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SELECTED PALEOZOIC FORMATIONS - MICHIGAN BASIN

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Raymond B. Moyer

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Master's degree in Geology

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THERMAL MATURITY AND ORGANIC CONTENT OF SELECTED PALEOZOIC FORMATIONS - MICHIGAN BASIN

Ву

Raymond B. Moyer

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

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ABSTRACT

THERMAL MATURITY AND ORGANIC CONTENT OF SELECTED PALEOZOIC FORMATIONS - MICHIGAN BASIN

by

Raymond B. Moyer

Thermal maturity and total organic carbon content have been determined for selected shale units in the Michigan basin. Results show that at least parts of all units studied have been sufficiently matured to generate oil, and some may have generated gas as a primary product.

Current geothermal gradients in the Michigan basin indicate that temperatures are not high enough in formations above the Precambrian to degrade oil. A contour map of thermal maturity data shows that the Dundee limestone is the deepest formation likely to contain oil in the central basin. Older formations may contain oil toward the basin flanks. In the north and northeast the Niagaran appears to be the oldest potential oil producer.

Thermal maturity and vitrinite reflectance data indicate that the Michigan basin may once have contained 4000 to 7000 feet of additional sedimentary cover, and that the Antrim shale experienced maximum temperatures of about 100°C.

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INTRODUCTION

The Michigan basin is a stable interior (gravity sag) basin which underwent subsidence from the Middle Ordovician through the Pennsylvanian. Stratigraphically the basin is dominated by carbonates and shales of Cambrian through Pennsylvanian ages with some Jurassic rocks in the center (Figure 1). There are no Permian or Triassic rocks in the basin and, except for glacial drift, there are no rocks younger than Jurassic age.

The Michigan basin has been a source of oil and gas since the discovery of the Port Huron field in 1886 (Michigan DNR, 1980).

Through 1979, cumulative production of Michigan oil and gas fields was 803,792,444 barrels of oil and 1,554,478,962,000 cubic feet of natural gas (Michigan DNR, 1980). The principal producing zones are the Michigan Stray-Marshall, Berea, Antrim, Traverse, Dundee-Reed City, Detroit River, Salina-Niagaran, and the Trenton-Black River Units. Minor amounts of gas have been produced from the glacial drift, and minor amounts of oil have been produced from the Prairie du Chien (Champion, 1967).

The deepest gas well is the Dart-Edwards #7-36, discovered in 1981, producing from 10,600 feet in the Prairie du Chien. The deepest well producing oil is in the Frederick Field in Crawford County (T28N R4W Sec 29). This well produces from a Niagaran reef at a depth of 7,420 feet.

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STRATIGRAPHIC SUCCESSION IN MICHIGAN



MICHICAN DEPARTMENT OF NATURAL RESOURCES Howard A. Tanner, Director

INFORMAL TERMS







Figure 1.

Source rock evaluation is an important part of any basin analysis. In addition, it is desirable to define the depth below which no oil will exist, the so called "oil death line." The primary objectives of this investigation are to define this depth in the Michigan basin and predict, in general, the type of hydrocarbons (oil or gas) that may have been generated from potential shale source rocks.

Under favorable conditions, part of the organic matter preserved in sedimentary rocks may be converted into crude oil. The rate of transformation and the amount transformed are primarily dependent on three factors: (1) the nature and amount of original organic matter, (2) the catalytic properties of the enclosing sediments, and (3) the thermal history of the potential source bed (Philippi, 1965). This study is not concerned with the rate of transformation. Therefore, only the amount of organic matter in the form of total organic carbon (TOC), and the thermal history of potential source beds have been considered.

Samples of cores and cuttings from the Michigan formation (Mississippian), Antrim shale (Devonian), Bell shale (Devonian), C shale (Silurian), Utica shale (Ordovician), Eau Claire shale (Cambrian) and Precambrian shales have been analyzed for TOC content and thermal maturity (degree of organic metamorphism). TOC is used to determine whether or not a rock contains the minimum organic content for hydrocarbon generation. Thermal maturation is used to determine whether or not a rock has been subjected to the minimum temperature required for hydrocarbon generation and to predict whether oil or gas has been generated.

Thermal history is a post-depositional factor and is the product of temperature, as a function of depth and heat flow, and the duration of burial beneath overlying strata. Of these factors, the maximum temperature to which a rock has been subjected for a significant amount of time is the more critical (Nixon, 1973). The depth interval of oil generation (the oil window) depends on the temperature history and age of the source sediments (Philippi, 1965). It is possible to define the interval by analyzing the thermal maturity of sediments at various depths throughout a basin. This requries the use of indirect methods which are based on irreversible diagenetic effects of temperature upon organic matter. These studies are performed in the laboratory on cores or cuttings samples.

Secondary objectives of this investigation are to define the present geothermal gradients in the Michigan basin, estimate the maximum paleotemperature of the Antrim shale and to address the question of whether the Michigan basin is overpressured; that is, whether it was once buried under an additional 5000 feet of sedimentary cover, as has been suggested by Price (1976) and Nunn (1981).

It is emphasized here that there is much controversy regarding this type of investigation, and the data are not conclusive. Studies of this nature, generally conducted by oil companies, are kept confidential by those companies and are not made available to the public. This is intended to be a reconnaissance study, and it is hoped that it will provide a starting point for more detailed studies of the thermal maturity of sediments in the Michigan basin.

SAMPLING AND SAMPLE PREPARATION

A total of 101 samples, both cores and cuttings, were obtained from oil an gas tests at locations throughout the Michigan basin. Patterns of coverage varied in each formation due to the limited availability of samples. For consistency, all samples, both cores and cuttings, were taken near the base of the formations. All cuttings samples were washed with distilled water to remove drilling mud. This was repeated as many times as was necessary to insure complete removal of the mud. The surfaces of all cores were washed in distilled water prior to crushing. All samples were allowed to dry at room temperature. Cores were crushed in a rock crusher to coarse sand size. All samples were divided into two fractions, one for titration and one for maceration. The samples to be used for titration were ground to a fine powder and passed through a 120 mesh sieve.

METHODS

Total Organic Carbon

Total organic carbon is a measure of the organic richness of a sample. The actual amount of organic matter is usually not determined because it is more difficult to measure accurately, but it is approximately 1.2 to 1.7 times the TOC content (Nixon, 1973).

There is a direct relationship between the organic carbon content of sediments and the quantities of hydrocarbons that can be generated during thermal maturation of organic matter (Demaison, 1972). Potential source rocks may be graded according to their TOC

contents by the following scale (Dow, 1977):

TOC % in shales	TOC% in carbonates	
<.5%	<.2%	marginal
.5 to 1%	.2 to .6%	fair
1 to 2%	.6 to 1.5%	good
>2%	>1.5%	excellent

method described by Gaudette (et al., 1974). The procedure is described in Appendix A. Excellent agreement of results between this method and the LECO combustion method have been demonstrated by Gaudette. This method measures the readily oxidizable organic carbon content through heat produced by chemical reaction and oxidation with potassium dichromate and concentrated H₂SO₄, and the titration of excess dichromate with 0.5N ferrous ammonium sulfate solution to a sharp one-drop end point. The results of the analysis are calculated by the following equation:

% organic carbon = 10(1-T/S)[0.336(0.003)(100/W)]

Where T = sample titration, ml ferrous solution

S = standardization blank titration, ml ferrous sulfate

0.003 = 12/4000 = mass equivalent weight of carbon

 $0.336 = \text{normality of } K_2Cr_2O_7 \text{ in ml}$

10 = volume of $K_2Cr_2O_7$ in ml

W = weight of sediment sample in grams

This equation differs from that published by Gaudette (et al., 1974)

in that the normality of the $K_2Cr_2O_7$ solution is actually 0.336 and not 1.0 as stated in the publication (D. Long, 1981, pers. comm.)¹.

Samples were randomly chosen for analysis a second or third time to test the reliability of this method. A total of 38 samples were analyzed more than once. In 25 cases the variation of results was less than 0.1%, and in five cases the variation was between 0.1 and 0.15%. In the remaining eight samples, all but one was analyzed three times. Variation between highest and lowest TOC values for these eight samples ranged from 0.20% to 0.52%. For those samples analyzed more than once, average TOC values were used. Results of TOC analyses were mapped for each formation and lines of equal TOC value were drawn.

Thermal Maturity

Samples from the formations under consideration were analyzed for their thermal maturity through color changes of organic material. This method has been described by Staplin (1969 and 1977), and is based on the color darkening of all types of biological remains as a result of temperature influence. The level of organic metamorphism is directly expressed by stages of thermal diagenesis (color change) of organic matter. The main limitation of this method is that appreciation of color changes is, to a degree, subjective. However, for this study a standard pollen and spore color chart (Figure 2) was used in order to overcome as much subjectivity as possible (Phillips Petroleum Co., 1981). In addition, a ten point scale, rather than

^{1.} Department of Geology, Michigan State University

POLLEN/SPORE COLOR "STANDARD" MUNSELL COLOR STANDARDS (MATTE FINISH)

ORGANIC FOSSIL COLOR MATURITY	TO O	LATION	HUE	VALUE	CHROMA	DOMINANT WAVE LENGTH	EXCITATION PURITY	MUNSELL PROD. NO.		
		TAI = 1-5	SCI= 1-10					. % .		
		1		7.5y	9	4	573.5	31	14,479	
		1+	1	7.5y	9	8	574	57.5	14,481	
MMATURE		2-	2	7.5y	9	10	574	68.5	12,992	
		2	3	5 y	8	12	576	82.5	13,618	
MATURE		2+	4	2.5y	8	12	579	80.5	14,253	
MAIN PHASE OF LIQUID PETROLEUM GENERATION PRESERVATIO		3-	5	10y,r	6	10	582	68.5	12,424	l
		3	6	10y,r	5	6	582	61	12,382	
		3+	7	10y,r	4		582	50	17,209	
DRY GAS		4-	8	10y,r	3		582	30	15,814A	
BARREN		4	9	10y,r	2.5		582.5	16	15,978	
		5	10							
J.										

Figure 8. Pollen/Spore Color Standard.

Staplin's five point scale was used for quantifying the color of organic matter. This scale is termed spore coloration index (SCI) as opposed to Staplin's thermal alteration index (TAI), and a comparison of the two scales and their interpretation can be seen in figure 2. A graphical representation of potential hydrocarbon type vs. maturation is shown in figure 3. In this study, thermal maturity of the Michigan formation and the Bell shale was determined on the basis of the color of terrestrial spores. The Antrim shale contained very few spores. Therefore, the color of Tasmanites, believed to be an algal cyst, which is abundant in the Antrim, was used. An attempt was made to correlate the color of Tasmanites with that of terrestrial spores to determine if there was any difference in their rates of color darkening. However, spores were not present in the Antrim in sufficient quantities to insure valid results and this attempt was abandoned. No spores were present in the other formations, as they are all Late Silurian or older. Therefore, thermal maturity was estimated for these formations on the basis of the color of amorphous kerogen.

The use of three different types of organic matter to determine thermal maturity introduces a potential for error in interpretations. The magnitude of this potential error cannot be calculated or estimated, because the relationships, with respect to color change, between the three types of organic matter are unknown. Therefore, this investigation was carried out under the assumption that the potential error was minimal, but the possibility of error should not be overlooked.

Samples were macerated and standard palynological slides were

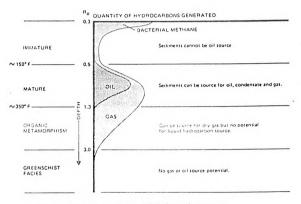


Figure 3. Variations of type of hydrocarbons as a function of thermal alteration.

prepared to study thermal maturity of the formations previously mentioned. The maceration procedure is described in Appendix B.

Slides for each sample were viewed under a Leitz Ortholux microscope. Twenty five counts were made for each sample and their SCI values recorded. The numerical average was considered to be the SCI for that sample. SCI values were plotted on maps for each formation and lines of equal SCI value were drawn.

It was noted in many samples that spores, and especially <u>Tasmanites</u>, were not equally well preserved. This often led to a wide variation of SCI values within one sample. Therefore, in order to provide as much precision and consistency as possible, only the best preserved palynomorphs were considered. This sometimes resulted in a relative sparsity of data, but it is felt that this is overcome by the more precise data that was obtained.

A surface contour map, defining what are believed to be the deepest formations in the Michigan basin capable of containing oil, was constructed from the data generated in the thermal maturity analyses. This map is based on SCI values in the Bell shale and deeper formations. SCI values for each formation were plotted on a single map and, by extrapolation, used to determine the formation in which a value of 8 would occur. It is assumed here that oil cannot exist in formations that have matured above this level. For example, a SCI value of 7.0 in the Bell shale was extrapolated downward to a value of 8 in the Salina, and a SCI value of 8.9 in the Eau Claire was extrapolated upward to a value of 8 in the Prairie du Chien.

Vitrinite Reflectance

In recent years, reflectance analysis of coal macerals has become an important technique in the study and evaluation of coals and has led to a useful and precise coal ranking scheme. It has also become a useful method of evaluating thermal maturity of potential petroleum source rocks.

Most vitrinite is the product of alteration of woody tissues, and its reflectance of incident light increases with increasing thermal maturity. Measurements are made microscopically, with reflected light amplified and measured by a photomultiplier tube which is attached to a photomultiplier indicator. The maximum reflectance value for each piece of vitrinite is recorded from a digital readout on the photomultiplier indicator as the microscope stage is slowly rotated through 360° (Stach et al., 1975).

For this study, a single coal sample was collected from an exposed Pennsylvanian coal seam at Grand Ledge, Michigan (T4N R4W Sec 3, Eaton Co.). This seam is about 50 cm thick and, in order to get as fresh a sample as possible, the sample was taken from the center of the seam after digging about 30 cm into the exposure. Two pellets were made from this sample and 25 reflectance measurements were made on each. The 50 readings were averaged to provide the mean maximum reflectance of the vitrinite macerals for this sample.

The relationships between vitrinite reflectance in oil values (R_0) , degree of thermal maturity, temperatures, and the types and quantities of hydrocarbons generated are shown in Figure 3. As seen in this figure, the transition from immature to mature sediments with a temperature history adequate for oil generation is thought to occur

at a temperature of about $150^{\circ}F$ ($65^{\circ}C$), which corresponds to a R_{O} value of 0.5% and an SCI value of about 4 (Figure 2). If reflectance values are below 0.5 and SCI values are below 4, the generation of oil within that formation is unlikely. If the temperature has been above $350^{\circ}F$ ($R_{O} > 1.3\%$ and SCI > 7) any oil initially generated would have undergone thermal cracking, and gas not oil, would be the expected hydrocarbon product. If the temperature had been such that reflectance values are greater than 3.0 (SCI = 10), even the gas would have been destroyed, and graphite would be the major carbon-containing product (Demaison, 1972).

The purposes of using vitrinite reflectance in this study are three-fold: (1) to relate, in a general sense, the $R_{\rm O}$ value of the Pennsylvanian coal to SCI values in the Michigan formation and Antrim shale; (2) to address the question of additional sedimentary cover in the Michigan basin; and, (3) to address the question of the maximum paleotemperature to which the Antrim shale has been subjected.

Geothermal Gradient

A map of present geothermal gradients in the Michigan basin was constructed using bottom hole temperatures (BHT) recorded on well logs. A gradient correction procedure was used to adjust for BHT's not being in thermal equilibrium with the true undisturbed formation temperature. This is the same correction procedure used by the American Association of Petroleum Geologists (AAPG) in their Geothermal Survey of North America project which was initated in 1968.

The following formula was used:

$$G = A_0 + A_1 D + A_2 D^2 + A_3 D^3$$

where:

G = gradient correction

D = depth

A = coefficients

For the Michigan basin the following coefficients are used:

 $A_0 = 1.0304107 \times 10^{-1}$ $A_1 = 1.4174583 \times 10^{-5}$ $A_2 = -2.5949825 \times 10^{-10}$ $A_3 = -2.6120884 \times 10^{-14}$

A linear gradient was assumed using the surface and an average annual surface temperature of 46°F (Michigan Weather Service, 1982) as one point and the BHT and the depth at which it was measured as the second point.

RESULTS OF ANALYSES

Total Organic Carbon and Thermal Maturity

Results of the TOC content analysis and the thermal maturity evaluation are combined for each formation for ease of interpretation. It was noted, especially in the Michigan formation and Antrim shale, that TOC values obtained from cores did not always fit the pattern generated by TOC values obtained from cuttings. The most probable explanation is that cuttings represent rock thicknesses of 30 to 200 feet and represent deposition over relatively longer periods of time. TOC values probably represent a fairly good average of the entire rock unit. On the other hand, core samples were usually about one inch thick (vertically) and represented deposition over a relatively short time interval. Local conditions may have been such that during this short interval of time the amount of organic matter deposited was not representative of the entire rock unit. Therefore, values from cores were not used in the contouring of TOC maps, but their locations and values have been plotted for reference. SCI values from both cores and cuttings were used in every case. The areal distribution of producing zones in the Michigan basin is provided on SCI maps for comparison.

Michigan Formation

TOC content and SCI values for the Michigan formation are plotted on Plates 1 and 2 respectively. For cuttings samples in the coverage area TOC contents range from a high of 0.53% to a low of 0.25%, with TOC content decreasing toward the center of the basin.

Evidence of the variability of TOC content at different depths in the same well is shown by the core taken from the MCG-Six Lakes 175A well (T12N R7W sec 9), which was sampled at 1257 feet and 1271 feet. The higher sample had a TOC content of 0.27% and the lower had a TOC content of 0.56%. Also, the highest TOC content of any sample was 0.75% in a core taken from a well in very close proximity to the well in which the lowest (0.25%) TOC content was found. As the Michigan formation extends beyond the 0.5% contour line, it is suggested that, based on TOC content, the most likely locations for generation of hydrocarbons is outside the contoured area.

SCI values for the Michigan formation range from a high of 5.8 to a low of 4.1, with a tendency for thermal maturity to increase toward the center of the basin. Based on the color of spores, therefore, it appears that the entire Michigan formation, with the possible exception of southern Osceola and Lake counties, has been heated to temperatures high enough to generate oil.

A comparison of Plates 1 and 2 indicate that the most likely area of hydrocarbon generation was in the southwestern Mecosta, eastern Newaygo and northern Montcalm Counties area. This area appears to have a TOC content > 0.5% and a SCI > 5.

The Michigan stray sandstone is the producing zone of the Michigan formation. Production has been mainly dry gas, although the Clare City field in Clare County has produced minor amounts of oil. The areal distribution of Michigan stray gas fields (Plate 2) shows that several of the larger fields are located in the area previously cited as most likely to generate hydrocarbons. However, other fields, specifically the Cranberry Lake, Winterfield, and Freeman Lincoln are

located in areas that, based on TOC content of the Michigan formation, are unlikely to contain hydrocarbons. Although these rocks have low TOC contents and are considered as marginally potential source beds, they are sufficiently mature to generate hydrocarbons, and may have done so. However, pay zones are relatively thin and production low throughout the Michigan stray (Michigan DNR, 1980) as might be expected from the relatively low TOC values.

Although a kerogen type analysis was not undertaken in this study, it was noted in palynological slides that most kerogen was structured. This type of kerogen is most likely to produce gas rather than oil (Staplin, 1969), which is consistent with production from the Michigan Stray.

Since most of the gas produced from the Michigan Stray is dry, the question of possible biogenic origin arises. Analysis of gas produced from the Austin Field in Mecosta County shows this gas to be 74.8% methane, 16.9% ethane with smaller amounts of propane and heavier components. Gas from the Marion field in Clare and Osceola Counties has been analyzed at 81.62% methane, 9.61% ethane, 2.86% propane with smaller amounts of heavier components (J. King, 1982, oral comm.). The fact that the gas is not entirely methane and that some oil has been produced from the Clare City field suggests that at least some of the gas is not biogenic and was probably generated in Michigan formation shales.

Antrim Shale

TOC content and SCI values for the Antrim shale are plotted on Plates 3 and 4 respectively. TOC contents of cuttings samples in the

¹ Michigan Department of Natural Resources.

Antrim range from a high of 2.61% to a low of 0.29%, with TOC content decreasing toward the center of the basin. A reversal of this trend is noted toward the northeastern and eastern flanks of the basin.

TOC contents throughout the Antrim suggest that, with the possible exception of areas of Osceola and Mecosta Counties, the entire unit was capable of generating hydrocarbons.

SCI values in the Antrim range from a high of 7.0 to a low of 4.0, with a pattern of increasing thermal maturity toward the center of the basin. A core from Newaygo County (T14N R14W Sec 5) was actually from the Ellsworth shale, but it was used in this analysis because the Ellsworth is the approximate time equivalent of the Antrim. Slides made from a core from St. Clair County (T9N R15E sec 8) contained little recognizable organic material and were not used. Based on SCI values, therefore, the Antrim, except for the eastern and southern flanks is capable of generating oil. In addition, kerogen in these slides was primarily amorphous, the type most favorable for oil generation (Staplin, 1969). A comparison of Plates 3 and 4 reveals that the Antrim was probably an excellent source for oil and gas throughout the Michigan basin.

The areal distribution of oil and gas fields in the Berea sandstone is shown on Plate 4. Important Berea oil fields are the Birch Run and Saginaw fields in Saginaw County and the Logan in Ogemaw County. The stratigraphic relationship between the Berea and the Antrim suggests that the source of hydrocarbons in these fields may have been the Antrim.

On the west side of the basin, a lentil of sandy dolomite and limestone in the Ellsworth formation produces oil and gas in Kent,

Muskegon, Ottawa, Oceana and Newaygo counties. Because it is believed to be a time-equivelent of the Berea sandstone of eastern Michigan, this unit is also referred to as Berea. These fields may have had a hydrocarbon source in the Antrim by means of vertical and lateral up-dip secondary migration of oil and gas generated in the Antrim. However, it is more likely that hydrocarbons were derived from the Sunbury or Ellsworth shales, because hydrocarbons generated in the Antrim would have had to pass through the Ellsworth to reach these fields.

The Traverse Group (see Plate 4) has been a major producer of oil throughout southwestern and western Michigan as well as in the central basin area. Gas has been an important by-product in several western Michigan oil fields. It is suggested here that the Antrim may have been the source of hydrocarbons in the central basin fields from above and the western fields through lateral up dip migration from the central basin areas.

Bell Shale

TOC content and SCI values for the Bell shale are plotted on Plates 5 and 6 respectively. TOC contents of cuttings samples range from a high of 0.52% to a low of 0.15%, with TOC content decreasing toward the center of the basin. A reversal of this trend is noted toward the north side of the basin. TOC values of cores tend to fit this pattern very well. Based on TOC content, the most likely areas of hydrocarbon generation are along a thin east-west band between 0.50% contours from Arenac through Wexford counties and southward through Lake and Newaygo counties. The area south of the 0.50 contour line from Barry to St. Clair County may also be favorable.

SCI values in the Bell shale range from a high of 7.8 to a low of 5.7, with thermal maturity generally increasing toward the center of the basin. Slides made from a core from Shiawassee County (T5N R2E SEC 23) contained few recognizable palynomorphs and were not evaluated. The pattern indicates that the entire rock unit, based on thermal maturity, was capable of generating oil and that the area within the 7.0 contour has reached the post-mature stage, and may have generated gas as a primary product, as well.

Comparison of Plates 5 and 6 show that the area of highest thermal maturity roughly corresponds to the area of lowest TOC content. Therefore, although the rocks were heated to high enough temperatures, this area is an unlikely source for hydrocarbons. The most likely areas that may have produced hydrocarbons are those based on TOC content mentioned above.

Plate 4 also shows many Traverse oil fields in western and southwestern Michigan. It is possible that the source of the hydrocarbons in these fields, as well as several fields in Missaukee, Roscommon and Gladwin counties, was through vertical migration of oil generated in the Bell shale.

The areal distribution of oil fields in the Dundee limestone (Plate 6), reveals that many of these fields are located in the central basin below the area enclosed by the 7.0 SCI contour line. As this area of the Bell shale also has a low TOC content, it appears that the source of hydrocarbons in these fields was not the Bell. Oil in these fields was most likely generated by the same rocks in which it is found, or by vertical migration from deeper source rocks. However, a large number of oil fields exist to the west, north and

northeast of the central basin, the hydrocarbons of which may have been from the Bell through lateral up dip migration.

As there is a fairly large area of the Bell shale (within the 7.0 contour) that, according to organic coloration, appears to have reached the post-mature stage, the question of how hydrocarbons continue to exist in the oil phase below this area arises. First, the oil-death line is not a line, but a zone. It is in this zone that thermal cracking takes place, converting larger hydrocarbon molecules to smaller ones. Also, a SCI value of 7 does not represent the deepest depth at which oil can exist, but, rather, the base of the zone of peak oil generation. Oil may be generated and may accumulate in this zone, but it would be expected to have undergone some thermal cracking and to have a relatively high API gravity of between 40° and 60° (D. Pearson, 1982, oral comm.). This is, in fact, the case with oil in the Dundee limestone in the central basin area. For example, oil from the Coldwater field (Tl6N R6W) has an API gravity of 48° (Michigan DNR, 1980). Other fields in this area contain similar oil, and there is a tendency for API gravity to increase toward the center of the basin.

Plate 8 shows the distribution of Detroit River oil fields.

Three fields, the Reed City, Cedar, and Fork are located below the

7.0 SCI contour area of the Bell shale. Detroit River producing

zones in these fields are about 1200 feet below producing zones in

the Dundee. API gravity in oil produced from these zones ranges from

44.7° in the Cedar field to 54.8° in the Fork field (Michigan DNR,

1980). These figures indicate that some thermal cracking may have

taken place and that this zone is near the base of the "oil window"

There are no known oil reservoirs in the Michigan basin below these producing zones in Lake, Osceola, Mecosta, Montcalm or Isabella counties.

C Shale

plotted on plates 7 and 8, respectively. Titration of cuttings samples yielded TOC values from a high of 2.1% to a low of 0.04%. However, several samples, identified with the notation H₂SO₄ Rx on plate 11, reacted very strongly to the addition of H₂SO₄. Visual analysis revealed that these samples were primarily evaporites and, although identified as C Shale on driller's logs, actually contained little, if any, shale. Therefore, the results of TOC determination for these samples are considered invalid and they are not used. Of the remaining samples, the highest TOC content was 0.26%. The pattern developed from the results is vague, but it may show a weak tendency toward a decrease of TOC content toward the center of the basin. In any event, TOC content is low throughout the unit, and there appears to be little likelihood that hydrocarbons were generated in the C Shale.

No spores and little amorphous kerogen was observed in palynological slides made from these samples. However, estimates of thermal maturity, based on color of amorphous material, are shown on Plate 8. No discernible pattern appears, except for slightly higher values in the northern and southern parts of the basin. Results of this analysis are not considered to have any degree of accuracy, because the standard color chart is not generally applicable to evaluating the color of amorphous kerogen (D. Pearson, 1982, oral

comm.). It may, however, give additional insight into the depth limits of liquid hydrocarbon accumulation. There is no control in the central basin area, but it appears that oil can exist in the Salina throughout much of the basin. The locations of Salina and Niagaran fields (Plate 8) show that this is indeed the case. Plate 9, Michigan oil and gas fields, 1980, shows the location of Salina-Niagaran fields along the northern reef trend from Mason to Presque Isle Counties. These fields are prolific producers of oil and gas and are certainly within the oil window.

Utica Shale

TOC contents and SCI values for the Utica shale are plotted on Plates 10 and 11 respectively. Titration of cuttings samples yielded TOC values from a high of 0.43% to a low of 0.15%. Coverage is sparse and TOC values are low, but oil may have been generated in the southwest and southeast corners of the state, areas in which TOC content tends to increase.

A core taken from the Shell-Taratuta #1-13 well in Presque Isle County had a TOC content of 1.87%. Although it may not be representative of the entire unit, it does indicate the possibility of increased organic content toward the northeastern part of the basin.

SCI values in the Utica shale appear to have a slight tendency to increase toward the center of the basin and indicate that the entire formation is near the base of the oil window. However, it must be kept in mind that results of this analysis are tenuous, since it is based on the color of amorphous kerogen. One exception to this

is the sample from Presque Isle County, in which all organic material was black. This area is definitely below the oil window, supported by the fact that the Shell-Taratuta #1-13 well, which penetrated the Trenton-Black River, resulted in a dry hole.

Plate 11 also shows the areal distribution of oil fields producing from the Trenton-Black River group. This group lies immediately below the Utica shale, and all production is confined to the southern and southeastern flanks of the basin. Major production from the Trenton-Black River is from the Albion-Pulaski-Scipio trend field in Calhoun, Jackson and Hillsdale Counties (Michigan DNR, 1980). A large gas cap in these pools may indicate that some thermal cracking has taken place and that they are in the transition zone near the base on the oil window. Based on TOC contents in the Utica shale in this area, it is unlikely that the source of hydrocarbone in this field was the Utica.

Eau Claire Shale

TOC contents and SCI values for the Eau Claire shale are plotted on Plates 12 and 13, respectively. Coverage was sparse and TOC contents were low in all cases. Results of this analysis are inconclusive, but it appears that the Eau Claire did not generate hydrocarbons in the areas sampled.

Evaluation of thermal maturity in the Eau Claire was based on color of amorphous material and was also inconclusive. However, it does appear that most, if not all, of the Eau Claire is in the post-mature stage, and reservoired oil is unlikely.

The Eau Claire is Late Cambrian in age, and there is no oil or

gas production from rocks of this age in the Michigan basin. Small amounts of oil have been produced from the Prairie du Chien group (Early Ordovician) in southern Michigan (see Plate 11) and gas has been produced from the Prairie du Chien in Missaukee County but, based on TOC contents, it is unlikely that the Eau Claire was the source of either.

Precambrian

The only available samples from Precambrian rocks were cores from three locations. TOC contents and SCI values are plotted on Plates 14 and 15 respectively. Results in both cases are inconclusive, but these rocks are definitely below the oil window in Gratiot and Wayne counties. The core from Branch County, described as a meta-shale on the drillers log, contained no organic material, and nothing was learned from it.

Present Geothermal Gradients

The present average geothermal gradients in the Michigan basin are shown in Plate 16. Gradients vary throughout the basin and range from a high of 1.74°F./100 ft (T17N R1E SEC 3) to a low of 0.90°F/100 ft (T6N R6W SEC 22). At these geothermal gradients, oil is capable of existing at any depth in the basin above the Precambrian and well into the Precambrian in most areas. For example, where the geothermal gradient is 1.74°F/100 ft, the temperature will reach 350°F (the "oil death line") at a depth of about 17,470 feet. The deepest exploratory well drilled in Michigan, 17,466 feet, was the McClure-Sparks et al. #1-8 well in Gratiot County (T10N R2W SEC 8).

This well, south of the central basin area, penetrated the Precambrian at a depth of 12,176 feet (-11,414 feet with respect to sea level).

Plate 17 is an isotherm map showing the temperatures at the top of the Traverse formation. This map was constructed from the geothermal gradient information (Plate 16) and clearly demonstrates that oil is capable of existing in the Traverse at any location in the basin.

For reference, a generalized structure contour map on the top of the Traverse formation (the base of the Antrim) was constructed (Plate 18). Comparison of Plates 17 and 18 demonstrates the influence of depth on temperature.

As previously noted, the base of the oil window in the central basin is probably just below the Detroit River Group, where these rocks were at one time subjected to temperatures of about 350°F. The deepest producing zone in this area is the Detroit River group at 5060 feet in the Cedar Field (Michign DNR, 1980). At the present geothermal gradient in this area (1.5°F/100 ft) the static formation temperature in the rocks is about 122°F. In order for these rocks to have been subjected to temperatures of 350°F, there must have been (1) additional overburden, (2) a higher geothermal gradient, or (3) a combination of both. At the present geothermal gradient, and assuming the same mean annual surface temperature of 46°F, the overburden required to bring these rocks to 350°F would be 20,267 feet, 15,207 feet more than at present. At their present depth, a 350°F. temperature would require a geothermal gradient of about 6°F/100 ft. If a paleogeothermal gradient of 3°F/100 ft is assumed,

the additional overburden required would be about 5100 feet. This question will be explored further in succeeding sections.

Vitrinite Reflectance

Vitrinite reflectance measurements were made on a single Pennsylvanian coal sample from Grand Ledge, Michigan (Figure 4). This analysis yielded a mean maximum reflectance (R_0) of 0.541%, giving this coal a high volatile "C" bituminous rank (Hood et al., 1975).

Figure 5 shows the relationship between several organic metamorphism scales. A R_O value of 0.541% corresponds to an SCI value of between 4 and 5. The location of Grand Ledge is shown on Plate 2, and extrapolation from the 5.0 SCI contour line indicates that the Michigan formation in the Grand Ledge area would be expected to have a SCI value of about 4.0 to 4.5. The Michigan formation lies 200 to 300 feet below Pennsylvanian sediments in the Grand Ledge area. Therefore, it would not be expected that there would be much difference in thermal maturity between Pennsylvanian sediments and sediments in the Michigan formation, and it is concluded that SCI values in the Michigan formation correlate fairly well with vitrinite reflectance of this coal sample. In addition, SCI values for the Antrim shale, which lies about 2100 feet below the surface at Grand Ledge are about 5.5 (see plates 4 and 18) which also correlates fairly well with the vitrinite reflectance value.

The presence of coal at the surface implies the former presence of additional sedimentary cover. One way to estimate the additional amount of sedimentary cover is to use the vitrinite reflectance value

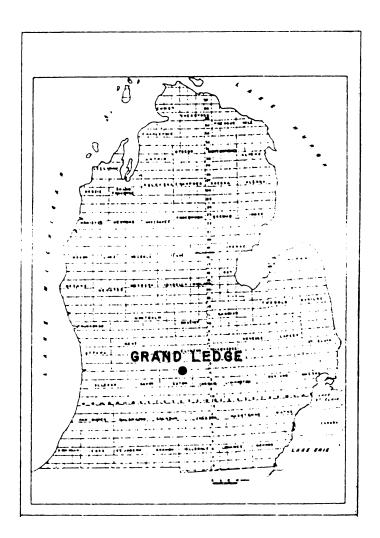


Figure 4. Location of Grand Ledge, Michigan.

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Figure 5. Some organic metamorphism scales (modified after Hood, Gutjahr, and Heacock, 1975).

to determine the maximum temperature to which the coal sample has been subjected and then, using a reasonable geothermal gradient, extrapolate to the surface. Coal rank, as well as thermal maturity of sediments, depends not only on the maximum temperature to which the coal was heated but also on the amount of time it was heated.

Karweel (1956), used a thermal chemical reaction rate of 8.4 kcal/mole for the coalification process to determine the effect of time and temperature on the degree of organic metamorphism.

Hacquebard and Donaldson (1970) modified Karweil's graph (Figure 6) to include vitrinite reflectance and the system of coal classification employed by the American Society for Testing and Materials (ASTM). According to this graph, the coal sample used in this study was heated to a temperature of 135°C (275°F) for a period of 10 MY to achieve its present rank. Alternatively, a heating period of 50 MY yields a temperature of about 85°C (185°F) and a period of 100 MY yields a temperature of about 55°C (131°F).

Hood (et al., 1974) developed the Level of Organic Metamorphism (LOM) scale (see Figure 5) which included the effects of both time and temperature on organic metamorphism. According to this figure, the coal used in this study has a LOM value of about 7.7. Figure 7, based on data from boreholes and rocks of known burial history, shows the relationship of LOM to maximum temperature with respect to effective heating time. Cordas (1978) modified the figure to include a LOM value of 8 (dotted line in Figure 7). Based on this figure the coal sample in this study would have been subjected to a maximum temperature of about 50°C if the heating time was 10 MY. Longer periods of heating time result in lower maximum temperatures.

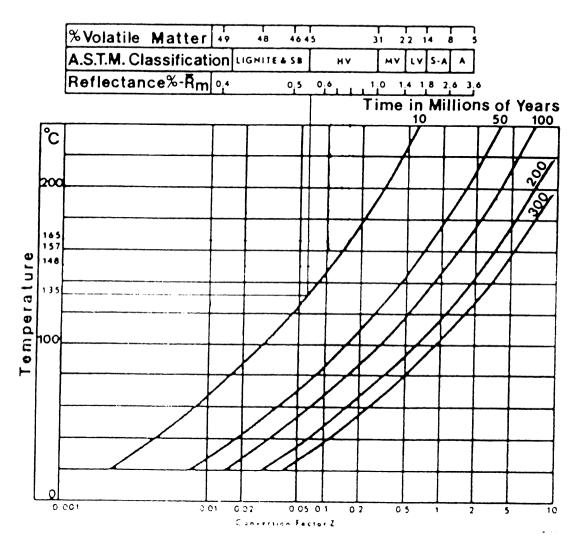
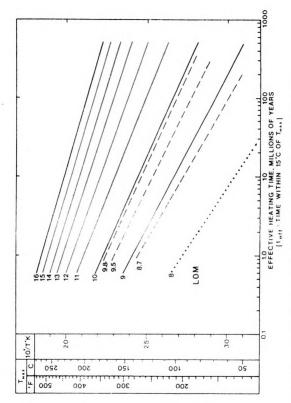


Figure 6. Relationship between rank, temperature and time, and the plot of the Grand Ledge coal sample (from Hacquebard and Donaldson, 1970, after Karweil, 1956).



Relationship of maximum temperature to LOM and effective heating time (from Cordas, 1978, modified after Hood, Gutjahr, and Heacock, 1975). Figure 7.

Cordas (1978) used vitrinite reflectance to study Permian coals in the Parana Basin, Brazil. One of his samples has a R_0 of 0.541%, the same value as the sample used in this study. Using five different methods developed by various investigators, and assuming a 10 MY heating time, he concluded that this sample was subjected to a maximum temperature of 95°C (203°F). The actual range of estimates was 50°C (Hood et al., 1975) to 135°C (Hacquebard and Donaldson, 1970). The three other estimates ranged from 87°C to 105°C.

Obviously, there is much controversy among various investigators regarding the time-temperature relationship in organic metamorphism, and this question will not be pursued further here. However, based on the study of the coals in the Parana basin, and on the older age of the Pennsylvanian coal, it seems reasonable to assume that the coal sample in this study was subjected to a temperature of about 70°C (158°F). This is slightly higher than the minimum temperature thought to be required for oil generation, and correlates well with thermal maturity of sediments in the Michigan formation and the Antrim shale. Assuming this temperature to be correct, and assuming the present mean annual surface temperature of 46°F, what remains is to estimate a paleogeothermal gradient. For this purpose, the relationship between SCI values at various depths in the McClure-Sparks et al #1-8 well may provide a clue.

Thermal Maturity vs. Depth in the McClure-Sparks et al #1-8 Well

SCI values of formations in the McClure-Sparks et al # 1-8 well are given in Table 1. A plot of these values vs. depth in this well shown in Figure 8. Several investigators have shown that there is an

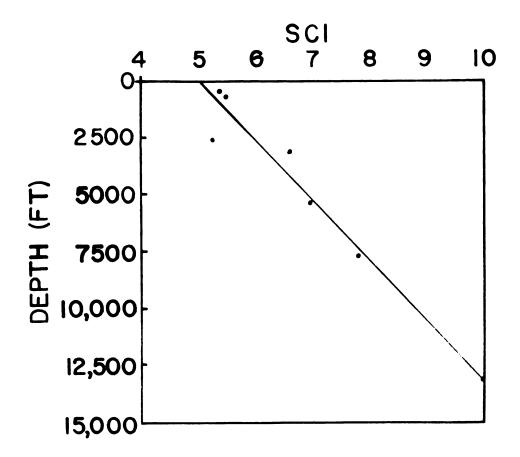


Figure 8. SCI vs. depth of samples from the McClure-Sparks et al #1-8 well.

Table 1. Thermal maturity in the McClure-Sparks et al #1-8 well.

Formation	Depth	SCI
Saginaw	400-470	5.4
Michigan	670-700	5.5
Antrim	2520-2600	5.3*
Bell	3095-3135	6.6
C Shale	5430-5500	7.0
Utica	7600-7700	7.8
Precambrian	13,417	10

*SCI for this sample was rechecked twice. This low value may be the result of an abundance of poorly preserved <u>Tasmanites</u> or it may be due to the experimental error inherent in the method. A nearby sample from the Antrim (T10N R3W Sec 6) had a SCI of 6.4.

Table 2. SCI values and corresponding temperatures.

SCI	Temp (°F)
4	150
5	217
6	283
7	350

exponential relationship between the reflectance of vitrinite and depth of burial (Costano and Sparks, 1974; Dow, 1978). However, the upper end of the scale approaches linearity, and linearity is assumed in this study. The following is not intended to be definitive of a paleogeothermal gradient but, rather, to estimate what a reasonable geothermal gradient might have been. Assuming a linear relationship between SCI and depth, the method of least squares (Swartz, 1973) yields a slope of 1.06 for the line of best fit, which indicates that SCI changes by a factor of one unit for each 2650 feet of depth (see appendix C for calculations). SCI values of 4 and 7 correspond to temperatures of 150°F and 350°F respectively (Figure 3). If there is a linear relationship between these values, each increase of one SCI unit represents an increase of 67°F (Table 2). Therefore, an increase of 67°F for each 2650 feet corresponds to a paleogeothermal gradient of 2.53°F/100 ft.

Figure 8 indicates that rocks at the surface would be expected to have a SCI of about 5, corrsponding to a maximum temperature of 217°F. Assuming the present surface temperature and a geothermal gradient of 2.53°F/100 ft. these rocks must have been buried to a depth of about 6760 feet to reach their present level of thermal maturity. Making the same assumptions, the coal at Grand Ledge must have been buried to a depth of about 4425 feet to reach its present rank. Therefore, it is concluded that the Michigan basin may once have had an additional sedimentary cover, and the amount of this cover may have been between 4000 and 7000 feet.

Temperature of the Antrim Shale

It has altready been shown, by the thermal maturity of organic material, that the Antrim shale is sufficiently mature to have generated oil. Therefore, it must have been heated to a temperature of at least 150°F (65°C). However, other evidence (Nunn, 1981) suggests that only Middle Ordovician and older rocks in the Michigan basin have been heated to high enough temperatures to generate liquid hydrocarbons. In order to address this inconsistency, an estimate of the maximum temperatures to which the Antrim shale was subjected is warranted.

Hathon (1979) studied the origin of authigenic quartz in the Antrim and estimated a maximum temperature in the Antrim of 50°C (122°F). This estimate was based on a vitrinite reflectance value of 0.46% in a sample of the Antrim shale from Alpena County. He equated this value to a LOM of 7.3 (figure 5) and made his temperature estimate from Hood's (et al., 1975) unmodified graph (figure 7). Estimates of temperatures from LOM values below 9 on this graph appear to be unreliable (Cordas, 1978). Therefore, Hathon's estimate may be low.

Wardlaw (1981) studied the origin of carbonate concretions in the Antrim shale in the same area as Hathon's (1979) study. Based on oxygen isotope analysis, she concluded that the minimum temperature of the precipitating pore fluids was 83°C (181°F). Evaluation of this analysis is not made here, but the results are presented to show independent evidence that the Antrim shale was sufficiently heated to generate oil.

The Grand Ledge coal sample used in this study was estimated to

have reached a temperature of about 158°F (70°C). The Antrim shale lies about 2100 ft (640 m) below the surface in this area. Applying the geothermal gradient of 2.53°F/100 ft (4.554°C/100m) the Antrim would have reached a temperature of 211°F (100°C) in this area. The present geothermal gradient at Grand Ledge (see Plate 16) is about 1.2°F/100 ft (2.16°C/100 m). Applying this figure, the Antrim would have reached a temperature of 183°F (84°C).

Based on the above, it is apparent that the Antrim shale was heated to high enough temperatures to generate liquid hydrocarbons, and that Nunn's (1981) conclusions regarding the generation of oil in the Michigan basin are incorrect.

Base of the Oil Window

It has already been shown that, based on today's geothermal gradients, oil may exist down to the Precambrian at any location in the Michgian basin. However, analysis of the thermal maturity of organic material throughout the basin indicates otherwise.

Plate 19 is a surface contour map showing the deepest formations, based on thermal maturity data, in which oil can exist at any location in the Michigan basin. This map is based on the assumption that oil will be degraded in formations where SCI values are above 8. Gas, however, may exist below these formations.

The maximum depths at which gas can exist in the Michigan basin cannot be determined from the data available. However, the SCI of the Utica shale (see plate 11) in the Shell Taratuta #1-13 well (T33N R5E SEC 13) indicates that even gas may have been degraded below the Utica in that area. It is also likely that deeper formations in

Mecosta and Isabella Counties are barren of gas.

Construction of this map was based primarily on extrapolation of SCI data from several formations. As most of these data were determined from color of amorphous kerogen, the results are tenuous. However, the results do conform to the location of known oil fields and it is believed to be a good approximation of the base of the oil window in the Michigan basin.

DISCUSSION

It was noted in the previous sections that TOC concentrations in each formation had a tendency to decrease toward the center of the basin. Studies of other basins (Nixon, 1973 and Dow, 1974) show increases of TOC to a maximum in the central basin. Plates 3 and 5 shown that there is actually a reversal in the general trend toward the flanks of the basin in the Antrim and Bell shales. In these formations, TOC concentrations increase away from the central basin and then decrease toward the flanks. Interpretation of these observations involve consideration of the source of organic material and the depth of wave base.

Organic material is deposited in sedimentary basins in the same way as any other type of sediment. Coarse material is deposited closer to its source in relatively high energy environments. Fine material, capable of remaining in suspension longer, is carried farther from its source and deposited where currents are no longer strong enough to carry it. Therefore, it would be expected that most terrestrially derived organic matter would be deposited close to its source, with finer material carried a greater distance to relatively low energy environments. Clay minerals, being finer than most organic materials, and of a platy nature, would remain suspended longer and be carried farther from the shoreline. Coarse material, deposited in near-shore locations above wave base, would be subjected to oxidation, resulting in less preservation and lower TOC concentrations. This would result in a pattern of increasing TOC concentrations away from the shoreline where energy is highest to a maximum in the area below wavebase. Thereafter, concentrations would decrease toward the central basin in response to the decreasing amounts of organic material that were deposited.

Marine organisms tend to be most abundant in areas of upwelling, which provides the nutrients necessary to sustain life (Demaison, 1972). These areas are nearshore, and as these organisms die and fall to the bottom those deposited above wave base will be oxidized, winnowed and destroyed. Those deposited in areas below wave base will be better preserved. The pattern of TOC concentration would be similar to that of terrestrial organic material, with lower concentrations in areas above wave base, higher concentrations in areas immediately below wave base and decreasing concentrations toward the central basin. These interpretations are diagrammed in figure 9.

The above interpretations are consistent with observations in the Antrim and Bell shales, and it is suggested that these are the most likely explanations of the TOC patterns generated. However, this explanation is a broad generalization and doesn't consider such factors as location of deltas or lagoons, where organic concentrations would be highest. It is presented only as a possible explanation for the TOC patterns observed. In addition, as the epeiric seas at the time of Antrim and Bell deposition were shallow, upwelling may not have been a factor in concentration of marine organisms. Sufficient data is not available from other formations to determine if these interpretations may also be applied to them.

An alternative explanation of the TOC patterns observed may be that larger amounts of hydrocarbons were generated and expelled from rocks in the central basin, thus reducing the residual TOC content. However, even under favorable conditions (high organic content and

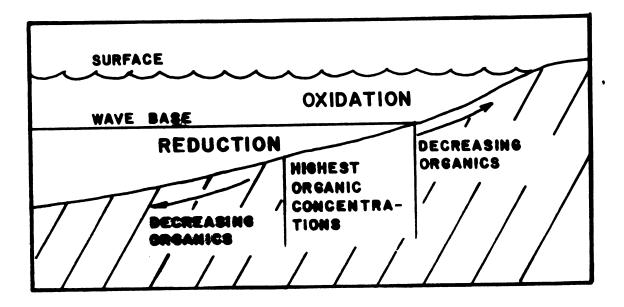


Figure 9. Interpretation of TOC distribution in the Antrim and Bell shales.

required temperature for hydrocarbon generation), only a small percentage of the organic matter present is converted into hydrocarbons and only a small percentage of that is expelled from the source rock. It is unlikely, therefore, that TOC content would be reduced enough to explain the patterns observed. Nothing was found in the literature addressing this question.

SCI data in each formation shows a pattern of generally increasing thermal maturity toward the central basin area. This is to be expected since the central basin was buried deepest and, therefore, subjected to the highest temperatures. Plates 17 and 18 show that this is, indeed, the case in the Traverse formation today. The only exception to this pattern seems to be in the northeast area of the basin, where SCI values in the Utica shale are 9 to 10. The reason for this inconsistency is unknown. However, it may indicate the presence of a mantle hot spot or local igneous activity.

It has been shown that the Michigan basin probably contained between 4000 and 7000 feet of additional overburden at one time. Similar conclusions were reached by others (Price, 1976 and Nunn, 1981). The time that this additional sedimentary cover was present is unknown. Peak oil generation in the Michigan basin would have coincided with its presence, since the Michigan formation and Antrim shale would not otherwise have been buried deep enough to attain the temperatures required to generate hydrocarbons. No attempt is made here to determine the time of peak oil generation, because the complete burial history of the Michigan basin is unknown. Only a provenance study in areas that may have received sediments from the former overburden could resolve this question.

CONCLUSIONS

Based on total organic carbon and thermal maturity data, the following are the most salient conclusions reached in this study:

At least some parts of all formations studied have been heated to high enough temperatures to generate oil and some may have been subjected to temperatures high enough to generate gas as a primary product. This conclusion is supported by vitrinite reflectance of the Grand Ledge coal.

The presence of wet gas and minor amounts of oil in the Michigan stray sandstone suggests that at least some of the gas is not of biogenic origin and was probably generated in Michigan formation shales.

Total organic carbon content indicates that the Antrim shale was the formation most likely to have generated the largest amounts of hydrocarbons, and was probably an excellent source for oil and gas thorughout the Michigan basin. The Antrim was probably the source for many of the oil and gas fields in the Traverse group.

Total organic carbon content is low throughout the C Shale, and it is unlikely that hydrocarbons were generated in this unit.

In general, the Utica shale does not appear to have been a good source for hydrocarbons, but oil may have been generated in the southwest and southeast corners of Michigan. It is unlikely that the Albion-Pulaski-Scipio field was sourced by the Utica.

Data was sparse in both the Eau Claire shale and the Precambrian sediments, but it is unlikely that hydrocarbons were produced by either in the areas sampled.

At the present geothermal gradients in the Michigan basin, oil

is capable of existing at any depth down to the Precambrian.

However, thermal maturity of organic material indicates that

paleogeothermal gradients were higher and that there is a base of oil

accumulation, which is defined by Plate 19. The deepest formation

capable of containing oil at the Mecosta-Isabella county line is the

Dundee limestone. Outward from this area older formations are

capable of containing oil. This trend reverses toward the north and

northeast where it appears that the Salina is the deepest formation

capable of containing reservoired oil.

With the possible exceptions of deeper formations in the northeastern and Mecosta-Isabella county areas, gas can exist at any depth in the Michigan basin. Sufficient data is not available to define the deepest formations which may contain reservoired gas.

The Michigan basin probably once contained between 4000 and 7000 feet of additional sedimentary cover. The time of its presence is unknown.

The maximum temperature to which the Antrim shale was subjected was probably between 84°C and 100°C (183°F - 211°F) at Grand Ledge and may have been higher in the center of the basin.



APPENDIX A

TITRATION PROCEDURE

Between 0.2 and 0.5 grams of the sediment sample is placed in a 500 ml Erlenmeyer flask. 10 ml of the K₂Cr₂O₇ solution is added and mixed by swirling the flask. 20 ml of concentrated H₂SO₄ is then added and mixed by gentle rotation of the flask for one minute. The mixture is allowed to stand for 30 minutes. A standardization blank without sediment is run with each new batch of samples. After 30 minutes, the solution is diluted to 200 ml volume with distilled water. 10 ml of 85% H₃PO₄, 0.2 grams of NaF, and 15 drops of diphenylamine indicator are then added to the sample flask. The solution is back-titrated with 0.5N ferrous ammonium sulfate solution. The color will progress from an opaque green-brown to green upon addition of about 10 ml and continue to shift to a bluish-black-grey. At this point, the addition of 10 to 20 drops of ferrous solution will shift the color to a brilliant green giving a one-drop end point (Gaudette et al., 1974).

APPENDIX B

MACERATION PROCEDURE

Approximately 5 grams of dried sediment sample are placed in a 250 ml polyurethane flask. About 100 ml of 10% HCl is added to dissolve the carbonates. The sample is stirred and allowed to settle for about 12 hours. Additional HCl is added to insure all carbonates are dissolved. When there is no further reaction to the HCl, the solution is diluted with distilled water and allowed to settle. This step is repeated two more times, each time siphoning off the solution. About 50 ml of 48% HF is then added to dampened sediment to dissolve the silica. The mixture is stirred and allowed to stand for 12 to 24 hours, and more HF is added. After an additional 24 hours, distilled water is added and the sediment allowed to settle. The solution is then decanted into an HF waste container. This step is repeated two more times to insure that all HF has been safely disposed. The final time the solution is siphoned off. No bleaching treatments are used, as these would alter the color of organic material. The sediment is then filtered through a 15 micron screen to remove as much clay as possible. The remaining sediment is put into one dram vials in a solution of Hydroxyethyl Cellulose (HEC) until palynological slides are prepared.

APPENDIX C

Least squares calculation of rate of SCI increase with depth.

No.	Formation	x	<u>y</u>	$\underline{\mathbf{x}^2}$	<u>ху</u>
1	Saginaw	5.4	0.188	29.16	1.0152
2	Michigan	5.5	0.28	30.25	1.54
3	Antrim	5.3	1.04	28.09	5.512
4	Bell	6.6	1.254	43.56	8.2764
5	C Shale	7.0	2.2	49	15.4
6	Utica	7.9	3.08	62.41	24.332
7	Precambrian	10	5.3668	100	53.668

Total 47.7 13.4088 342.47 109.7436

where x = SCI

$$y = depth (1y = 2500 ft)$$

y = mx + b (linear relationship)

$$m = \frac{k + (x_1y_1) - x_1 + y_1}{k + x_1^2 - (x_1)^2}, \text{ where } k = \text{number of samples}$$

$$m = \frac{(7)(109.7436) - (47.7)(13.4088)}{(7)(342.47) - (47.7)^2} = 1.06$$

The slope of the line of best fit = 1.06. Since each depth unit = 2500 ft, SCI increases by one unit for each 2650 ft of depth. $(1.06 \times 2500 \text{ ft} = 2600 \text{ ft})$.

$$b = \frac{x_{i}^{2} \quad y_{i} - x_{i} \quad x_{i}^{2}}{k \quad x_{i}^{2} - (x_{i})^{2}}$$

$$b = \frac{(342.47)(13.4088) - (47.7)(109.7436)}{(7)(342.47) - (47.7)^2} = -5.268$$

when
$$x = 5$$
, $y = (1.06)(5) - 5.268 = 0.032$

when
$$x = 9$$
, $y = (1.06)(9) - 5.268 = 4.272$

APPENDIX D

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
SAGINAW	SAGINAW FORMATION					
1-S	29739	Cuttings	McClure-Sparks et al #1-8 TION R2W Sec 8	400-470		5.4
MICHIGAN	MICHIGAN FORMATION					
1 –M	30884	Core	MCG-NH 162A TION R4W Sec 4	957	0.49	2.0
2-M	31497	Core	MCG-Six Lakes 175A Ti2N R7W Sec 9	1271	0.56	2.0
2a-M	31497	Core	MCG-Six Lakes 175A T12N R7W Sec 9	1257	0.27	5.6
3-M	31530	Core	MCG-Six Lakes 217A Ti3N R7W Sec 34	1235	0.27	5.8
W-7	26447	Core	MCGC-Herring #1 T13N R10W Sec 5	1155	0.51	5.8
5-M	24239	Core	Sun-Yake #1 T20N R4W Sec 20	1499	0.54	6. 8
W-9	25995	Core	MGSC 831 T20N R6W Sec 4	1417	0.39	2
7 – M	25462	Core	MGSC 831 T20N R6W Sec 7	1341	0.75	5.2

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
MICHIGAN	MICHIGAN FORMATION					
₩-8	15387	Cuttings	Basin-Badour #1 T14N R6E Sec 15	245–260	0.50	4.6
₩ - 6	10639	Cuttings	Cities-Methner #B-1 T16N R3W Sec 33	980-1010	0.35	5.2
10-M	11582	Cuttings	Taggart-McCormick #1 T17N R8W Sec 9	1190-1210	0.51	4.1
11-M	3815	Cuttings	Ide-Cooley #1 T10N R4W Sec 3	915-940	0.35	8 • 4
12-M	7770	Cuttings	Taggart-Wooden-Baugham #30 T20N R6W Sec 19	1379-1387	0.25	4.7
13-M	10595	Cuttings	Gordon-DeKraker #1 T21N R6W Sec 34	1400-1420	0.35	5.0
14-M	8775	Cuttings	Union-Newland #1 T20N R4W Sec 19	1525-1540	97.0	5.1
15-M	26002	Core	MGSC-MGSC #972 T 19N R7W Sec 12	1453-1543	0.58	5.0
16-M	11394	Core	SOHIO-Hoffman #2 T16N R6W Sec 29	1412	0.62	5.7
17-M 29739	739	Cuttings	McClure-Sparks et al #1-8 T10N R2W Sec 8	002-029	0.53	5.5

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
ANTRIM SHALE	HALE					
1-A		Core	Dow-Rover #102 T9N R51E Sec 1	1458	0.23	
2-A	9582	Core	Pure-Nix #1 T23N R5W Sec 11	2462	0.24	0.9
3-A		Core	Jennings-Vanderlay #1-15 T14N R14W Sec 5	1622(E11s.)	0.19	4.5
4-A	11597	Cuttings	Riddell-Trautner #1 Tl3N R4E Sec 20	2277-2315	1.13	5.1
5-A	10639	Cuttings	Cities-Methner #B-1 T16N R3W Sec 33	2955-2970	1.03	5.6
6-A	11995	Cuttings	Ohio-Mio Unit Area #1 T25N R3E Sec 30	1870-1900	1.19	5.8
7-A	13632	Cuttings	Sun-State-Secord #A-1 T19N RIE Sec 9	2217–2250	1.61	5.6
8-A	8482	Cuttings	Drake-Gladstone #1 T10N R3W Sec 6	2490-2520	0.74	9. 9
9-6	16690	Cuttings	Hook-McClear #1 TIN R3E Sec 28	1177-1198	1.21	4.8
10-A	8270	Cuttings	Bridger-Basin-Harden #1 T2N RllW Sec 7	1530-1558	2.61	4.3

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
ANTRIM SHALE	HALE					
11-A	10936	Cuttings	Sinclair-McIntyre #1 T9N R9E Sec 28	1759-1790	1.64	5.4
12-A	3298	Cuttings	Columbia-Satterlee #1 T13N R8W Sec 24	s690-2733	0.39	8.9
13-A	10661	Cuttings	Hilliard-Fox-Larson #1 T22N R10W Sec 24	27772-2808	0.97	4.5
14-A	16734	Cuttings	Cities-Cities #1 T6N R9W Sec 12	1960–1975	1.45	6.3
15-A	9897	Cuttings	Sun-Rice #1 T17N R8W Sec 15	8904-8933	0.29	7.0
16-A	10792	Cuttings	Chamness-Roddenberry Comm. #1 IIS R7E Sec 27	748-777	1.29	4.1
17-A	30974	Cuttings	McClure-Hewett et al #1-20 T12N R15E Sec 20	1025-1230	1.09	6.4
18-A	29739	Cuttings	McClure-Sparks et al #1-8 T10N R2W Sec 8	2520-2600	1.03	5.3
BELL SHALE 1-B	<u>LE</u> 13816	Core	Sun-Bradley #4 T12N R13W Sec 11	2750	0.62	8.9

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
BELL SHAI	BELL SHALE (cont.)					
2-B	26799	Core	MCGC-Shuttleworth #1 T10N R4W Sec 5	3242	0.28	9•9
3-B	12376	Core	Pure-Mulder #1 T17N R6W Sec 18	3885	0.35	7.5
4-B	27390	Core	Benedum-Corlew #1 T19N R5W Sec 3	4001	0.73	6.9
5-B	27191	Core	MCGC - Reiman #1 T17N R9W Sec 4	3708	0.38	7.4
6-B	16738	Core	PEPL - Nemcik #1 T5N R2E Sec 23	1750	0.35	
7-8	10572	Core	Bolger-State-Adams #1 T19N R3E Sec 14	2896	0.53	5.7
8-B	10511	Cuttings	Gulf-Lassiter #1 T13N R9E Sec 5	2725-2740	0.29	6.3
8-6	17892	Cuttings	Strickler-State-Clearwater #1 T27N R5W Sec 27	2707-2742	0.23	6.8
10-B	10661	Cuttings	Hilliard-Fox-Larson #1 T27N R5W Sec 27	3605-3624	0.52	6.8
11-B	2686	Cuttings	Sun-Rice #1 T17N R8W Sec 15	3873-3914	0.33	7.2

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
BELL SHA	BELL SHALE (cont.)					
12-B	13275	Cuttings	Degenther-Ellens #1 T8N R10W Sec 32	2600-2605	0.19	6.9
13-B	14418	Cuttings	Smith-Schultz #1 T10N R9W Sec 18	3038-3062	0.18	7.0
14-B	11995	Cuttings	Ohio-Mio Unit Area #1 T25N R3E Sec 30	2970-2985	0.15	6.4
15-B	10913	Cuttings	Tamblyn-Jordan #1 T9N R5E Sec 29	2545-2610	0.23	6.5
16-B	10977	Core	SOHIO-Cummings #4 T16N R6W Sec 32	3663-3690	0.30	7.8
17-B	10015	Core	Maguire-State #Al T18N R9W Sec 34	3873-3887	0.37	7.6
18-B	30974	Cuttings	McClure-Hewett et al #1-20 T12N R15E Sec 20	1710-1770	0.25	6.2
19-B	29739	Cuttings	McClure-Sparks et al #1-8 T10N R2W Sec 8	3095-3135	0.16	9.9
C SHALE						
1-C	BD151	Core	CPC-CPC BDW1 T5N R17E Sec 7	1891	0.07	9•9

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
C SHALE (cont.)	(cont.)					
2-C	30974	Cuttings	McClure-Hewett et al #1-20 T12N R15E Sec 20	4170-4230	0.12	6.5
3-C	29739	Cuttings	McClure-Sparks et al #1-8 T10N R2W Sec 8	5430-5500	0.10	7.0
7-4	30475	Cuttings	Amoco-Pkg Corp of Amer. T24N R13W Sec 13	5020-5070	0.56 H ₂ SO ₄ Rx	9.9
5-C	31335	Cuttings	Marathon-Cupp #1-11 T6S R10W Sec 11	1520-1580	0.20	8.9
0-9	31253	Cuttings	Marathon-Ella Rzepka #1-27 T6S R5W Sec 27	1670-1710	0.16	7.3
7-C	31295	Cuttings	Marathon-Russel #1-21 T6S R4W Sec 21	1810-1860	0.26	7.2
ပ 8	31584	Cuttings	Amoco-Carpenter Unit #1-4 TlS R6W Sec 4	2690-2740	0.19	7.0
D-6	28546	Cuttings	Amoco-Garland #1 T28N RIE Sec 16	6210-6290	0.04	7.0
10-C	28999	Cuttings	Amoco-DePeel #1-31 T2N R2W Sec 31	3230-3270	0.12	7.3
11-C	29099	Cuttings	Amoco-State-Charlton #1-28 T31N R1W Sec 28	4480–4520	0.12	7.2

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
C SHALE (cont.)	(cont.)					
12-C	29474	Cuttings	SME Co & Amoco-USA et al T27N R9W Sec 36	2600–5690	1.1 H ₂ SO ₄ Rx	6.4
13-C	30137	Cuttings	Amoco-Timm-Kennedy #1-14 T3N R8W Sec 14	3090-3130	0.18	6.7
14-C	30814	Cuttings	Amoco-Hansen #1-19 T8N RL5W Sec 19	2990–3040	0.13	7.3
15-C	31067	Cuttings	Amoco-Sorgett #1-26 T34N R4E Sec 26	2630-2680	1.3 H ₂ SO ₄ Rx	7.3
16-C	31293	Cuttings	Amoco-State-Mancelona E#3-33 T29N R5W Sec 33	5880-5940	2.1 H ₂ SO ₄ Rx	7.2
UTICA SHALE	ALE					
1-U	13816	Core	Sun-Bradley #4 T12N R13W Sec 11	5963	0.32	7.5
2-U	25536	Core	CPC-CPC 204 T1S R7E Sec 1	4124	0.21	7.2
3-N	5441	Cuttings	Gulf-Bateson #1 T14N R4E Sec 2	9375–9390	0.15	7.8
n−4	6364	Cuttings	Violette-Warren #1 T8S R20W Sec 8	1292-1315	0.37	7.1

Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
UTICA SH	UTICA SHALE (cont.)					
2-U	10792	Cuttings	Chamness-Roddenberry Comm. #1 IlS R7E Sec 27	4062-4104	0.38	7.5
Ω -9	30974	Cuttings	McClure-Hewett et al #1-20 T12N R15E Sec 20	6295–6375	0.25	7.6
7-U	29739	Cuttings	McClure-Sparks et al #1-8 T10N R2W Sec 8	7600-7700	0.28	7.8
n−8	31335	Cuttings	Marathon-Cupp #1-11 T6S R10W Sec 11	2600-2700	0.43	7.2
n-6	31253	Core	Marathon-Rzepke #1–27 T6S R5W Sec 27	3102	0.20	7.0
9a-U	31253	Cuttings	Marathon-Rzepke #1-27 T6S R5W Sec 27	3030-3100	0.36	
10-U	31295	Core	Marathon-Russell #1-21 T6S R4W Sec 21	3221	0.25	7.2
10a-U	31295	Cuttings	Marathon-Russel #1-21 T6S R4W Sec 21	3100-3220	0.29	
11-U	31338	Cuttings	Amoco-Rau #1-21 T22N R2E Sec 21	9770-9840	0.15	7.6
12-U	30137	Cuttings	Amoco-Timm-Kennedy #1-14 T3N R8W Sec 14	4650-4700	0.20	7.5

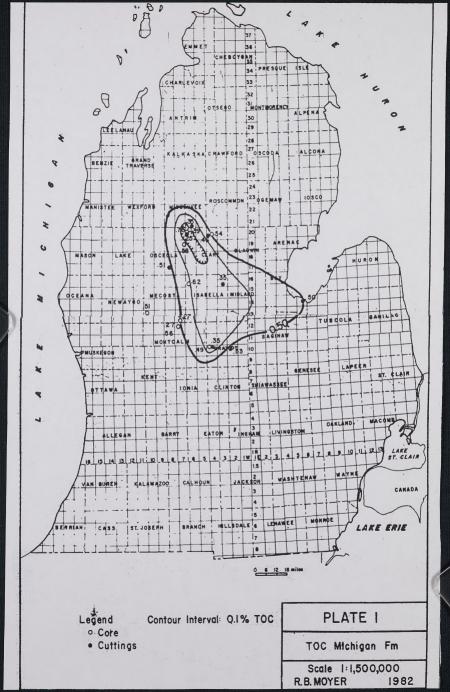
Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
UTICA SH	UTICA SHALE (cont.)					
13-U	33680	Core	Hunt-Winterfield Deep Unit A#1 T20N R6W Sec 30	9885	0.39	7.9
14-U	29372	Core	Shell-Taratutta #1-13 T33N R5E Sec 13	4740	1.87	0.6
EAU CLAI	EAU CLAIRE FORMATION	NC				
1-EC	80604	Core	Allied-Disposal #2 T2S RllE Sec 26	3827	0.15	7.6
2-EC	BD151	Core	CPC-CPC BDW 1 TSN R17E Sec 5	4586	0.12	
3-EC	80663	Core	GPC-BD 152 #2-7 T5N R17E Sec 7	4573	0.05	7.8
4a-EC	25099	Core	Sun-Brazos-State-Foster #1 T24N R2E Sec 28	12,481	0.24	8.2
4 b-EC	25099	Core	Sun-Brazos-State-Foster #1 T24N R2E Sec 28	12,085	0.07	
4c-EC	25099	Core	Sun-Brazos-State-Foster #1 T24N R2E Sec 28	11,642	0.15	
4 d -EC	25099	Core	Sun-Brazos-State-Foster #1 T24N R2E Sec 28	12,937	0.14	

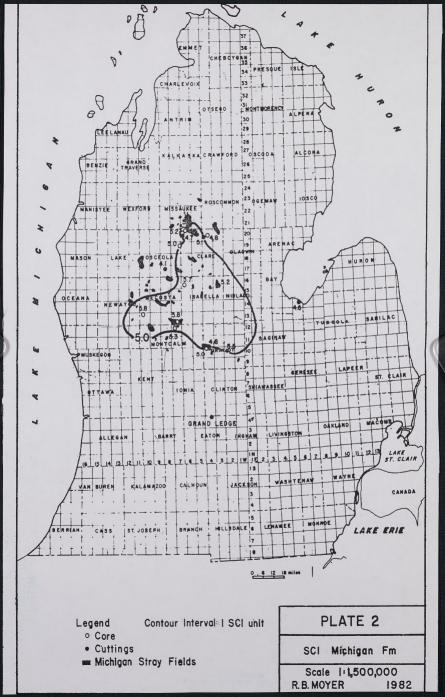
Sample No.	Permit No.	Core or Cuttings	Well Name Location	Footage Sampled	TOC(%)	SCI
EAU CLAI	RE FORMATI	EAU CLAIRE FORMATION (cont.)				
5-EC	31335	Cuttings	Marathon-Cupp #1-11 T6S R10W Sec 11	4330–4460	0.12	8° . 9
PRECAMBRIAN	IAN					
1-PE	80604	Core	Allied Disposal #2 T2S R11E Sec 26	4042	0.19	0.6
2a-PE	29739	Core	McClure-Sparks et al #1-8 T10N R2W Sec 8	13,417	0.03	10.0
2b-PE	29739	Core	McClure-Sparks et al #1-8 T10N R2W Sec 8	15,072	0.03	
2c-PE	29739	Core	McClure-Sparks et al #1-8 T10N R2W Sec 8	16,418	0.02	
Meta Shale	29969	Core	CPC-Clark #1 T5S R8W Sec 8	5426	00*0	

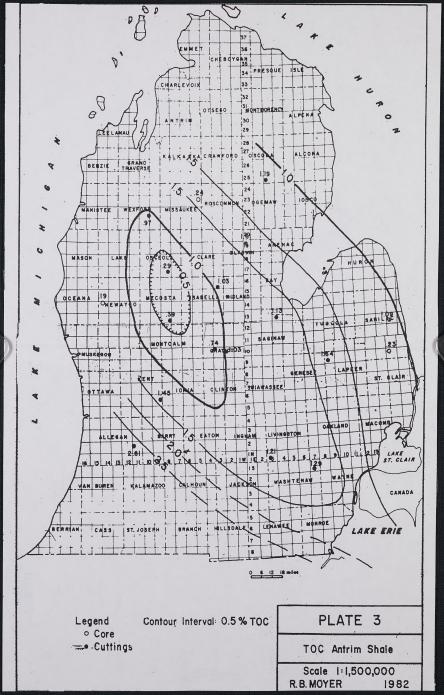
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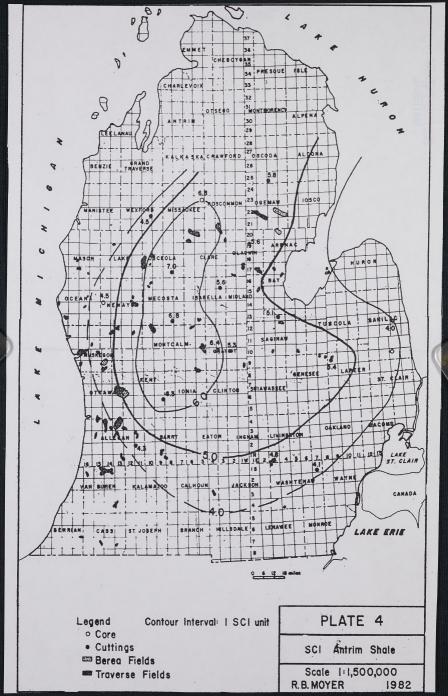
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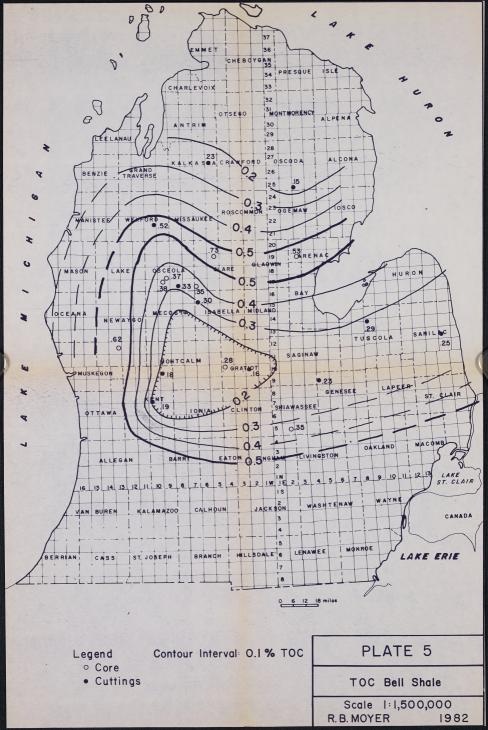
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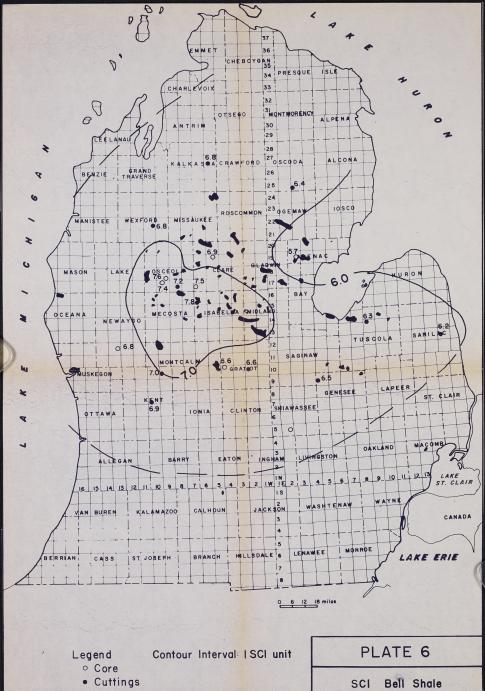






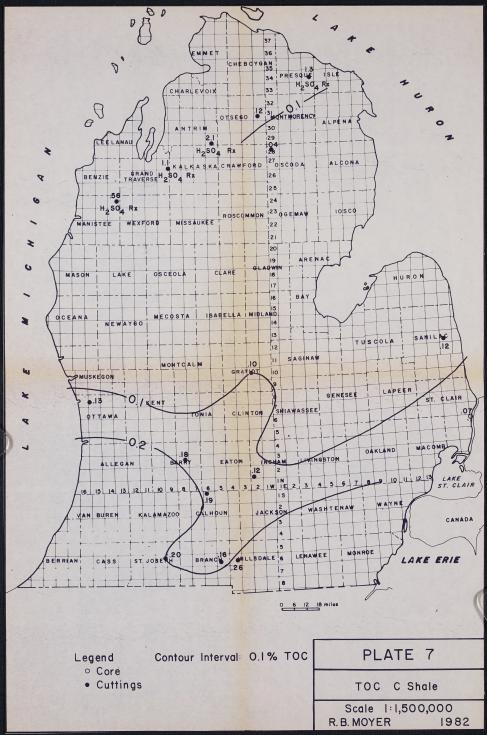


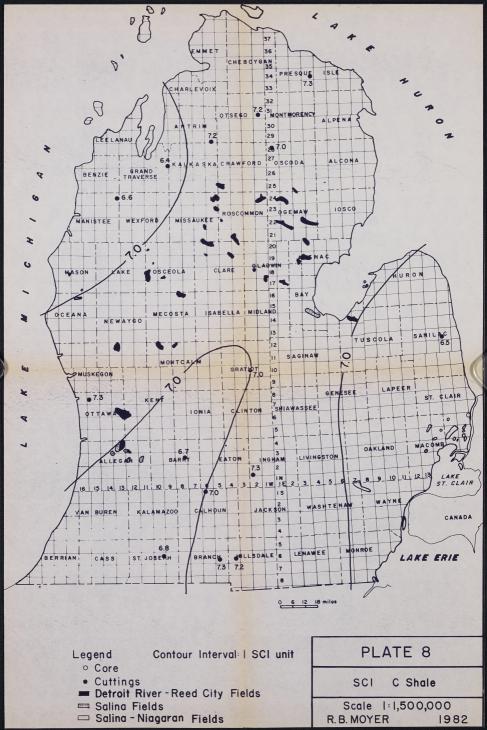




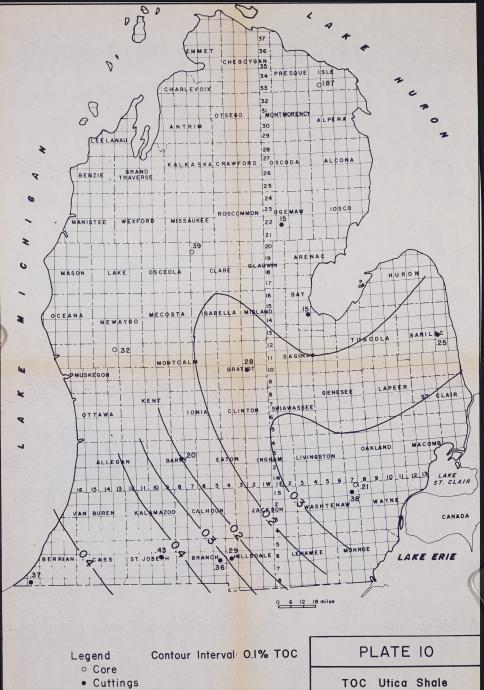
Dundee Fields

| Scale | 1:1,500,000 |
| R.B. MOYER | 1982





DEPARTMENT OF NATURAL RESOURCES GEOLOGICAL SURVEY DIVISION MICHIGAN OIL AND GAS FIELDS, 1980 0 BERRIEN INDIANA онго PLATE 9

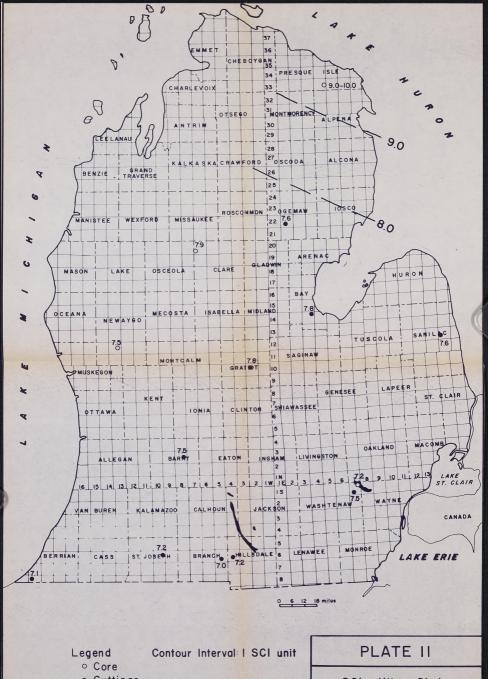


• Cuttings

TOC Utica Shale

Scale 1:1,500,000

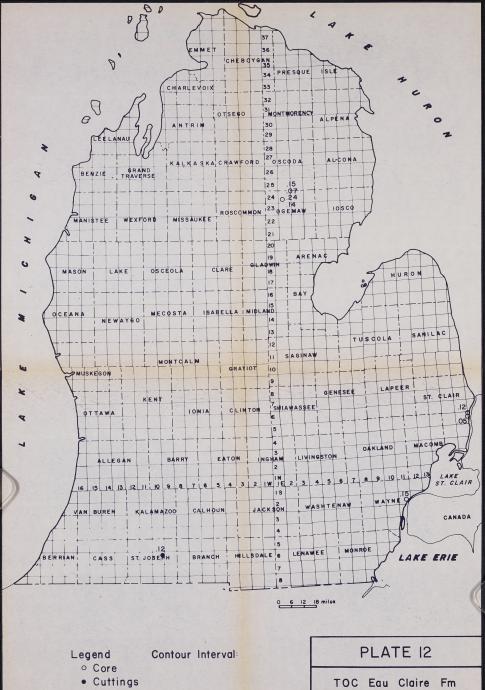
R.B.MOYER 1982



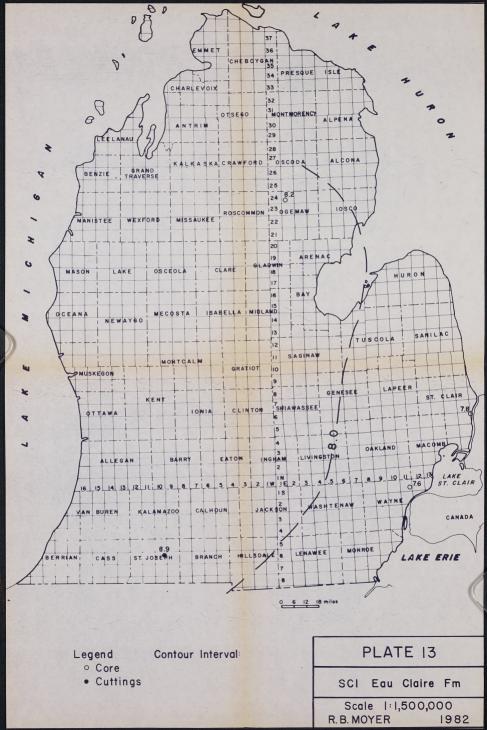
CuttingsTrenton-Black River Fields

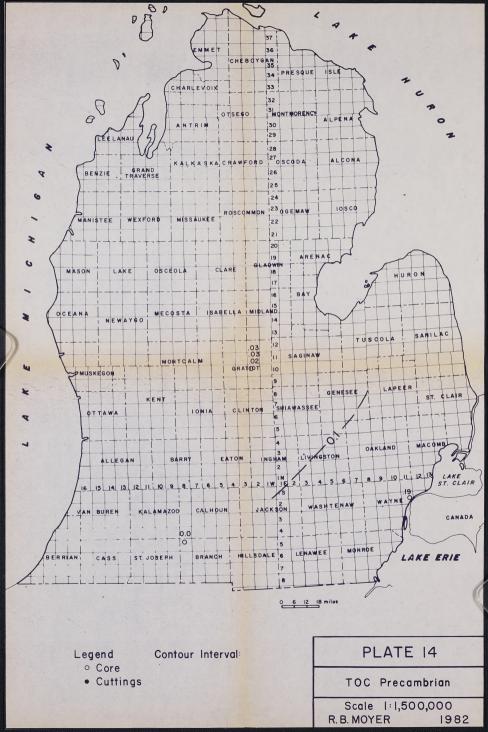
SCI Utica Shale

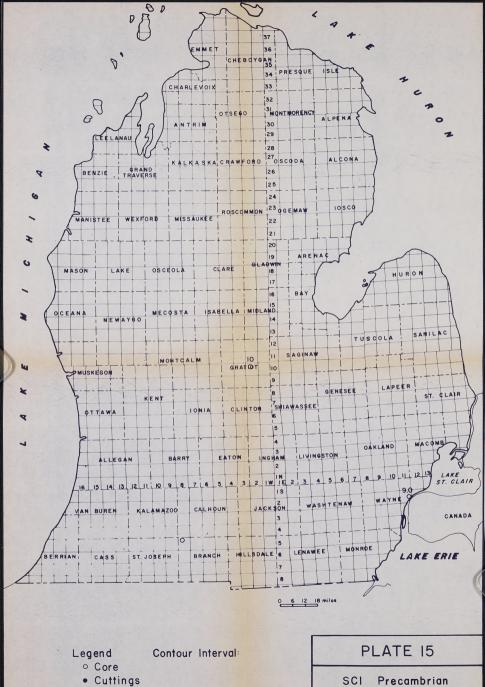
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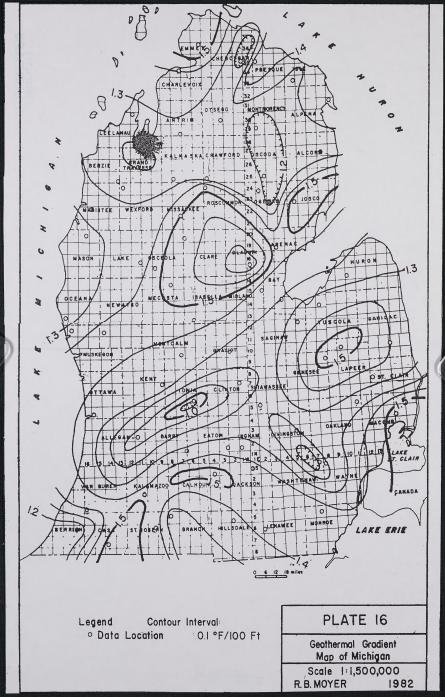
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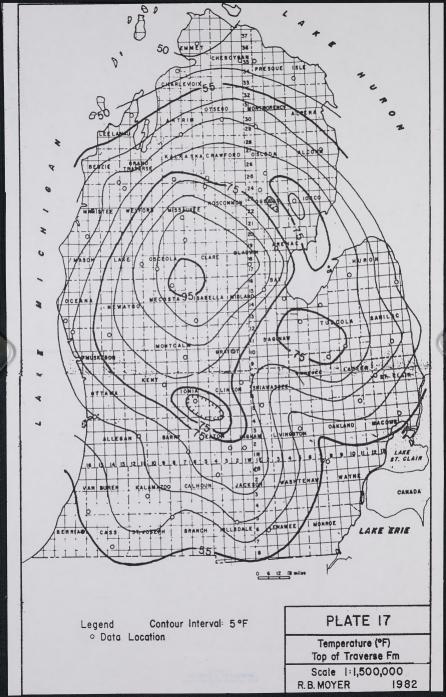


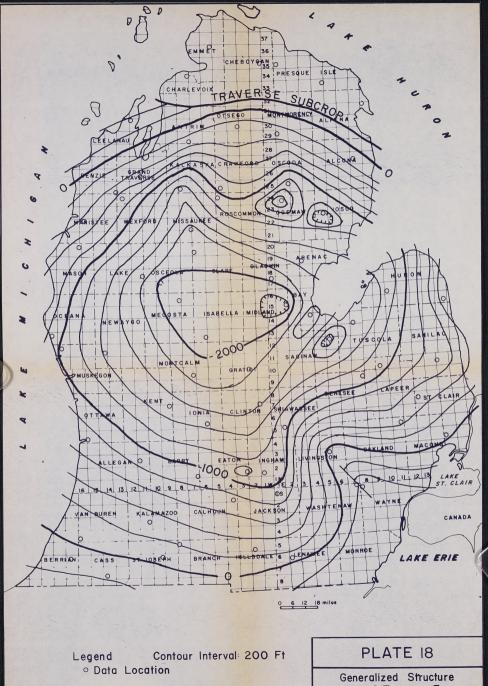




Scale 1:1,500,000 R.B. MOYER 1982







Top of Traverse Fm

Scale 1:1,500,000

R.B. MOYER 1982