UNITED STATES DEPARTMENT OF THE INTERIOR GEOLOGICAL SURVEY

Hydrocarbon Source Rock Evaluation--Solor Church Formation (Middle Proterozoic, Keweenawan Supergroup) Southeastern Minnesota

Ву

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This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature.

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ABSTRACT

In the type section (Lonsdale 65-1 core, Rice County, Minnesota) the Solor Church Formation (Middle Proterozoic, Keweenawan Supergroup) consists primarily of reddish-brown mudstone and siltstone and pale reddish-brown sandstone. The sandstone and siltstone are texturally and mineralogically Hydrocarbon source-rock evaluation of bluish-gray, greenish-gray immature. and medium-dark-gray to grayish-black beds, which primarily occur in the lower 104 m (340 ft) of this core, shows: (1) the rocks have low organic carbon contents (<0.5 percent for 22 of 25 samples); (2) the organic matter is thermally very mature ($T_{max} = 494^{\circ}C$, sample 19) and is probably near the transition between the wet gas phase of catagenesis and metagenesis (dry gas zone); and (3) the rocks have minimal potential for producing additional hydrocarbons (genetic potential <0.30 mgHC/gm rock). Although no direct evidence exists from which to determine maximum depths of burial, the observed thermal maturity of the organic matter requires significantly greater depths of burial and(or) higher geothermal gradients. It is likely, at least on the St. Croix horst, that thermal alteration of the organic matter in the Solor Church took place relatively early, and that any hydrocarbons generated during this early thermal alteration were probably lost prior to deposition of the overlying Fond du Lac Formation (Middle Proterozoic, Keweenawan Supergroup).

INTRODUCTION

Recent publications by Gustavson (1983), Lee and Kerr (1983), and Petroleum Information, Inc. (1984) have speculated that sedimentary rocks of the Middle Proterozoic Keweenawan Supergroup associated with the North American Midcontinent rift system (fig. 1) have a potential for producing They base their speculations on comparisons with hydrocarbon hydrocarbons. potential of present-day rift basins and on known occurrences of organicmatter-rich rocks in the Nonesuch Shale of the Oronto Group in northern Unfortunately, there is very little information regarding the Michigan. hydrocarbon source-rock potential of Keweenawan sedimentary rocks in the remainder of the rift system. One of the few areas in the rift system outside of northern Wisconsin and the Upper Peninsula of Michigan, where unweathered samples of sedimentary rocks from the upper part of the Keweenawan Supergroup are available, is in the pre-Paleozoic Twin Cities basin of southeastern Here, cores of the Solor Church Formation were collected during exploration for gas-storage reservoirs in the 1960's. The purpose of this report is to appraise the hydrocarbon source-rock potential of the Solor Church Formation in the Twin Cities area based on geochemical analyses of samples from the core containing the greatest part of the Middle Proterozoic section.

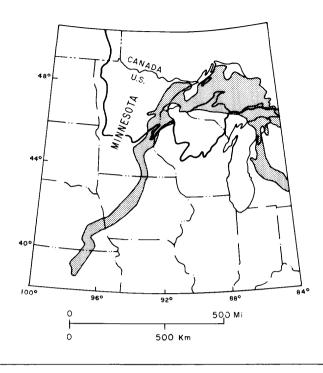


Figure 1.—Map showing general location of the Midcontinent rift system (shaded area) and the area of the pre-Paleozoic bedrock. Modified from Klasner and others (1982). Shaded area includes that part of the rift system having a gravity anomaly greater than -20 milligals (-40 milligals in Kansas). Area of pre-Paleozoic bedrock is to the north and east of the heavy black line.

GEOLOGIC SETTING

The geographic distribution of various kinds of sedimentary rocks in the Middle Proterozoic Keweenawan Supergroup in southeastern Minnesota is closely related to the geometry of the Midcontinent rift system. The most prominent expression of the Midcontinent rift system in southeastern Minnesota is a linear gravity anomaly known as the Midcontinent Gravity High. demonstrated that the positive part of the anomaly originates from dense mafic the flanking negative anomalies result rocks. whereas Craddock and others (1964) contrasting low-density sedimentary rocks. suggested that the volcanic rocks were elevated from 60 to 100 m (200 to 300ft) to around 4.6 km (15,000 ft) above adjacent strata to form part of what they call the St. Croix horst. Alternatively, Morey (1972) suggested that the horst stood as a positive area that supplied detritus to half-graben-like Figure 2 shows the basins that subsided along the flanks of the horst. southern part of the St. Croix horst in Minnesota, where it is bounded on the northwest by a series of steeply inclined northeast-trending faults, including the Douglas and Pine faults, on the southeast by the Hastings and Cottage Grove faults, and on the southwest by northwest-trending faults, including the Belle Plaine fault (Morey, 1977). Sims and Zietz (1967) have shown that the magnetic patterns and basalt subcrops delineate a fault-bounded, sedimentary rock-filled basin along the axis of the horst. This basin, called the pre-Paleozoic Twin Cities basin, underlies and conforms approximately in outline to the much younger Twin Cities basin developed in overlying Paleozoic strata (Thiel and Schwartz, 1941; Mossler, 1972). Thus, sedimentary rocks of the

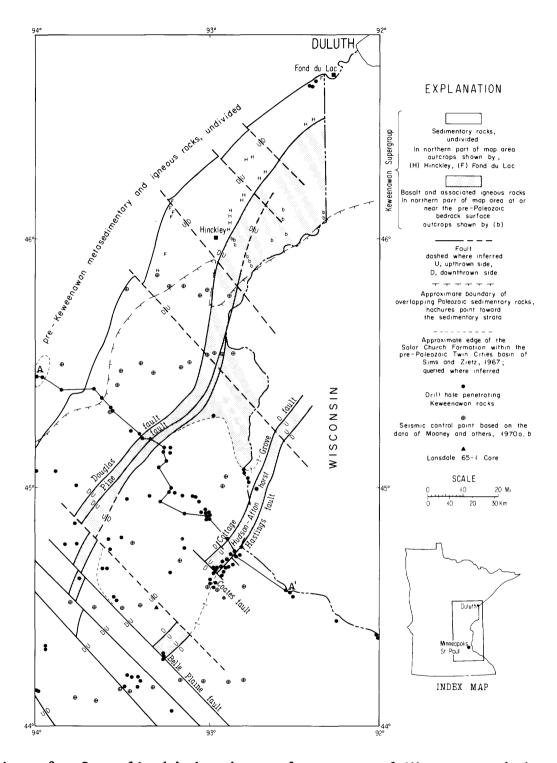


Figure 2.—Generalized bed rock map of east-central Minnesota and the inferred distribution of pre-Paleozoic rocks in southeastern Minnesota. Modified from Morey (1974, fig. 1; originally modified from Sims and Zietz, 1967 and Sims, 1970).

Keweenawan Supergroup occur in two discrete tectonic settings: 1) in half-grabenlike basins on the flanks of the St. Croix horst, and 2) within the pre-Paleozoic Twin Cities basin on the horst itself.

Sedimentary rocks within the pre-Paleozoic Twin Cities basin occupy an elongate area that is at least $100~\rm km$ $(60~\rm mi)$ long in a northeasterly direction and $50\text{--}55~\rm km$ $(30\text{--}35~\rm mi)$ wide. These rocks range in thickness from less than $10~\rm m$ $(33~\rm ft)$ on the flanks of the horst to at least $975~\rm m$ $(3,200~\rm ft)$ under the central part of the basin (Sims and Zietz, 1967). Keweenawan rocks east of the Hastings fault are $2,400\text{--}3,700~\rm m$ $(8,000\text{--}12,000~\rm ft)$ thick (Volz, 1968), whereas they are much thinner in the flanking basin to the west of the Douglas fault.

A generalized east-west cross section across the St. Croix horst is shown in figure 3. The structural configuration is based largely on data obtained by geophysical methods (Mooney and others, 1970a), whereas the various lithostratigraphic units are identified by petrographic criteria developed by Kirwin (1963) and somewhat refined by Morey (1972).

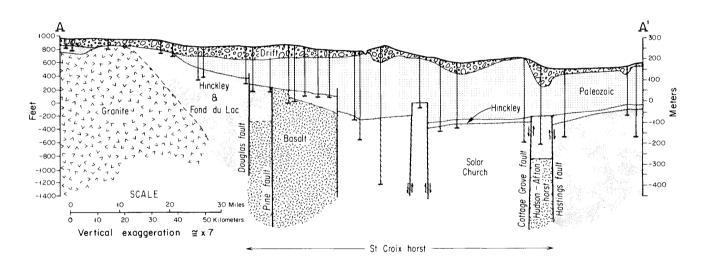


Figure 3.--Generalized east-west cross section across the St. Croix horst in the vicinity of Minneapolis-St Paul, Minnesota.

Location of cross section shown in figure 2. Figure from Morey (1974, fig. 4).

Stratigraphy

Keweenawan sedimentary rocks in east-central and southeastern Minnesota are divided into three formations (fig. 4). In descending order: (1) Hinckley Sandstone, a buff to tan sandstone generally containing 95 percent or more quartz; (2) Fond du Lac Formation, consisting of red-colored feldspathic sandstone, arkose, and abundant shale; and (3) Solor Church Formation consisting of dark reddish-brown mudstone, shale, and sandstone containing variable amounts of quartz, plagioclase of intermediate composition, and aphanitic igneous-rock fragments (Morey, 1974). For comparison, the stratigraphic nomenclature used for sedimentary rocks in the upper part of the Keweenawan Supergroup in Wisconsin is included in figure 4.

	WISCON	ISIN	1	VINNESOT.	A
ТуІ	Thwaites, 1912 as modified by er & athers, 1940	Ostram, 1967	Surface exposures Tyler & others, 1940	Sub-surface Kirwin, 1963	Sub - surface Morey, 1977
	Chequamegon Sst	Chequamegon Fm.			
Group	Devits Island Sst. (nearly pure qtz. sst.)	Devils Island Fm	Hinckley Sandstone >99 % qtz.	Unit 1 >95% qtz., minor K-spar, no rock fragments.	Hinckley Sandstone >95 % qtz.
Bayfield	Orienta Sandstone 75% qtz., 25% feldspar- mostly K-spar	Orienta Fm	Fond du Lac Fm. 40-60% qtz, 20-25% feldspar early Proterazaic rocks.	Unit 2 Sst., feldspathic, grading into an arkose having 60-85% qtz. K-spar = or > plagioclase. Subordinate rock fragments.	Fond du Lac Formatian
Group	30% qtz., 75% feldspar - mostly plag. Freda Sandstone <25% qtz 75% plagioclase & aphanitic rack fragments of basaltic composition.	Freda Fm.		Unit 3 Arkose, 50% quartz, plagioclase >>> K-spar Subordinate rock fragments. Unit 4 30% quartz, 40% volcanic rock fragments, remainder plag.	Solor Church Formation
Oronto G1	Nonesuch Shale "Virtually unalterea debris of basic eruptives".	Nonesuch Fm		DE 5-40% quartz, remainder volcanic rock fragments and plagioclase	
	Copper Harbor Conglomerate "boulder - sized conglomerate of basic eruptives."				
	Mid Keween basaltic lava			Mid Kewee basaltic lav	nawan a flows

Figure 4.--Stratigraphic nomenclature used for Keweenawan sedimentary rocks in Minnesota and Wisconsin (Morey, 1977, table 2).

It can be seen from figure 4 that the Solor Church Formation is lithologically similar to rocks of the Oronto Group in Wisconsin and Michigan and, therefore, the two may be broadly correlative. The age of deposition of the Solor Church Formation is unknown. The age of the Oronto Group, however, is bracketed between 1,072±25 m.y. (Chaudhari, 1972) for extrusive rocks that interfinger with the lower part of the Oronto Group and 985±25 m.y. (Chaudhuri, 1975) for a felsic intrusion that cuts the Oronto Group. Chaudhuri and Faure (1967) also report a questionable age of 1,052±50 m.y. from the Nonesuch Shale itself.

The geographic extent of the Solor Church Formation has been very poorly documented. Sparse drill-hole data combined with seismic studies (Mooney and others, 1970a, b) have shown that it occurs within the pre-Paleozoic Twin cities basin on top of the St. Croix horst. Seismic data indicate that Solor-Church-like rocks also may occur as a thin wedge in the lower part of the western flanking basin and as an appreciable part of the sedimentary fill in the eastern flanking basin. The presence of Solor Church Formation in the flanking basins, however, has not been confirmed by drilling.

The Solor Church Formation does not crop out anywhere in Minnesota. Therefore, its general chracteristics have been defined from drill cores. One core (Lonsdale 65-1) penetrates 578.5 m (1,898 ft) of Keweenawan strata and was subsequently defined as the type section for the Solor Church Formation (Morey, 1977). This type section, however, represents only part of the formation. Seismic geophysical evidence (Mooney and others, 1970b) indicates that the formation is at least 975 m (3,200 ft) thick at this locality.

Lithology

In general, the Solor Church Formation in the Lonsdale 65-1 core consists of a rather monotonous sequence of interbedded conglomerate, sandstone, siltstone, and shale or mudstone. There are a few thin beds of limestone, especially in the upper part of the formation. Abrupt changes in rock type are common, with individual beds generally being less than 3 m (10 ft) thick; a few sandstone beds, however, are as much as 10 m (30 ft) thick (Morey, 1977).

Sparsley distributed conglomeratic units near the base of the formation, as intersected in a nearby drill hole, contain pebble- and cobble-size clasts of basalt (Morey, 1977). Most of the conglomeratic material, however, is intraformational in origin and consist of angular to subangular pebble-size clasts of shale, mudstone, and siltstone set in a sand-size matrix. These intraformational conglomerates generally occur in the basal parts of thick sandstone beds, which are separated from underlying argillaceous rocks by scoured surfaces.

Beds of sandstone and siltstone of the Solor Church Formation are mineralogically immature in that they contain appreciable amounts of feldspar and aphanitic igneous rock fragments (Morey, 1972). Examination of about 100 thin sections by Morey (1977) show that approximately 2 percent of the sandstones are quartz arenite, 31 percent subarkose, 20 percent arkose, 22 percent lithic arkose, 14 percent feldspathic lithic arenite, 10 percent lithic subarkose, and 1 percent lithic arenite. The rocks are textually immature in that they contain more than 5 percent matrix material.

Siltstone in the Solor Church Formation is the fine-grained equivalent of the sandstone, and there is a more or less continuous gradation between the two rock types. Most of the siltstone is poorly sorted. Silt and very fine sand-size grains of quartz, feldspar, and rock fragments comprise about 30 to 60 percent of the rock. The matrix consists of very fine grained clay minerals, together with particles and irregular patches of iron oxides and calcite (Morey, 1977).

Mudstone in the Solor Church Formation has either a laminated or massive fabric; laminated rocks contain small amounts of silt concentrated in discontinuous layers less than a millimeter thick, whereas, structureless beds are very silty, and the silt-size detritus generally is randomly distributed. Hematite is a common constituent, imparting a red color to many beds, and calcite is locally very abundant (Morey, 1977).

Beds of mudstone and siltstone in the Solor Church Formation contain more iron than intercalated coarser grained strata and, thus, are more intensely stained by iron oxides. Beds of sandstone and conglomerate generally are

moderate red (5R4/6) or pale reddish brown (10R5/4) in color, whereas beds of shale, siltstone, and mudstone typically are dusky red (5R3/4) or dark reddish brown (10R3/4) in color (Morey, 1977). The entire Solor Church Formation is not, however, characterized by a red color, and there is a gradual downward decrease in the proportion of red-pigmented material leading ultimately to rocks, as at the bottom of the Lonsdale 65-1 core, which are light greenish gray (5GY8/1) dark greenish gray (5GY4/1) to 5G4/1 and medium dark gray (N4) to grayish black (N2).

Sedimentologic Framework

Two kinds of sedimentary cycles, each characterized by "fining-upward" attributes, are recognized in the Solor Church Formation: (1) Minor cycles, 1-15 m (3-50 ft) thick, consist of sandstone/conglomerate overlain by a siltstone/mudstone. Each minor cycle contains a vertical succession of primary structures and textures indicative of fluvial sedimentation by (2) Major cycles, which may be as much as 180 m (600 ft) meandering streams. thick, are characterized by a systematic upward increase in the amount of mudstone relative to sandstone. This fining upward trend reflects a more or less systematic increase in the thickness of the fine-grained lithologies whereas the thickness of the coarse-grained lithologies in each minor cycle remains more or less constant. As the proportion of siltstone/mudstone increases, there is a corresponding decrease in the grain size of the sandand silt-size detritus. Each major cycle is terminated by an abrupt vertical decrease in the relative amount of fine-grained detritus and a corresponding increase in the amount of sandstone (Morey, 1974).

The Solor Church Formation most likely was deposited by rivers flowing on an alluvial plain; in each minor cycle the conglomerate and sandstone were deposited in migrating channels, whereas the mudstone and limestone were deposited on interchannel flood plains and in shallow lakes. The general increase upward in the amount of silt and clay implies that the upper part of each major cycle was dominated by overbank or interchannel deposition rather than by channel deposition. Thus, each major cycle records a progressive change toward a balance between rate of subsidence and rate of infilling. The sudden reappearance of abundant conglomerate and sandstone, at the base of the succeeding major cycle, indicates an abrupt increase in the rate at which materials were supplied to the system. It is inferred that these abrupt changes record periods of tectonism during the evolution of the rift system (Morey, 1974).

SAMPLES

Twenty-five samples of the Solor Church Formation were collected from the Lonsdale 65-1 core. Depths for the samples and brief lithologic descriptions are listed in table 1. Detailed descriptions of the entire Lonsdale 65-1 core are in Morey (1974 and 1977). All samples were collected from the bottom 40 percent (225 m, 740 ft) of the core; 22 of the 25 samples are from the lowest 20 percent (104 m, 340 ft). The samples were collected specifically because of their bluish-gray, greenish-gray, brownish-gray, and medium-gray to grayish-black hues.

Table 1. Lithologic descriptions, depths, organic carbon contents and Rock-Eval pyrolysis results for 25 samples from the Lonsdale 65-1 core, Rice County, Minnesota.

[Core was collected from SW1/4SW1/4 sec. 14, T. 11 2N R. 21 W. HC = hydrocarbons; TOC = organic carbon; ---, indicates no data or data not calculable; one meter = 3.28 ft]

Sample number	Lithology	Depth (meters)	Organic carbon (percent)	¹ s ₁	² s ₂	³ s ₃	Temperature of 4 maximum yield (°C)	Hydrogen ⁵ index	0xygen ⁶ index
1	Siltstone, 5B 4/1	640.1	0.04						
2	Siltstone, 5G 3/1	642.8	.03						
3	Mudstone, silty,								
	laminated, N3	694.9	.35	<.01	.15	.13	486	42	37
4	Sandstone, fine-grained,								
	5G 5/1, N3 laminations	764.6	.03						
5	Do	767.0	.12						
6	Siltstone, 5G 3/1	780.3	.04						
7	Sandstone, fine-grained,								
	5YR 4/1	- 786.7	.12						
8	Mudstone, silty, N5, N4								
	laminations	788.2	.14						
9	Do	790.0	.13						
10	Mudstone, silty, N3	795.5	.13						
11	Siltstone, N4	798.0	•04						
12	Mudstone, silty, N3	804.4	.13						
13	Mudstone, sandy,								
	laminated, N4	804.7	.62	.01	.13	.07	414	20	11
14	Mudstone, sandy, N5,								
	N4, laminations	804.9	.21	<.01	<.01	.13		<5	62
15	Sandstone, N4, medium								
	grained	805.8	•01						
16	Siltstone, 5YR 4/1	813.2	.01						
17	Siltstone, N4		.19						
18	Mudstone, sandy, 5G 3/1	821.2	.19						
19	Mudstone, laminated, N2		1.77	.024	. 28	.30	494	15	17
20	Mudstone, laminated, N3		.45	.01	.16	.10	458	35	22
21	Do		.76	<.01	.15	.09	464	19	11
22	Mudstone, sandy, 5YR 3/1	855.1	.22	<.01	<.01	.14		<5	62
23	Do		.15						
24	Siltstone, N5		.15					-	
25	Siltstone, N3		.03						

 $^{^1{\}rm mg}$ volatile HC/g sample: Rock-Eval analysis $^2{\rm mg}$ pyrolyzable HC and HC like compounds/g sample: Rock-Eval analysis $^3{\rm mg}$ CO $_2$ /g sample: Rock-Eval analysis $^4{\rm mg}$

Temperature at which the yield of pyrolysis products (S_2) is at a maximum (T_{max}): Rock-Eval analysis S_2 /TOC, mgHC/gTOC

⁶s₃/TOC, mgCO₂/gTOC

METHODS

Total organic carbon content (TOC) was determined by a wet oxidation method slightly modified from Bush (1970). TOC provides the best measure of amount of organic matter, both soluble and insoluble, in the rock. Factors used to estimate organic-matter content from TOC depend on the type of organic matter and level of thermal maturation and range from about 1.1 to near 1.6 (Forsman and Hunt, 1958).

Pyrolysis assay was by Rock-Eval 1* using the instrument (Girdel) and methods of Espitalié and others (1977). This method measures contents of volatile hydrocarbons (S_1 peak, mgHC/g rock) pyrolytic hydrocarbons (S_2 peak, mgHC/g rock) pyrolytic carbon dioxide (S_3 peak, mgCO $_2$ /g rock) and the temperature of maximum pyrolytic hydrocarbon generation (T_{max}). S_1 , S_2 , S_3 , and TOC are combined mathematically in the form of various indicies used for hydrocarbon source-rock evaluation. These indicies include the genetic potential ($S_1 + S_2$, mgHC/g rock), hydrogen index (HI, S_2 /TOC, mgHC/g TOC), and oxygen index (OI, S_3 /TOC, mg CO $_2$ /g TOC). Genetic potential (GP) is used to estimate the source-rock potential and is a function of both the amount and composition of the organic matter in the rock. HI and OI are correlative with H/C and O/C atomic ratios of kerogen and can be used to help evaluate the type of organic matter (Espitalié and others, 1977; Orr, 1983). The temperature at which the S_2 peak reaches a maximum (T_{max}) increases with increased thermal maturation of the organic matter (Espitalié and others, 1977).

The sample (19), which had the highest TOC content, was pulverized (<100 mesh) and extracted with chloroform (CHCl $_3$) in a Soxhlet apparatus for 24 hours to determine the amount and composition of extractable organic matter (EOM) content. Sulfur was removed from the EOM by refluxing with polished copper metal. The filtered EOM was evaporated at room temperature under nitrogen to remove chloroform and the weight of the total extract used to calculate the EOM content. The EOM was diluted with N-heptane to precipitate asphaltenes. A concentrate of the solution was separated by column chromatography on silica gel, eluting successively with heptane, benzene, and benzene-methanol to collect the saturated hydrocarbons, aromatic hydrocarbons, and resin (NSO) fractions, respectively.

The saturated hydrocarbon fraction was analzyed further by gas chromatography on a SE54 bonded phase WCOT column, 30 m x 0.35 mm I.D. temperature programmed from $80^{\rm o}$ to $300^{\rm o}$ C at $4^{\rm o}$ C per minute. Identifications of peaks on the resultant chromatograms were based on relative retention times.

^{*}Trade and company names are for descriptive purposes only and do not imply endorsement by the U.S. Geological Survey.

RESULTS

Organic Carbon

Results of TOC determinations are listed in table 1. TOC for 22 of the 25 samples is less than 0.50 percent; for 18 of the 25 samples TOC is less than 0.20 percent. Sample 19 has the highest TOC (1.77 percent).

Rock-Eval pyrolyses

Rock-Eval pyrolysis analyses were performed on the seven samples with greater than 0.20 percent TOC. Results for the seven samples are listed in table 1. Contents of both the volatile (S_1) and pyrolytic (S_2) hydrocarbons are very low for all seven samples. Maximum S_1 is 0.024 mgHC/g sample (sample 19); maximum S_2 is 0.28 mgHC/g sample, (sample 19). Maximum genetic potential ($S_1 + S_2$) is 0.30 mg/g sample (sample 19). Hydrogen indicies range from <5 to <6 (mgHC/g TOC); oxygen indicies range from <6 (mg CO $_2$ /g TOC).

 $T_{\rm max}$ values for the five samples in which a measurable S_2 peak occurs range from 414° to 494°C. For four of the five samples (samples 3, 13, 20, and 21), however, $T_{\rm max}$ is considered unreliable because of the small amount of pyrolytic hydrocarbons (<0.16 mgHC/g sample) and the resultant broad, poorly defined S_2 peak. The fifth sample (19) produced a greater amount of pyrolytic hydrocarbon (0.28 mgHC/g sample), and the S_2 peak for this sample has a clearly defined maximum at 494°C.

Extractable Organic Matter

The amount and composition of the (EOM) from sample 19 is listed in table 2. A gas chromatogram of the saturated HC fraction of the EOM from sample 19 is shown in figure 5a. For comparison, a gas chromatogram of the saturated HC fraction from an oil sample from the White Pine mine of northern Michigan is shown in figure 5b. The saturated HC distribution of this oil is similar to the saturated HC distribution of extracts of the Nonesuch Shale in the White Pine mine area (Connan, 1976). Because all of the extract from sample 19 was blown down to near dryness to determine amount and composition of the EOM, comparisons between figures 5a and 5b must be limited to the $n-C_{15}+$ part of the saturated HC distribution. In this part of the saturated HC distribution, sample 19 is characterized by more abundant branched and cyclic alkanes compared to the n-alkanes $(n-C_{17}/pristane for the oil is 6.2; for sample 19 it$ Saturated HC from sample 19 also have a predominance of evennumbered over odd-numbered n-alkanes in the n-C $_{20}$ to n-C $_{26}$ range [carbon preference index (CPI) = 0.61]. CPI was calculated from the following formula (modified from Bray and Evans, 1961): $CPI = 1/2 [(n-C_{21} + n-C_{23} +$ $n-C_{25}$)/($n-C_{20} + n-C_{22} + n-C_{24}$) + ($n-C_{21} + n-C_{23} + n-C_{25}$) ($n-C_{22} + n-C_{24} + n-C_{25}$) The White Pine oil has a slight odd predominance (CPI = 1.07) in the same molecular weight range.

Table 2.—Amount and composition of extractable organic matter from a laminated mudstone (sampel 19) from a depth of 2,728.8 ft in in the Lonsdale 65-1 core.

[HC = hydrocarbon]

Organic carbon content (TOC)	1.77 pe	roont
Extractable organic matter (EOM)	_	rts per million
Saturated HC fraction	26	Do •
Aromatic HC fraction	27	Do.
Resins fraction	28	Do.
Asphaltene fraction	9 90	Do.
Total	90	
EOM/TOC	5 mg/	g
(saturated HC + aromatic HC)/TOC =	3 mg/	g
saturated HC/aromatic HC =	1.0	_

DISCUSSION

Hydrocarbon source-rock evaluation is based on the amount of organic matter in the rock, on the potential of the rock to produce hydrocarbons, and on the level of organic matter thermal maturity. amount of organic matter is measured by the organic carbon content, the potential to produce hydrocarbons by the genetic potential $(S_1 + S_2)$, and the level of organic matter thermal maturity by T_{max} . value of organic carbon proposed by Ronov (1958) for a potential shale source rock is about 0.5 percent. Based on this minimum, rocks at the type section of the Solor Church Formation are generally organic lean (22 of 25 samples contain <0.5 percent TOC) and have a poor source-rock These rocks also have a minimal potential to produce potential. hydrocarbons suggested by the following as genetic classification of Tissot and Welte (1978):

G.P. <2 mg/g: little or no source-rock potential 2 mg/g <G.P. <6 mg/g: moderate source-rock potential G.P. >6 mg/g: good source-rock potential.

Genetic potentials of the seven samples are <<2 mg HC/g sample.

The one apparently useful $T_{\rm max}$ value (494°C, sample 19) shows that the rocks of the Solor Church Formation are thermally very mature at the type locality. A $T_{\rm max}$ of about $460^{\rm o}$ C is suggested by Espitalié and others (1977) as the transition between the oil and wet gas generation zones of catagenesis. The $T_{\rm max}$ of $494^{\rm o}$ C for sample 19 suggests that organic matter in this rock is probably near the transition between the wet gas zone of catagenesis and the zone of metagenesis where methane remains as the only hydrocarbon (dry gas zone). Organic matter in the much more deeply buried, stratigraphically equivalent rocks, in the

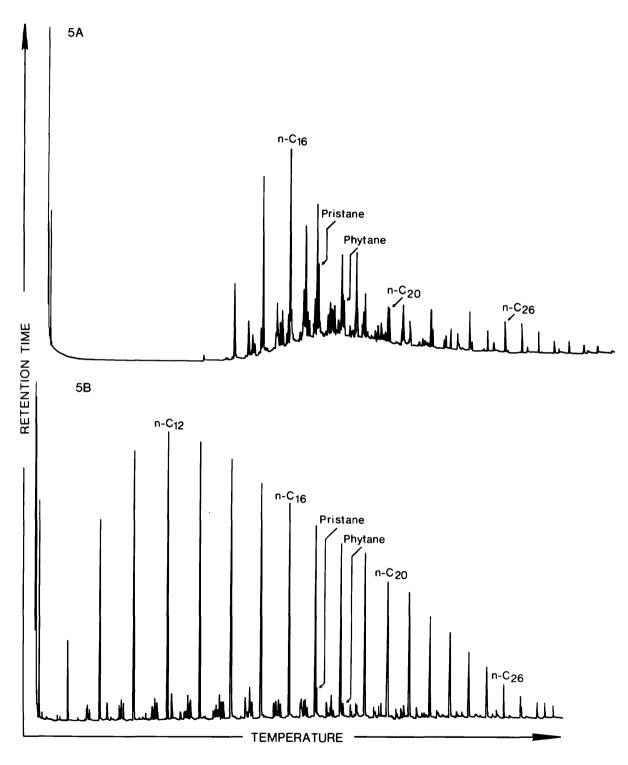


Figure 5.—Saturated hydrocarbon distributions for: sample 19 (fig. 5a) and oil from the White Pine Mine, Michigan (fig. 5b).

flanking basin east of the St. Croix horst, is probably at least as thermally mature, if not more so, than organic matter at the type locality. The low hydrogen indicies of organic matter in these samples are a likely result of the advanced level of thermal maturation.

The 5 mgEOM/g TOC for sample 19 is very low and is comparable to values (<10 mg/g) obtained from samples from great depths in the Douala Basin, Cameroon (>3,000 m, >9,800 ft) (Albrecht and others, 1976), Uinta Basin, Utah (>6,000 m, >19,700 ft) (Tissot and others, 1978), and from Phosphoria Formation shales, southeastern Idaho, northeastern Utah, and southwestern Wyoming that are inferred to have had burial depths of greater than 5,000 m (16,400 ft) (Claypool and others, 1978). The very low EOM/TOC for sample 19 is an additional measure confirming that organic matter in the Solor Church Formation is thermally very mature.

The dissimilar saturated HC compositions of the oil from the White Pine mine and sample 19 suggests that organic matter in the Solor Church Formation is dissimilar in composition to that in the Nonesuch Shale, the presumed source of the White Pine oil. This dissimilarity may be the result of different levels of organic-matter thermal maturity, or because of the very low saturated HC content (26 ppm), the saturated HC distribution of sample 19 may, in part, be a result of contamination during sample handling and analysis.

Burial Depths and Time-Temperature Relationships

Independent geologic evidence to help determine maximum burial depths or a time-temperature history of the Solor Church Formation at this location does not exist. The Keweenawan Fond du Lac Formation is absent, and only the presence of a 12 m (40 ft) thick regolith at the top of the Solor Church Formation and 11 m (37 ft) of Keweenawan Hinckley Sandstone mark the approximately 500 m.y. period between deposition of the Solor Church Formation and deposition of the basal beds of the Upper Cambrian Mount Simon Sandstone.

The geochemical composition of the organic matter, as indicated by pyrolysis behavior and content of extractable organic matter, suggests that thermal maturity is quite advanced; equivalent to vitrinite reflectance of 2.0-2.2 or a time-temperature-index (TTI) of 1,500 (Waples, 1980). If it is assumed that (1) heating has been only due to burial, (2) maximum burial was one km (3,300 ft) or less for the approximately 1,000 m.y. since deposition of the Solor Church Formation, and (3) a normal geothermal gradient (30°C/km, 87°F/mi) has always been present, then calculated thermal maturity as measured by TTI would only be near 30, equivalent to a vitrinite reflectance of about 0.8. observed level of thermal maturity (TTI about 1,500) requires a higher thermal history, which is a result of greater depth of burial and (or) a higher geothermal gradient. A TTI of about 1,500 can be achieved, for example, by assuming the high geothermal gradient of 75°C/km (220°F/mi) characteristic of present-day Salton Sea, California geothermal area (Muffler and White, 1969), burial over a 25-m.y. period to depths of about 2 km (6,600 ft), remaining near that depth for 50 m.y., then uplift and erosion combined with a decreased geothermal gradient over a

100 m.y. period. Any reasonable TTI senario requires significantly greater depths of burial and higher geothermal gradients than at present.

Morey (1977) observes Solor Church-like rock fragments in the Fond du Lac Formation. This suggests that the greatest burial depth and thermal alteration of the organic matter in the Solor Church Formation, at least in the rocks on the St. Croix horst, occurred fairly early, and that any hydrocarbons generated were probably lost during the subsequent uplift and erosion that produced the clastic sediments included in the Fond du Lac Formation.

SUMMARY

- 1. Hydrocarbon source-rock evaluation of the bluish-gray, greenish-gray and medium-dark-gray to grayish-black beds primarily in the lowest 104 m (340 ft) of the Solor Church Formation in the Lonsdale 65-1 core shows: (a) the rocks are generally organic lean (TOC <0.5 percent for 22 of 25 samples); (b) the organic matter present is thermally very mature ($T_{max} = 494^{\circ}\text{C}$, sample 19) and is probably near the transition between the wet gas phase of catagenesis and metagenesis (dry gas zone); and (c) the rocks now have a minimum potential for producing additional hydrocarbons (genetic potential $\approx 0.30 \text{ mgHC/gm rock}$).
- 2. Saturated HC distributions from a laminated mudstone (sample 19) in the Solor Church Formation and oil from the Nonesuch Shale at the White Pine mine, northern Michigan, are dissimilar, suggesting geochemically dissimilar organic matter in the rocks. This dissimilarity may be the result of different levels of thermal maturity.
- 3. Although no direct evidence exists from which to determine maximum depths of burial or time-temperature relationships, the observed thermal maturity of the organic matter requires significantly greater depths of burial and (or) higher geothermal gradients.
- 4. The thermal alteration of organic matter in the Solor Church Formation on the St. Croix horst probably took place relatively early, prior to deposition of the overlying Fond du Lac Formation. Any hydrocarbons that might have been generated during this early thermal alteration were probably lost during the subsequent uplift and erosion that produced clastics sediments included in the Fond du Lac Formation.

REFERENCES CITED

- Albrecht, P., Vandenbroucke, M., Mandengue, M., 1976, Geochemical studies on the organic matter from the Douala Basin (Cameroon). I. Evolution of the extractable organic matter and the formation of petroleum: Geochimica et Cosmochimica Acta, v. 40, p. 791-799.
- Bray, E. E. and Evans, E. D., 1961, Distribution of n-paraffins as a clue to recognition of source beds: Geochimica et Cosmochimica Acta, v. 22, p. 2-15.
- Bush, P. R., 1970, A rapid method for determination of carbonate carbon and organic carbon: Chemical Geology, v. 6, p. 59-62.
- Chaudhuri, S., 1972, Radiometric ages of Keweenawan intrusions and extrusions in Michigan and adjacent areas: Geological Society of America Abstracts with Programs, v. 4, p. 470.
- _____1975, Geochronology of upper and middle Keweenawan rocks of Michigan: Marquette, Northern Michigan University, 21st Annual Institute on Lake Superior Geology, Proceedings, p. 32.
- Chaudhuri, S., and Faure, G., 1967, Geochronology of Keweenawan rocks, White Pine, Michigan: Economic Geology, v. 62, p. 1011-1033.
- Claypool, G. E., Love, A. H., and Maughan, E. M., 1978, Organic geochemistry, incipient metamorphism, and oil generation in black shale members of Phosphoria Formation, Western Interior United States: American Association of Petroleum Geologists Bulletin, v. 62, no. 1, p. 98-120.
- Connan, J., 1976, Etude geochimique d'un echantillon d'hule de la mine de White Pine (Michigan, U.S.A.): informal report, centre De Recherches-Pau, Dept. Recherches en Geologie, 5 p., 3 figs.
- Craddock, Campbell, Thiel, E. C., and Gross, B., 1963, A gravity investigation of the Precambrian of southeastern Minnesota and western Wisconsin: Journal Geophysical Research, v. 58, p. 6015-6032.
- Espitalié, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P., Paulet, J., and Boutefeu, A., 1977, Méthode rapide de caractérisation des roches mères, et de leur potentiel pétrolier et de leur degré d'evolution: Revue de l'Inst. Français de Pétrole, v. 32, no. 1, p. 23-42.
- Forsman, J. P. and Hunt, J. M., 1958, Insoluble organic matter (kerogen) in sedimentary rocks of marine origin, *in* Weeks, L. G., ed., Habitat of Oil: Tulsa, Okla., American Association of Petroleum Geologists, p. 747-778.
- Gustavson, J. B., 1983, Basement rift control on oil production in eastern Kansas: American Association of Petroleum Geologists, v. 67, no. 8, p. 1324-1325.
- Kirwin, P. H., 1963, Subsurface strtigraphy of the Upper Keweenawan red beds in southeastern Minnesota: University of Minnesota, Unpublished M.S. Thesis, 74 p.
- Klasner, J. S., Cannon, W. F., and VanSchmus, W. R., 1982, The pre-Neweenawan tectonic history of southern Canadian Shield and its influence on formation of the Midcontinent Rift, in Wold, R. J., and Hinze, W. J., eds., Geology and tectonics of the Lake Superior basin: Geological Society of American Memoir 156, p. 27-46.

- Lee, C. K., and Kerr, S. D., 1983, Mid-continent rift system--A frontier hydrocarbon province: American Association of Petroleum Geologist, v. 67, no. 8, p. 1325.
- Mooney, H. M., Craddock, Campbell, Farnham, P. R., Johnson, S. H., and Volz, G., 1970a, Refraction seismic investigations of the northern Midcontinent Gravity High: Journal Geophysical Research, v. 75, p. 5056-5086.
- 1970b, Seismic studies over the Midcontinent Gravity High in Minnesota and northwestern Wisconsin: Minnesota Geological Survey Report of Investigations 11, 191 p.
- Morey, G. B., 1972, Petrology of Keweenawan sandstones in the subsurface of southeastern Minnesota, in Sims, P. K., and Morey, G. B., eds., Geology of Minnesota: A centennial volume, Minnesota Geological Survey, p. 436-449.
- 1974, Cyclic sedimentation of the Solor Church Formation (Upper Precambrian, Keweenawan), southeastern Minnesota: Journal of Sedimentary Petrology, v. 44, p. 872-884.
- _____1977, Revised Keweenawan subsurface stratigraphy, southeastern
 Minnesota: Minnesota Geological Survey Report of Investigations
 16, 67 p.
- Mossler, J. H., 1972, Paleozoic structure and stratigraphy of the Twin City region, in Sims, P. K., and Morey, G. B., eds., Geology of Minnesota: A centennial volume, Minnesota Geological Survey, p. 485-497.
- Muffler, L. J. P. and White, D. E., 1969, Active metamorphism of upper sediments in the Salton Sea geothermal field and Salton Trough, Southeastern California: Geological Society of America Bulletin, v. 80, p. 157-82.
- Orr, W. L., 1983, Comments on pyrolytic hydrocarbon yields in source-rock evaluation, in Bjoroy, J., and others, eds., Advances in organic geochemistry, 1981: John Wiley & Sons Limited, p. 775-787.
- Ostrom, M. E., 1967, Paleozoic stratigraphic nomenclature for Wisconsin: Wisconsin Geological and Natural History Survey Information Circular 8, 1 sheet.
- Petroleum Information, Incorporated, 1984, Keweenawan Rift--A play in the making?: Petroleum Information, Inc., Kansas Report, March 23, 1984, p. 5-6.
- Ronov, A. B., 1958, Organic carbon in sedimentary rocks (in relation to presence of petroleum): Translation in Geochemistry, No. 5, p. 510-536.
- Sims, P. K., 1970, Geologic Map of Minnesota: Minnesota Geological Survey Miscellaneous Map M-14.
- Sims, P. K., and Zietz, I., 1967, Aeromagnetic and inferred Precambrian paleogeologic map of east-central Minnesota and part of Wisconsin: U.S. Geological Survey Map GP-563.
- Thiel, E. C., 1956, Correlation of gravity anomalies with the Keweenawan geology of Wisconsin and Minnesota: Geological Society of America Bulletin, v. 67, p. 1079-1100.
- Thiel, G. A. and Schwartz, G. M., 1941, Subsurface structure of the Paleozoic rocks of southeastern Minnesota: Geological Society America Bulletin, v. 52, p. 49-60.

- Thwaites, F. T., 1912, Sandstones of the Wisconsin coast of Lake Superior: Wisconsin Geological and Natural History Survey Bulletin 25, 117 p.
- Tissot, B. P., Deroo, G., and Hood, A., 1978, Geochemical study of the Uinta Basin--formation of petroleum from the Green River Formation: Geochimica et Cosmochimica Acta, v. 42, p. 1469-1485.
- Tissot, B. P. and Welte, D. H., 1978, Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration: Berlin, Springer Verlag, 538 p.
- Tyler, S. A., Marsden, R. W., Grout, F. F., and Thiel, G. A., 1940, Study of the Lake Superior Precambrian by accessory-mineral methods: Geological Society of America Bulletin, v. 51, p. 1429-1537.
- Volz, G. A., 1968, Seismic investigation of the River Falls basin in western Wisconsin and part of the St. Croix horst in southeastern Minnesota: Univerity of Minnesota, unpublished M.S. Thesis, University of Minnesota.
- Waples, D. W., 1980, Time and temperature in petroleum formation—
 Application of Lopatin's method to petroleum exploration: American
 Association of Petroleum Geologists Bulletin, v. 64, p. 916-926.