface. Sufficient diagnostic zones exist, however, to indicate by both sample study and gamma ray-neutron logs that most of the St. Croxian sequence is encountered in the Foster Well, essentially the section below 11,055 feet to a depth nearly 13,000 feet below the surface.

The Cambrian rocks in the Michigan area are typically dolomite with varying degrees of quartz sand concentrations as mentioned above in the Prairie du Chien Group, and which developed in much the same manner in the transgressing Upper Cambrian sea. The source of the Upper

Cambrian quartz sands of the Appalachian foreland were recognized as coming from the west (Prouty, 1948) presumably from the Wisconsin "highlands" or southern Ontario. The shift in source direction to the proximal west in pre-Middle Ordovician (Chazyan) sediments could be of significance to this study in terms of the provenance and distance of transport effecting the clay mineralogy.

The shale content in the State-Foster Well though quantitatively small is anomalously high for Upper Cambrian sediments. This factor together with the dark carbonaceous pyrite-bearing composition of the shaly interlayers appears to be related to the location of the well in the deep Cambrian depocenter (Figure 2). The deeper somewhat isolated environment within the depocenter likely would account for the reducing condition inferred by the pyrite and carbonaceous characteristic of the sediment. Samples for x-ray analysis were taken from the thin shaly zones as indicated in Table 1.

CLAY MINERALOGY

Review of Clay Mineral Structure

The clay-size fraction is an important component of many sedimentary rocks and is composed of both non-clay as well as clay mineral types. In some shales, clay minerals may account for up to sixty percent of the clay fraction (Yaalon, 1962). Clay minerals play an influential role in shales, especially in post-depositional environments. Such factors as surface area and cation exchange are critical in dewatering and compaction of mudrocks.

Clays belong to the mineral group known as the hydrous aluminum silicates. They are represented by a definite structure and chemical composition. Structurally, the crystalline clay minerals belong to the phylosilicates, which have sheet structure with a hexagonal pattern somewhat like that of the micas.

In classifying the clay mineral types, the arrangement of two structural units, the silica tetrahedron (SiO_4) and the aluminum or magnesium octahedron is used.

The silica tetrahedron is composed of a silicon atom equidistant from four oxygens or hydroxyls, depending upon charge of the structure. They are arranged in a hexagonal framework, with the bases of all tetrahedrons in the same plane. The height of the unit is 2.1Å In some cases, aluminum will replace silica in the tetrahedral layer.

The octachedral layer is represented by two sheets of oxygens or hydroxyls. The ion present is dependent upon the charge requirements of the structure. The thickness of the octahedral layer is 5.05Å. Excluding allophane minerals, which are amorphous to x-ray diffraction, the combination of the tetrahedral and octahedral unit layers are used to classify the various clay minerals.

The two layered type mineral, which is composed of one layer of silica tetrahedron and one layer of aluminum ocathedron (1:1), is represented by the kaolinite group. Analysis indicates that substitution of ions occurs on the edges of the kaolinite mineral where charge deficiencies occur. The first order d-spacing (001) of kaolinite is 7.15 - 7.20Å.

The three layer type minerals (2:1), composed of one dioctahedral or trioctahedral layer between two silica tetrahedral layers, include the non-expanding illite and expanding clays such as montmorillonite.

Illite has a resultant charge deficiency when some of the silicons are replaced by aluminum. This charge is then balanced by potassium ions. Illite has a first order d-spacing of 10Å.

The expanding clays of 2:1 structure are represented by montmorillonite and vermiculite. Structurally, montmorillonite is like illite, however, the ability to absorb water or organic compounds between layers warrants the term "expanding clay." Vermiculite, also an "expanding clay" is structurally like montmorillonite. However, because of a higher charge in the vermiculite structure, the expansion is only two water layers thick. This gives a first order d-spacing (001) of about 14Å. The montmorillonite with a lower charge can expand indefinitely. However, with glycerol treatment it gives a first order d-spacing of 18Å.

Chlorite represents the clay mineral classified as regular mixed. Structurally, it consists of the three layer type (2:1) with a brucite (Mg_3OH_6) or gibbsite (Al_2OH_6) interlayer. The first order d-spacing is 14Å.

Methodology of X-Ray Analysis

As noted in the previous section on sample preparation, the clay suspension was deposited on a porous plate for further treatment and mineral identification.

The method employed in this study for mineral identification was a series of treatments with organic compounds, salts and finally heat (Table 2). Each treatment used showed a particular characteristic of a clay mineral.

The samples were first leached with increments of 0.1$\underline{N}$ $MgCl_2$ followed with several rinses of water, 10% glycerol by volume. This caused the expansion of the "swelling clays." Samples were then air dried and placed

Table 2. Flow-Sheet of X-Ray Procedure

<u>SUSPENSION</u>

Na-clay suspension
deposited on a porous
platelet--Oriented in
the z-direction.

<u>APPLICATION</u>

Three increments (.1N $MgCl_2$-Glycerol)
Rinse (Distilled water-10% Glycerol)
Dry (Room temperature and dessicator)

<u>X-RAY</u> (First)

<u>APPLICATION</u>

Three increments (1N KCl)
Rinse (Distilled water)
Dry (Room temperature)

<u>X-RAY</u> (Second)

<u>HEAT</u> (Two hours at 300°C)

<u>X-RAY</u> (Third)

<u>HEAT</u> (Two hours at 550°C)

<u>X-RAY</u> (Fourth)

in a dessicator containing $CaCl_2$ for complete drying. They were then ready to x-ray as an oriented, magnesium saturated, glycerol solvated sample.

Following the first x-ray, the samples were treated with 1<u>N</u> KCl solution for cation saturation and rinsed with several increments of distilled water. They were then dried and x-rayed.

The samples were then heated to 300°C and 550°C in two separate stages and x-rayed between each separate heat treatment.

After the completion of the various treatments and x-raying, each diffractogram was examined. Each peak was measured and a record of its 2θ angle and peak intensity completed. Tables from Fang and Bloss (1966) were consulted to convert all angles to d-spacings. For identification of minerals, tables of d-spacing for common clay minerals by Grim (1968) and Mortland (Table 3; Table 4) were used for interpretation.

In order to derive a relative proportion of the clays present, a ratio of the (001) peak intensities was used. It is realized that the (001) peak intensity is not solely related to amount, but also by grain size, crystallinity, composition and various other factors of the clay structure.

TABLE 3. X-Ray Diffraction for Clay Minerals and Quartz.*

Quartz		Illite		Kaolinite		Chlorite		Montmorillonite	
d(A)	hkl	d(A)	hkl	d(A)	hkl	d(A)	hkl	d(A)	hkl
4.26	100	10.0	001	7.15	001	14.2	001	18.0	001
3.34	101	5.0	002	3.56	002	7.1	002	9.0	002
2.46	110	3.33	003	2.38	003	4.71	003	6.0	003
2.28	102	2.5	004	1.78	004	3.56	004	4.5	004

*Data after Dr. Max Mortland, Department of Crop and Soil Science and Department of Geology, Michigan State University.

TABLE 4. X-Ray Diffraction Data for Clay Minerals (Different Treatments).*

Clay Minerals	Natural	Mg-Glyc.	K sat. Heat 100°C	K sat. Heat 555°C
Illite, mica	10.0Å	10.0A	10.0A	10.0A
Kaolinite	7.15A	7.15A	7.15A	--
Chlorite	14.5A	14.5A	14.5A	13.8A
Vermiculite	14.5A	14.5A	10.0A	10.0A
Montmorillonite	13-15A	18A	10.0A	10.0A

*Data after Dr. Max Mortland, Department of Crop and Soil Science and Department of Geology, Michigan State University.

Previous Work on Clays

Argillaceous sediments undergo various changes during initial weathering, transportation and burial. Dependent upon the stage and environment in which the change occurs, terms such as transformation (Millot, 1970), alteration and diagenesis are but a few that are used. Because of the numerous arguments in literature with the use of the word "diagenesis" and its meaning, "clay alteration" will be used when possible for simplicity. It is intended to cover the various changes of clays in this study such as potassium replacement, dewatering, changes in clay mineral species, and increasing/decreasing percents of clays present.

Excluding initial weathering of material, two environments are important when alterations of argillaceous sediments are studied: fresh water (aquatolysis) and marine (halymyrolysis). The differences of clay mineral formation in fresh-water and marine environments are the variable chemical and mineralogical changes in each. During transportation, weathering and the pre-burial diagenesis in the fresh-water environment, fine-grained mica minerals are mainly altered into clay micas (illite and ledikite) as a result of potassium loss. In the marine environment, the cations in the exchange positions of clay minerals are changed (Mg substituted for Ca). In some cases of marine environments chlorite and illite-like materials are formed by the fixation of magnesium and potassium in montmorillonite or degraded illite (Müller, 1967). By the deep burial stage, illite is thought to form at the expense of montmorillonite (via mixed-layer intermediate stage-illite/montmorillonite); and chlorite (plus illite) at the expense of kaolinite. In the final stages of diagenesis, the clay mineralogy is represented by a uniform "illite-chlorite," during the alteration to an end product of "sericite-chlorite."

The term "weathering" is critical when used in various concepts of sediment accumulation. The initial stage of rock breakup, whether or not it results from exogenic forces such as insolation, frost, water, atmosphere, or organisms, can play a very important role in the development of the initial clay mineral suite delivered to the sediment basin. It has been thought that the (1:1) structure minerals (kaolinite) form in an environment of "base removal." For the kaolin minerals to form, an efficient removal of metal cations other than aluminum and silica must occur with an adequate amount of H^+ ions supplied. These criteria may be met in an environment of high precipitation, warm temperatures and strong leaching. The leaching removes the Ca^{++}, Mg^{++}, Na^+ and K^+ with iron compounds forming insoluble oxides (Keller, 1956).

Montmorillonite, however, represents a reversal of the kaolinite environment. Keller (1956) believes that parent material must contain a significant content of magnesium, iron and calcium, or which readily releases high concentrations of these elements into solution along with physical conditions that maintain a high activity of these ions to favor the formation of minerals in the montmorillonite group. Divalent metal cations are essential because they flocculate and hold silica in the reaction. Their presence decreases the activity of the H^+ ions and supplies the cations which form montmorillonite.

The climate usually associated with the formation of montmorillonite is dry where evaporation exceeds precipitation. Such an environment allows an accumulation of bases. This can also occur in areas of accumulation of ash or tuff. Montmorillonite has also been observed in very small zones over a regional area dominated by (1:1) clay mineralogy. It was suggested (Keller, 1956) that such occurrences may represent microclimates within a regional magnaclimate zone, such as areas of less moisture and thus less leaching.

Environmental control in the formation of illite appears to be related to a climate of moderate rain with wetting and drying and the retention of potassium and calcium ions particularly (Müller, 1967).

In summary, during the weathering of source materials, the clays that form in a climate and topography, which are not favorable to the leaching and removal of alkalies and alkaline earths, are the three-layered clay minerals (illite, montmorillonite, chlorite and sepiolite-attapulgite),which will form depending on the prevalence of potassium and magnesium. In the absence of the alkalies and alkaline earths, the stable phase is kaolinite at moderate to low temperatures and pressures (Grim, 1958).

In addition to alteration of minerals in the initial weathering of source material, physical and chemical alteration of clays continues to occur during transportation in both fresh-water and marine environments. Since the work of Dietz (1941) the question arises as to whether the clays of marine sediments are representative of the continental source or are in an evolutionary stage of development in a marine environment.

From various studies (Grim and Johns, 1954; Grim, Dietz, and Bradley, 1949; Milne and Earley, 1958; and others) of marine sediments off the east coast, Gulf Coast and off the California Coast, the clay minerals appear to represent the drainage areas as they enter the marine environments. At this point, the clays appear to undergo a transformation process with montmorillonite absorbing potassium to form illite and kaolinite undergoing changes into chlorite. Milne and Earley (1958) found evidence in the Gulf Coast that montmorillonite, the dominant mineral carried to the Gulf Coast, alters slowly to illite where sedimentation is slow. However, Grim (1958) suggests that some illites and chlorites form quickly where fresh-water muds enter the marine environments. The changes are primary in the regeneration of degraded illite and chlorite which appear to occur before the river muds reach the sea floor.

The sequence of alteration of argillaceous sediments appear to occur in three phases: 1) pre-burial, 2) shallow burial, and 3) deep burial. The pre-burial stage represents the fresh-water and marine environments discussed previously. The shallow burial stage is certainly important in determining the initial material present which may be further altered after deeper burial. The previous work shows some variable conclusions, Correns (1938), Locher (1952), and Debyser (1959) studied cores of shallow burial (up to 20 meters) which indicated no transformation of clay minerals. However, Milne and Earley (1958) observed in a core, a decrease of kaolinite downward in a depth of seven feet. The decrease may have been related to an alteration of the sediment after deposition or difference in clay material being deposited.

The final stage of alteration in argillaceous sediments due to deep burial is of prime interest in this study. Often it is difficult to differentiate alteration which has occurred in the shallow stage from that resulting from deep burial. Overburden pressures are thought to be the factor for separation of the two stages. This may be important, because there are indications that overburden pressures account for the initial expulsion of pore fluids and compaction of the argillaceous sediments. It is unlikely to be responsible for complete dewatering and alteration of clay minerals.

From the previous work done on clay reactions in deep burial, various conclusions have been drawn. In recent years, the work indicates that differential sedimentation is not solely responsible for the clay mineral type in burial but that some transformation does occur (Millot, 1970).

Models and Studies of Deep Burial

As stated previously, it was the intention of this study to identify the clay mineralogy of the various shale units and compare the data to deep burial models established in literature. In this section a description and comparison of the models will be presented and used later in analysis of Michigan Basin data.

Van Olphen (1963) indicated that overburden pressures were not solely responsible for the dewatering of deeply buried mudrocks. As a result of this and other work (Powers, 1967; Burst, 1969; and others), a new fluid release theory developed to account for compaction of argillaceous sediments. Burst (1969) referred to this as an illitization process which consists of the transformation of montmorillonite (expanding clay) to illite (non-expanding). The alteration of the montmorillonite, thought to be due to the replacement of potassium in the structures, causes the montmorillonite to collapse and release the associated water. Burst (1969) concluded that the transformation process is temperature dependent and closely related to burial depths in terms of burial temperatures. Most work completed thus far indicates that at a depth of about 6,000 feet a transformation of montmorillonite begins; and at 10,000 feet either a mixed-layer of illite/montmorillonite or complete illitization has occurred. If mixed-layer clays persist at 10,000 feet, it is generally thought that this material is removed by 15,000 feet.

Three dewatering models (Burst, 1969; Powers, 1967; Perry and Hower, 1972) which have been explained in detail in literature may merit consideration.

Burst's Model is composed of a three stage dewatering process. Stage one accounts for the removal of pore water and excessive water interlayers by overburden pressure. This represents the greatest volume of water removed in sediment dehydration. The second stage, considered to be geothermally controlled, occurs when there is a release of one or two of the interlayers of water associated with the clays. The final stage, thought to be geothermally controlled, is identified by the complete collapse of the clay structure and final dewatering of the sediment.

The model derived by Powers (1967) is a two stage model which Burst altered to his three stage model. The first stage of sediment dewatering occurs when montmorillonite is buried by a few hundred feet of sediment. The water retained in the sediment reaches a balance with the water-retaining properties of montmorillonite. The process of montmorillonite alteration to illite continues through depth. At 6,000 to 9,000 feet, the associated water is no longer strongly oriented by the clays and thus overburden pressures compact the water until a balance is attained. At this stage the clays resemble an illite alteration product.

Perry and Hower (1972) proposed a quite different four stage dewatering model. Their work showed that no discrete montmorillonite occurred in the samples from the wells they examined. Rather it occurred as a randomly mixed component with illite which altered to a regular mixed component with increasing amounts of illite through depth. From this data, they concluded that the decrease in montmorillonite with depth was geothermally controlled. According to their model, stage one removes interstitial and interlayered water present in excess of two water layers. This is due to burial pressures. At 6,000 to 8,000 feet in the Gulf Coast, the alteration of montmorillonite to illite begins. Stage two accounts for random collapse of montmorillonite layers and interlayer water expulsion.

Stage three is marked by a transition from random to ordered interlayering. In the final stage there is complete removal of the remaining five percent of interlayered water and alteration of interlayered illite. (Refer to Figure 4 for dehydration models.)

Alteration of clay minerals in deeply buried sediments is not solely restricted to change in montmorillonite

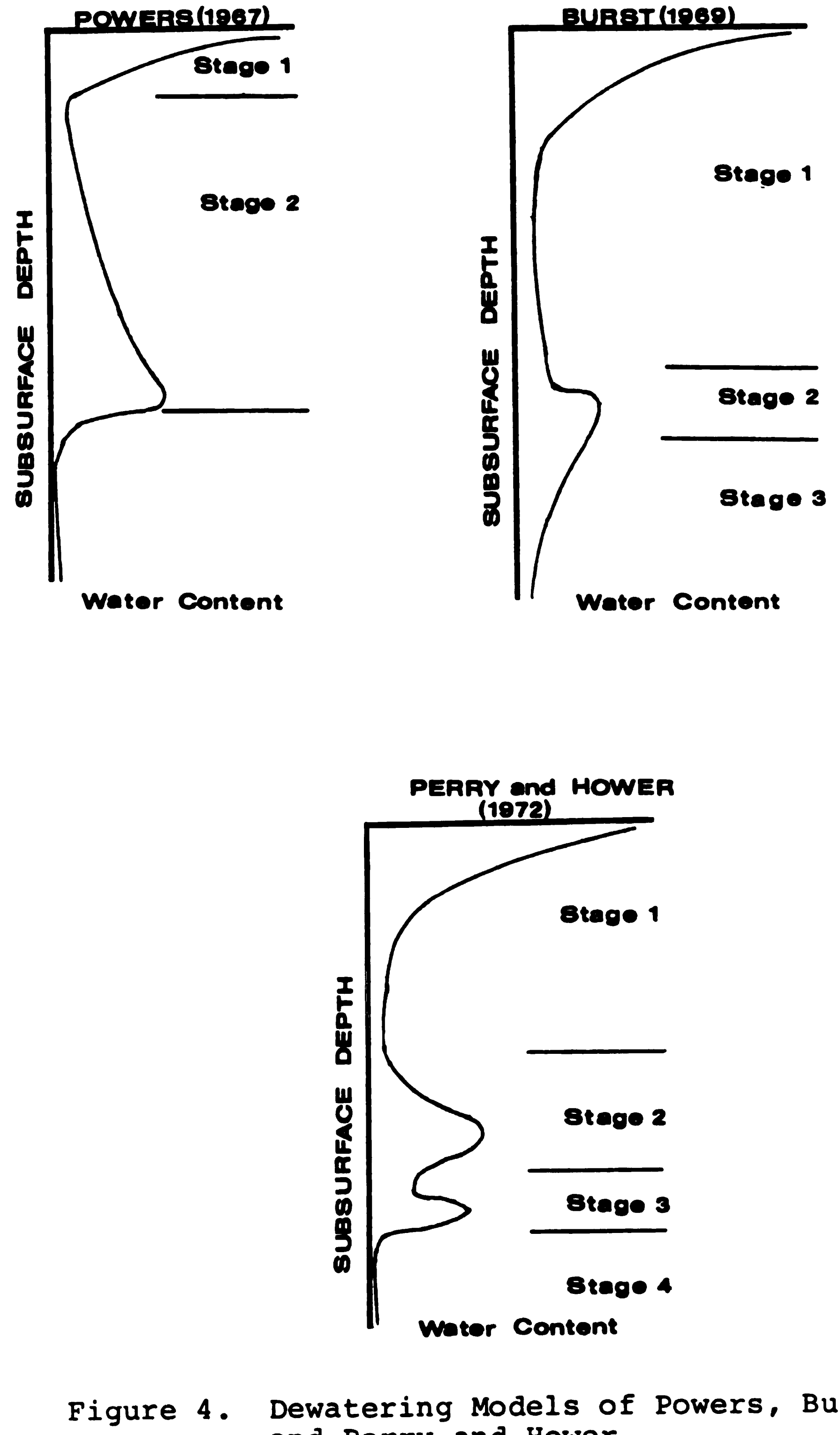


Figure 4. Dewatering Models of Powers, Burst, and Perry and Hower

to illite. Although this concept is usually associated with dewatering and compaction of sediments, it is the purpose of this study to show these and other forms of clay alteration at depth. Weaver (1960) indicated that illite becomes more crystalline in depth. This can be seen by observing the increased sharpness of the (001) illite peak in sediments from greater depth.

Michigan Basin "Model"

The clay mineralogy of the selected shale units in the State-Foster No. 1 Well was identified to detect any clay alterations that may have occurred as a result of burial. A comparison might then be made to results of previous works, most of which are concentrated in the Gulf Coast area, to determine if the changes are comparable to those in the Michigan Basin samples.

From the forty-seven samples, the magnesium chloride and glycerol diffractograms were initially analyzed for the presence of discrete montmorillonite or interlayered "expanding clays."

The lack of an 18Å peak in all diffractograms suggests an absence of discrete montmorillonite.

From observation of the 10Å illite peak, the asymmetrical shape of the peak to the lower angle suggests inter-layering with other clay(s). In order to determine the types of clays present, a series of measurements were made. A proportional measurement of the 14Å peak (vermiculite and chlorite) and the 10Å peak (illite) from the magnesium chloride and glycerol saturated diffractograms was compared to the same measurements from the potassium chloride saturated plus 300°C heat-treated diffractograms. With the potassium and heat treatment any vermiculite or montmorillonite present would collapse to 10Å and increase the intensity of the 10Å peak.

A slight reduction in the ratio values does occur which indicates some expanding clays present. However, the change is very small, except for sample 12,114 which indicates the presence of vermiculite, and is difficult to identify the type of clay present. Only a trace of "expanding clays" could be verified.

Another technique (Weaver, 1960) was utilized to observe the interstratification of clay minerals. A measurement of the 10Å and the 10.5Å values was made of the basal (001) illite peak from the magnesium chloride plus glycerol and the potassium chloride plus 300°C and 550°C diffractograms. With increasing temperatures, any expanding material present would collapse and sharpen the 10Å peak with decreasing interstratification. The values were similar for each treatment, which may infer interstratification with a non-expanding clay such as chlorite.

The general absence of montmorillonite in the Michigan Basin may be related to the complete alteration of expanding clays to essentially a non-expanding clay suite (time may be a factor); or there was initially an absence of montmorillonite in the Basin because of various conditions such as climate and topography in the source area.

It is difficult to ascertain that the alteration process is so complete that total removal of all montmorillonite would occur. It might be probable that discrete montmorillonite would be removed but some interlayered material would likely remain. This was observed in all studies reviewed in the Gulf Coast, ranging as an intermediate stage between discrete montmorillonite and illite (Powers, 1967; Burst, 1969) to a primary stage of interlayered material transforming to totally illitic clay (Perry and Hower, 1972).

However, if the trace of expanding clays in the Michigan Basin represents the remaining portion of an altered sequence of clays, recent work by Price (1976) and Perry and Hower (1972) in relation to primary migration of hydrocarbons may help explain the presence of small amounts of expanding clays.

In recent years, some research indicates that the expulsion of oriented water associated with montmorillonite accounts for the drive mechanism which flushes hydrocarbons from shale source beds. The slight trace of expanding clays may be evidence that this happened in the Michigan Basin. However, if the expanding clays were transported to the Basin rather than formed by in situ alteration, then an alternate explanation such as compaction might be called upon to account for the migration of petroleum from potential source beds (shales) such as the Utica shale.

Time, in relation to clay alteration, has been refuted by most researchers in recent years as a primary factor. This has been based on studies mainly of the thick Tertiary accumulations in the Gulf Coast. However, the Michigan Basin data is restricted to the Paleozoic section. Grim (1968) indicated that montmorillonite is generally absent in sediments older than the Mesozoic. This may be related to the slow absorption of potassium and magnesium for changes encompassing the units studied in the Michigan Basin and thus the removal of montmorillonite.

Work by Asseez (1967) and Chung (1973) also showed a lack of montmorillonite in the Upper Devonian-Antrim and the Mississippian-Coldwater shales respectively. From the present study and previous work, it could be inferred that conditions did not favor the accumulation of montmorillonite in the Michigan Basin. The absence may be related to initial clay formation rather than alteration at depth.

Work by Milne and Earley (1958) suggests the importance of climatic conditions in the source area. The Mississippi and its tributaries, which carry a montmorillonite enriched clay suite, have drainage basins in rocks of all type and ages. The drainage area is predominantly associated with the drier western United States. However, three rivers, the Wolf and Pascagoula, which are restricted to Tertiary sediments, and the Mobile, which extends to the southern Appalachian Highlands with mostly Paleozoic rock types, carry a kaolinite enriched clay fraction from an area of higher rainfall, the southeastern United States. This would suggest climatic control for the clay types.

Further analysis of the x-ray diffractograms indicate the shale horizons studied were uniform in clay mineralogy. Individual clay minerals were identified by their diagnostic peaks (Table 4) with relative quantities related to the intensity of the basal (001) peak reflections. Illite, chlorite and kaolinite are the predominant clay minerals present throughout the shale horizons (Table 1). The Salina and parts of the Cambrian showed the highest content of chlorite and kaolinite with illite the highest in Ordovician samples. Traces of "expanding clays," as previously mentioned, were found throughout but did not show a concentration at any level. Feldspars, both sodium and potassium, were present in many of the samples with exceptionally intense peaks in the Cambrian samples, possibly indicating proximity from source. The 4.26Å peak indicated the presence of quartz in all samples.

Much of the recent work on alteration of clay minerals with increasing depth is directed towards the consideration of absorption of potassium by montmorillonite and its resulting transformation to illite. Because of a lack of montmorillonite in the Michigan Basin, direct comparisons are difficult to make to previous studies. In an attempt to detect variations in the prominant clay minerals present, a relationship between kaolinite + chlorite to illite was established by plotting depth against the intensity of the 7Å peak divided by the intensity of the 10Å peak (7Å/10Å). Similarly, depth versus chlorite + vermiculite divided by illite (14Å/10Å) was plotted. However, as previously discussed, the presence of vermiculite (expanding clay) occurs only in trace amounts, except sample 12,114; thus it is felt that the 14Å/10Å represents essentially chlorite in relation to illite. The final method utilized in the study was previously described as the 10Å/10.5Å measurements from the basal (001) illite peak.

The measurements for all graphs were taken from the magnesium chloride and glycerol diffractogram patterns. An average value for the top, middle and bottom of each horizon (Antrim, Bell, Utica), the average values for the Salina and Glenwood and values for Upper Cambrian (Appendix 1) were used for all graphs.

The first graph compiled indicates the relationship of chlorite + kaolinite to illite (7Å/10Å). Figure 5 shows the chlorite + kaolinite increasing through the Salina with illite becoming more abundant in Utica. From Utica through Upper Cambrian, the chlorite + kaolinite values fluctuate through depth.

Figure 6 shows a relationship of chlorite to illite. Again the 14Å/10Å values appear very similar to the 7Å/10Å

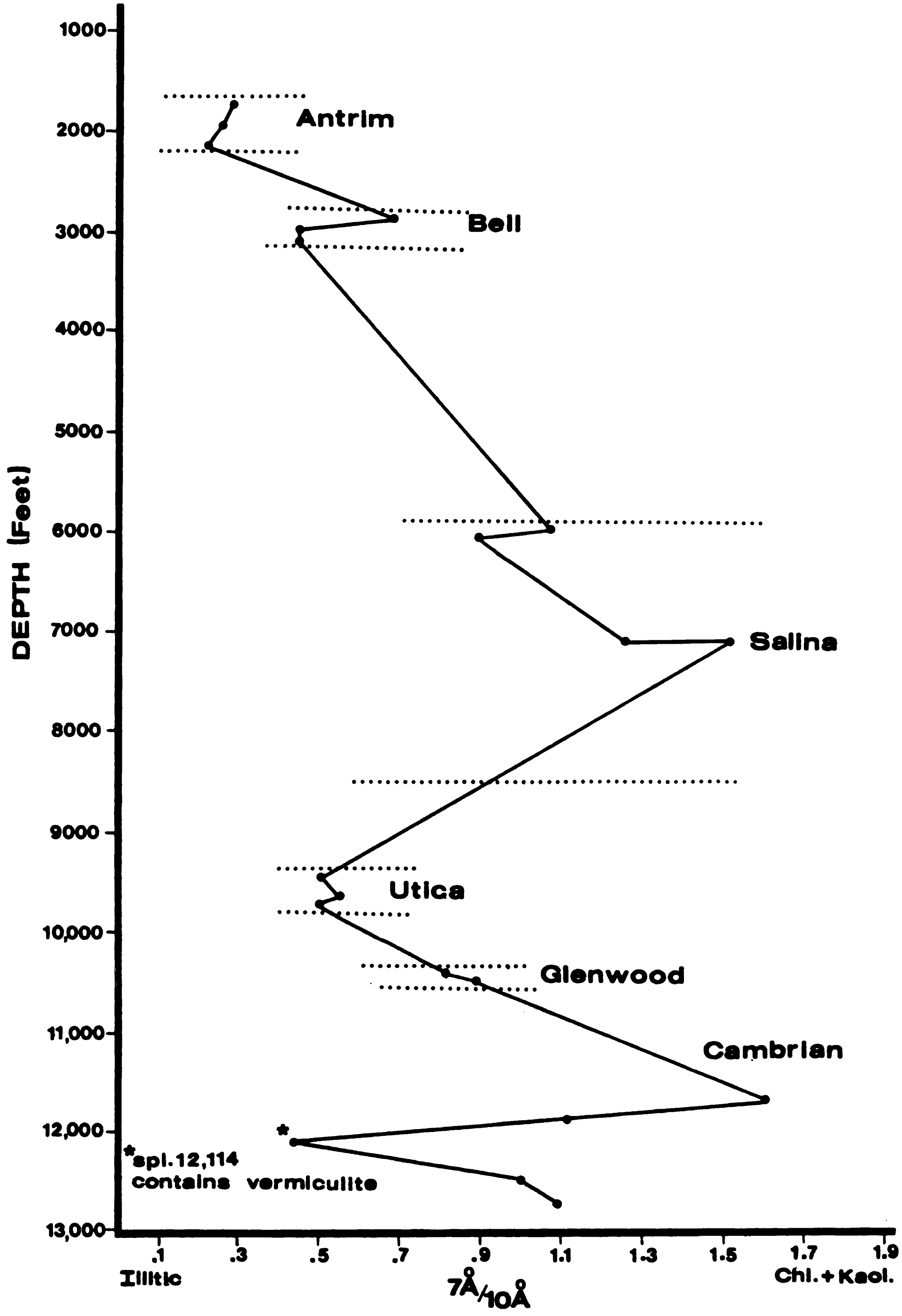


Figure 5. The Relationship of Chlorite + Kaolinite/ Illite with Increased Depth of Burial

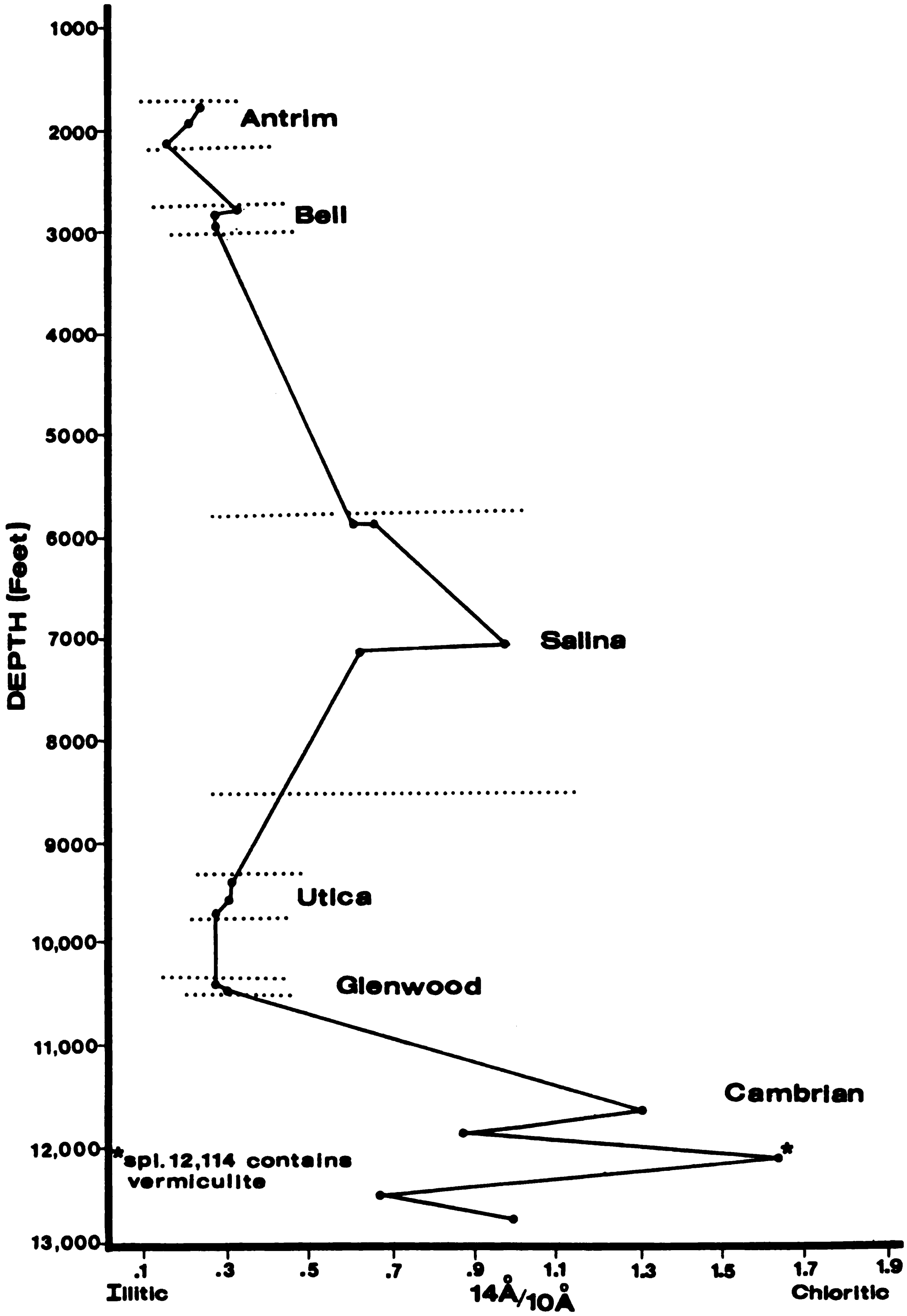


Figure 6. The Relationship of Chlorite/Illite with Increased Depth of Burial

values. There is a general increase of chlorite through the Salina samples and a reversal with illite greater in the Utica and Glenwood. By Upper Cambrian, the chlorite content has increased once again but shows some fluctuation.

From the review of the diagrams, the question arises whether the variable mineralogy is an alteration product or reflects the detrital material delivered to the sediment basin. Weaver (1958) argued that detrital material plays more of a significant role in the clay mineral suite present rather than diagenetic altered material. Powers' (1957) work in the Chesapeake Bay area indicated that diagenetic changes in clays often exceed the detrital clay fraction. This problem has been approached by many others (Grim, 1942; Rateyev, 1963; Bradley, 1945; Milne and Earley, 1958; Larsen and Chilingar, 1967; Johns and Grim, 1958 are but a few of the publications). Pawlowicz (1978) from work in the Gulf Coast indicated that the chlorite in shallow zones was related to detrital material and not until around 9,000-12,000 feet that a "chlorite-like material" appeared due to diagenetic changes.

From the data (Figures 5 and 6) assembled from shales of the Michigan Basin, the chlorite and kaolinite content increases in relation to illite from Antrim through Salina which infers a change due to depth. This is suggested based upon the fact that the increase is not restricted to any boundaries. After calculating the 7Å/10Å and 14Å/10Å values within the individual sampled horizons, the results varied insignificantly except for the Upper Cambrian. Excluding Upper Cambrian, this may suggest that changes are not restricted to stratigraphic horizons but more to depth.

Interesting similarities exist in the clay mineralogy which may suggest detrital origin with some in situ alteration. The clay mineralogy of the shale units, Antrim, Bell, Utica and Glenwood indicate very similar illite content in relation to chlorite (Figure 6). The Antrim, Bell and Utica represent a time of greater influx of fine clastics due to major movements in the Appalachian region. The Antrim and Bell are related to the Acadian Orogeny and Utica to the Vermontian Disturbance. The Blountian accounts for the Glenwood shale. The data from these shale units suggests detrital origin based on very similar clay mineralogy.

The chlorite/illite ratio of the shales in the Salina Group shows a higher chlorite content. This may suggest an alteration of the clay minerals in situ. The Salina samples represent the only shale studies above the Cambrian which are interlayered with dolomite, except for the Glenwood which is associated with a dolomitic limestone (Table 1). This may suggest that a magnesium source for chlorite was associated with the dolomitic rocks.

The Upper Cambrian also shows a higher chlorite content (Figure 6). In comparison to the Salina, the Upper

Cambrian shales are also associated with dolomite. However, Prouty (1948) concluded the source for the Upper Cambrian and Lower Ordovician sediments was from the craton to the west. The difference of the clay mineralogy in Upper Cambrian compared to the younger shale horizons studied may reflect this changing source.

The final method utilized in the study was developed by Weaver (1960). By dividing the 10Å by the 10.5Å measurement, Weaver showed the values to increase with depth. This indicated that the illite peak became less interstratified with depth.

Each horizon was examined as previously mentioned. The illite (Figure 7) shows decreasing interstratification through the Salina samples and once again, as in previously measured parameters, shows a change in the Ordovician (Utica). The interstratification generally increases through the Ordovician and into Upper Cambrian and then very quickly decreases at a depth of nearly 1000 feet into the Upper Cambrian. Such a quick change might indicate that illite forming from weathering of source material on the craton had become degraded because of longer exposure in Trempealeau and Upper Eau Claire times, in contrast to material being supplied in Lower Eau Claire time (Figure 3). The changes in the curve around Ordovician time may suggest the change of sources discussed earlier.

In essence, the results indicate suggestive evidence for the origin of the clay minerals in the shale units

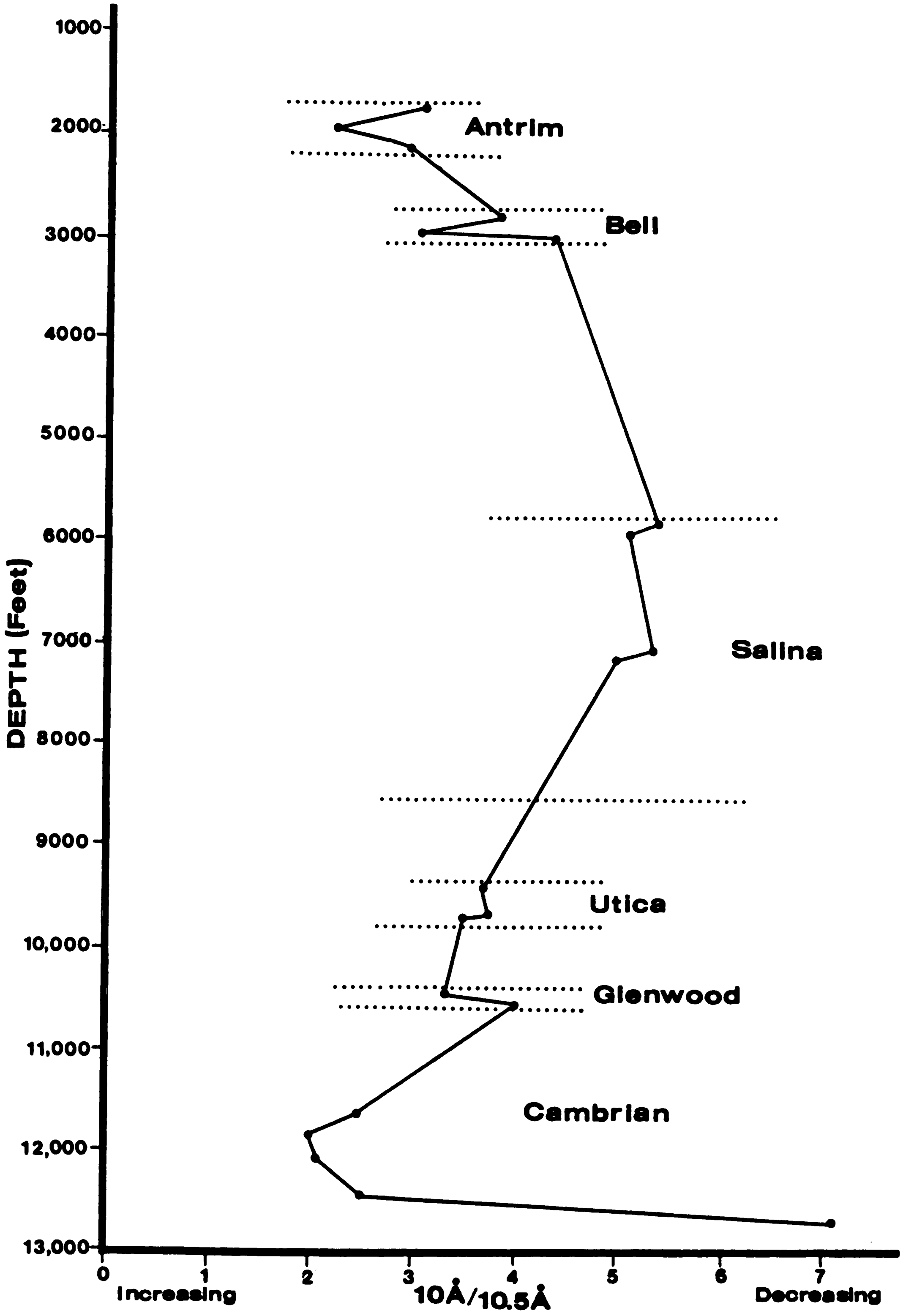


Figure 7. Interstratification of the Basal (001) Illite Peak with Increased Depth of Burial

analyzed in the Michigan Basin. It is unlikely that either diagenetic or detrital origin are solely responsible.

CONCLUSIONS

Some significant conclusions that can be drawn from the study are:

1. The clay mineralogy of the Antrim shale, Bell shale, shale interbeds from the Salina Group, Utica shale, Glenwood shale and shale partings from Upper Cambrian is very uniform and dominated by illite, chlorite and kaolinite.

2. Discrete montmorillonite does not occur in the Michigan Basin. Evidence for appreciable amounts of "expanding clays" is lacking in all but one sample. The lack of montmorillonite may be attributed to conditions (climate and topography) in the source area or a diagenetic transformation of montmorillonite to illite with a trace of expanding clays remaining.

3. Chlorite and kaolinite increased in relation to illite downward from Antrim shale through the Salina samples. A reversal occurs in the Ordovician with illite showing an increase. By Upper Cambrian, the relation of kaolinite and chlorite to illite fluctuates from higher to lower values. The increase of chlorite and kaolinite from Antrim through Salina may suggest a diagenetic change.

4. The clay mineralogy of shales from Antrim, Bell,

Utica and Glenwood show close similarities in illite content which may suggest relationship to orogenic activity in the Appalachian region at their respective times.

5. A change from a chlorite dominated mineralogy in Upper Cambrian to an illitic clay mineralogy in Late Cambrian may suggest the changing source from the craton to the west in Upper Cambrian to an easterly source in post-Middle Ordovician time. The higher feldspar content in the Upper Cambrian also suggests the proximity of a western (cratonal) source in contrast to a distant easterly source in the Upper Ordovician.

6. The values for interstratified clays show decreasing interstratification through the Salina samples; higher stratification or degraded illite in the Ordovician and once again decreasing interstratification through Upper Cambrian. The rather quick change from a lower interstratified illite to a highly interstratified material through Upper Cambrian may infer the degree of weathering in the source area. The change in the interstratification curve through depth at the Ordovician may once again reflect the geological occurrences at this time.

RECOMMENDATIONS

A reversal in all measurements of the Ordovician in the Michigan Basin certainly suggests variabilities not clearly understood. This somewhat anomalous area suggests future studies of interest.

A lateral clay mineralogy study encompassing the Antrim, Bell, Salina, Utica, Glenwood and Upper Cambrian throughout the Michigan Basin may reveal additional data on sedimentary environments, paleogeography, source distances and rock types, and other parameters that might help account for the anomalies in the clay mineralogy of that part of the geologic section. A detailed study of the Ellsworth shale of western Michigan, a partial equivalent of the Antrim shale, may reveal answers to the problem of the effects of a definite westerly source as opposed to sediments derived from the east (Appalachian). Answers from such studies may shed light on the interesting clay mineralogy problem in the Michigan Basin.

APPENDICES

APPENDIX I

MICHIGAN BASIN DATA

APPENDIX I

MICHIGAN BASIN DATA

Sample Number	Depth (Feet)	7Å/10Å	14Å/10Å	Sharpness Ratio 10Å/10.5Å
At-1	1790-95	.38	.18	3.03
At-2	1795-1800	.21	.22	3.4
At-3	1800-05	.24	.23	2.62
Am-4	1975-80	.19	.09	1.88
Am-5	1980-85	.31	.21	2.27
Am-6	1985-90	.29	.25	2.45
Ab-7	2150-55	.21	.09	3.23
Ab-8	2155-60	.15	.09	2.41
Ab-9	2160-65	.26	.23	3.09
Bt-1	2880-85	.50	.31	3.72
Bt-2	2885-90	.71	.32	4.11
Bt-3	2890-95	.90	.39	3.58
Bm-4	2915-20	.50	.28	2.98
Bm-5	2920-25	.32	.21	3.46
Bm-6	2925-30	.53	.26	2.60
Bb-7	2945-50	.46	.14	3.34
Bb-8	2950-55	.45	.28	4.83
Bb-9	2955-60	.45	.34	4.90
S-1	5850-55	1.12	.56	5.0
S-2	5855-60	1.02	.63	5.75
S-3	5860-65	.79	.49	5.33
S-4	5865-70	.98	.78	5.0
S-5	7025-30	.92	.80	5.38
S-6	7030-35	1.59	1.14	5.29
S-7	7060-65	1.75	.81	5.0
S-8	7065-70	1.31	.51	4.91
Ut-1	9440-45	.59	.27	3.49
Ut-2	9445-50	.45	.36	3.53
Ut-3	9450-55	.53	.19	3.47
Ut-4	9455-60	.33	.28	4.03
Um-5	9600-05	.65	.23	5.02
Um-6	9605-10	.55	.35	3.15
Um-7	9610-15	.52	.32	3.83
Um-8	9615-20	.49	.28	2.91

Sample Number	Depth (Feet)	7Å/10Å	14Å/10Å	Sharpness Ratio 10Å/10.5Å
Ub-9	9745-50	.40	.21	5.0
Ub-10	9750-55	.55	.31	3.2
Ub-11	9755-60	.66	.44	2.86
Ub-12	9760-65	.41	.27	2.78
G-1	10,415-20	.69	.32	3.0
G-2	10,430-35	.94	.25	3.6
G-3	10,435-40	1.0	.34	3.74
G-4	10,440-45	.80	.31	4.21
C-1	11,643	1.60	1.30	2.4
C-2	11,823	1.14	.86	1.95
C-3	12,114	.45	1.64	2.05
C-4	12,553	1.00	.67	2.5
C-5	12,707	1.07	1.0	7.1

APPENDIX II

SAMPLE PREPARATION

APPENDIX II

SAMPLE PREPARATION

The following contains a detailed description of sample preparation compiled by Dr. Max Mortland, Department of Soil Science and Department of Geology, Michigan State University.

Dissolution of Carbonates and Soluble Salts:

1. The initial amount of sample is placed into a 400 ml beaker. For each 5 gm portion of sample add 50 ml of 1 N sodium acetate (buffered to pH 5 with acetic acid) then bring the soil into suspension by stirring with a rubber policeman.

2. Digest the suspension for 30 minutes over a hot plate at low heat with intermittent stirring.

3. Centrifuge the suspension or filter under suction in a Buchner funnel. Discard the supernatant.

4. Highly calcareous material may require one or two additional washings with sodium acetate buffer.

Removal of Organic Matter:

1. The sample in the centrifuge tube, now free of soluble salts and carbonates, is wetted with NaOAc buffer and transferred to a 400 ml beaker with a minimum amount of water.

2. Add 5 ml of 30% H_2O_2 to the sample and stir carefully. Often the reaction will proceed so rapidly that constant care and stirring are required to prevent frothing over.

3. When the reaction has subsided, add a second 5 ml increment of H_2O_2 to the sample and digest on the hot plate. Repeat this procedure with 10 ml of H_2O_2 and digest for two hours to insure completion of the reaction and to remove excess peroxide in the solution.

4. The reaction of the suspension with H_2O_2 is essentially complete when the suspension loses its dark color or when conspicuous effervescence ceases. Some effervescence will always be present due to the decomposition of H_2O_2. The majority of suspension will also have color as a result of highly colored mineral particles and free iron oxides.

5. Evaporate excess liquid to a thin paste, but do <u>not</u> go to dryness. Add NaOAc and stir well. Filter or centrifuge the suspension to recover mineral matter. Wash once with distilled water and procede to the next step.

Removal of Free Iron Oxides:

1. Transfer the mineral matter to a 400 ml beaker and add 40 ml of 0.3N Na-citrate and 5 ml of 1N $NaHCO_3$.

2. Warm the suspension carefully to 75-80°C in a water bath or hot plate and add 1 gm of $Na_2S_2O_4$ with stirring. (Caution-Do not boil the suspension. Heating beyond

$80^{\circ}C$ can cause the precipitation of black FeS forms.) Digest the suspension for 15 minutes.

3. At this point the suspension can be cooled and centrifuged. The clear supernatant can be saved for Fe determination or can be discarded.

4. Iron-rich samples may require an additional treatment but most samples should be free of iron oxides at this point.

5. This procedure has rendered a sodium saturated sample and it is ready for particle size fractionation.

Fractionation by Gravity Sedimentation:

1. The sample is transferred to a sedimentation cylinder. The cylinder is filled with distilled H_2O.
   a. In the event the sample is not dispersed after 24 hours in the reciprocating shaker, transfer the suspension to a milkshake cup and place on the stirrer for 15 minutes before transferring to the sedimentation cylinder.
   b. If a large sample was used (sandy material), sieve the sample through a 270 mesh sieve before transferring to the sedimentation cylinder.

2. Stir vigorously with a stirrer. Note the time.

3. Take the first sample after 24 hours settling at the depth determined by Stokes law for <2μ clay, (plotted on graph). Decant the sample from the desired depth with a siphon. Refill the cylinder with distilled water and repeat the process (2 and 3) until the yields become small

(make 3 collections).

X-Ray Diffraction Prodedure:

1. A previously prepared porous plate is marked with the appropriate sample number and placed in the porous plate holder. The holder is then placed on a vacuum flask and the vacuum applied. The clay suspension is poured into the well of the holder and the clay is deposited on the plate as water is drawn through the plate. If the well will not hold all of the suspension at once, it may be added in parts.

2. After the film has been deposited, leach with three increments of 0.1N $MgCl_2$ which is 10 percent glycerol by volume. Wash with several increments of water/10 percent glycerol by volume, air dry, then complete drying in a dessicator over $CaCl_2$. The sample is ready for x-raying as a magnesium saturated, glycerol solvated, oriented aggregate.

3. After the initial x-raying of the magnesium saturated, glycerol solvated, oriented aggregates, the sample should be saturated with potassium (1N KCl), excess KCl washed out and the sample air dried, and x-rayed, then heated at 300°C and x-rayed. It should then be heated to 550°C, cooled, and x-rayed again. Heat treatments should be for 2 hours. These four x-ray tracings can then be used for qualitative identification of the clay minerals present.

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