

## The origin, distribution and hydrocarbon generation potential of organic-rich facies in the Nonesuch Formation, Central North American Rift System: A regional study

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**Abstract**—Precambrian, unmetamorphosed, organic-rich clastic rocks, whilst uncommon in the geologic record, are of interest with respect to their potential for hydrocarbon generation. The ~1.1 billion year old Nonesuch Formation is primarily a lacustrine deposit which is part of a thick sequence of volcanic and clastic sedimentary rocks that filled an aborted rift in central North America. Previous organic geochemical investigations of the Nonesuch Formation have been limited to isolated samples from the basal portion of the Nonesuch Formation at a copper mine (White Pine) in northern Michigan.

In the present study, 183 outcrop and core samples of the Nonesuch Formation from northern Wisconsin and Michigan (Upper Peninsula) were collected for sedimentologic and organic geochemical analyses. Total organic carbon (TOC) values for the samples ranged from 0.0 to 2.5% and showed a strong correlation between organic richness and depositional environment. Detailed petrographic analysis using incident white light and reflected blue light fluorescence revealed two major organic petrographies (1 and 2) which could be further distinguished using combined pyrolysis-gas chromatography/mass spectrometry (PY/GC/MS). Whereas the composition of Organic Petrography 1 kerogens is primarily aliphatic, the composition of Organic Petrography 2 kerogens is dominated by aromatic and/or phenolic constituents. The geographic and stratigraphic distribution of rocks bearing the two organic petrographies indicate that variable source-input or preservation, superimposed over maturity differences, is responsible for both organic petrographic and kerogen pyrolysis compositions.

**Key words:** kerogen, fluorescence petrography, Nonesuch Formation, pyrolysis-GC/MS, Precambrian sediments, Central North American Rift System, regional source rock analysis, Lake Superior region, lacustrine sediments, stable carbon isotopes

### INTRODUCTION

Regional occurrences of organic-rich, unmetamorphosed Precambrian sediments are rare in the geologic record. The Middle Proterozoic Nonesuch Formation, representing such an occurrence, is of great interest from the standpoint of Precambrian rift basin tectonics and sedimentology, the origin of stratiform metal deposits and the distribution and chemical character of pre-Paleozoic organisms. Recent interest has centered on the possibility that economic petroleum accumulations, sourced by the Nonesuch Formation, may exist in a region that has long been considered a classic example of a non-productive igneous and metamorphic province. The occurrence of crude oil seeps at the White Pine Mine locality (Fig. 1), widely believed to be indigenous to the Nonesuch Formation, lends credence to such speculations.

The tectonic and sedimentologic evolution of the Oronto group, which includes the Nonesuch Formation, has been examined by Chase and Gilmer (1973), Fowler and Kuenzi (1978), Elmore (1981, 1984) and Dickas (1986). The Oronto Group is a

thick, volcanic and clastic basin-filling sequence occupying the Keweenaw Trough, a northern extension of the Central North American Rift System. This system, which started as a proto-oceanic rift approximately 1.1 billion years ago, extends 1300 km from the Lake Superior region to northeastern Kansas. The rift system eventually failed, but not before 90 km of extension was achieved in the Lake Superior region.

Earlier sedimentologic and stratigraphic analyses of the Nonesuch Formation, primarily of the basal cupriferous zone (~10 m thick), resulted in nearshore and deltaic depositional environment interpretations (e.g. White and Wright, 1954; Ehrlich and Vogel, 1971). More recent studies involving detailed analyses of entire outcrop and core sections over an extensive area, however, reveal that the euxinic silts and shales, averaging 180 m in thickness, are likely to represent a lacustrine setting that evolved from marginal lacustrine to lacustrine to fluvial lacustrine (Elmore, 1981; Milavec, 1986).

The presence of organic matter in the basal Nonesuch Formation probably played an important role in copper mineralization. Copper-rich fluids are believed to have migrated through the underlying,

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conformable Copper Harbor Conglomerate into the Lower Nonesuch Formation where they were reduced to insoluble forms due to an organic-rich environment (e.g. Ensign *et al.*, 1968; Brown, 1971; Kelly and Nishioka, 1985). Micropaleontological investigations have shown that the Nonesuch shale contains a variety of organic remains. Analyses of shale extracts and the White Pine Mine seep oil resulted in the identification of a complex array of organic compounds. These investigations (discussed below), however, were made using only samples from the basal Nonesuch Formation at the White Pine Mine locality.

Barghoorn *et al.* (1965) and Moore *et al.* (1969) have described the distribution and appearance of organic matter in the Nonesuch Formation. Barghoorn *et al.* (1965) described aggregates or anastomosing aggregates of "thread-like" material, in addition to "globular spheroidal masses" and interstitial "opaque material." A possible algal affinity was proposed for the thread-like material, but it was acknowledged that little evidence was available for such an assignment. Organic matter was divided by Moore *et al.* (1969) into groundmass or matrix, and recognizable organic remains. The two categories of organic remains that were described are (1) preserved bacterial cells, fungal hyphae or actinomycete filaments attached to spore-like bodies and (2) solid "sporomorphs" (acritarchs) of unknown affinity but compatible with an algal origin. The thread-like associations of Barghoorn *et al.* (1965) were suggested by Moore *et al.* (1969) to be of possible fungal or actinomycete matte origin.

Eglinton *et al.* (1965, 1966) and Johns *et al.* (1966) have reported a number of organic compounds in the Nonesuch shale and Nonesuch oil seep. A range of normal alkanes, similar in carbon number range to those reported for Phanerozoic oils or source rock extracts, were found in both the Nonesuch oil and shale extract. Isoprenoid ( $C_{15}$ ,  $C_{16}$ ,  $C_{19}$ ,  $C_{20}$ ,  $C_{21}$ ), isoalkane ( $C_{16}$ ,  $C_{17}$ ,  $C_{18}$ ), anteisoalkane ( $C_{16}$ ,  $C_{17}$ ,  $C_{18}$ ) and cyclohexyl normal alkane ( $C_{16}$ ,  $C_{17}$ ,  $C_{18}$ ,  $C_{19}$ ) homologues were found in the oil. Only  $C_{16}$  and  $C_{18}$  isoprenoids were found in the Nonesuch shale extract. Barghoorn *et al.* (1965) reported the presence of at least two types of porphyrins (including a vanadyl porphyrin) in the Nonesuch shale. The porphyrins, although not detected in the Nonesuch oil, suggested that the sediments were never exposed to extreme temperatures. Hoering (1976) identified numerous isoprenoid and alkylcyclohexane homologs in the Nonesuch oil, but did not detect sterane and triterpane biomarker hydrocarbons in urea adducts or thiourea adducts and nonadducts. A more recent attempt to detect these biological marker compounds by hydrous pyrolysis of the Nonesuch shale met with the same results (Hoering and Navale, 1987).

Philp and van de Meent (1983) used pyrolysis-gas chromatography (PY/GC) and PY/GC/MS to characterize several Precambrian kerogens. They

determined that pyrolysates from the Nonesuch kerogen were similar in composition to those of the Fig Tree and Moodies (Swaziland Sequence, South Africa) and the Soudan Graphitic lens (northeast Minnesota). This group of kerogens was found to have a higher content of aromatic over aliphatic compounds when compared to the other group of kerogens, which was comprised of samples from the Onverwacht (Swaziland System, South Africa), Daspoort (Pretoria Series, South Africa), Kalgoorlie (Kalgoorlie, Western Australia) and from the Soudan Iron Formation (northeast Minnesota).

Although considerable progress has been made in characterizing organic matter from the Nonesuch Formation at the White Pine Mine locality (Fig. 1), a regional study assessing the origin, distribution and chemical nature of the kerogen associated with the Nonesuch shale has yet to be attempted. In the present study, 183 samples obtained from core and outcrop sections of the Nonesuch Formation were analyzed for organic carbon content and correlated with the results of sedimentologic analyses. Selected samples were described lithologically and characterized petrographically using reflected blue light fluorescence and incident white light. Representative samples were then analyzed by combined PY/GC/MS. The results of this study, elucidating the amount, type and maturity of organic matter, when used in conjunction with structural and geophysical data, should prove useful as a starting point for understanding Precambrian ecosystems in general and rift systems in particular, as well as facilitating petroleum exploration programs in the region.

## EXPERIMENTAL METHODS

### Sample collection

The Nonesuch Formation samples were collected from among eight core sections (housed at the U.S. Bureau of Mines Twin Cities Research Center, Minneapolis, Minnesota) and from four outcrop sections in Wisconsin and Michigan. The locations of these core and outcrop sections are shown in Fig. 1. Elmore (1981) previously used outcrop samples from the same sections to evaluate the sedimentologic history of the Nonesuch Formation. In conjunction with the present study, Milavec (1986) has interpreted the sedimentology of the Nonesuch Formation using samples from the same cores that were selected for organic geochemical analyses. A total of 183 samples were analyzed for organic carbon content. Fifty-five of these samples were examined macroscopically and microscopically under reflected blue light fluorescence for lithologic and petrographic characterization, respectively. Kerogen isolates from 9 representative samples were analyzed by PY/GC/MS. In addition, a bitumen extract from a solid hydrocarbon-impregnated sandstone taken from the White Pine Mine was also analyzed by

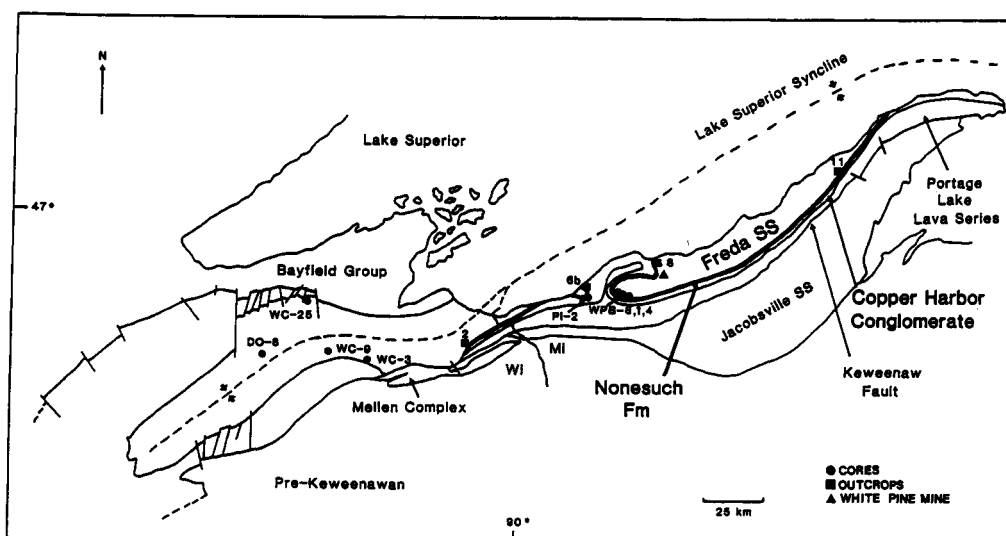


Fig. 1. Geologic map showing core and outcrop section locations. The White Pine Copper Mine locality is designated by the solid triangle. For the purpose of discussion, Michigan (Mi) is referred to as the eastern study area and Wisconsin (Wi) is referred to as the western study area.

PY/GC/MS. The experimental techniques that were employed for these analyses are described below.

#### Organic carbon determinations

Prior to TOC analysis, outcrop samples were scrubbed and exhaustively cleaned with distilled water to remove any traces of surficial dirt and plant growth. The core samples were also washed in an attempt to remove any possible drilling mud residues. The outcrop and core samples were crushed with a hammer to 5 mm fragments. After removal of pieces that were found to have traces of surficial oxidation, the rock fragments were ground for one minute using a micromill grinder (Bel Art Products, Pequannock, N.J.). The original oil-based lubricant used in the shaft adjacent to the grinding chamber was replaced with a silicone-based lubricant. Samples were sieved to pass 200 mesh and stored in glass vials. Care was taken at every step in the grinding and sieving process to prevent cross contamination of the samples.

Carbon analyses were performed using a LECO WR-12 Carbon Analyser (Leco Corporation, St. Joseph, Michigan). Four hundred to 600 mg samples were weighed out in porous crucibles. The samples were then treated with 2N HCl followed by 5N HCl and left overnight. Once the samples were thoroughly washed with distilled water (by vacuum aspiration) and dried overnight at 40°C, they were reweighed to determine %C carbonate. The Leco analyses were performed on the high carbon option (0.010–5.000%). Copper and iron were used as accelerators. The 70s combustion time provided complete burns in all cases. Duplicates were run for every fourth or fifth sample. In most cases, the duplicate TOC values differed by no more than 0.01%.

The results of previous control experiments (Imbus, unpublished results) indicated that time consuming solvent extraction procedures were un-

necessary for accurate organic carbon assessments of the samples analyzed. Extractable organic matter contributed about 10% by weight of total organic carbon. This is consistent with the determinations of Johns *et al.* (1966) who reported that 0.03–0.10% of the Nonesuch shale is comprised of indigenous extractable organic matter, corresponding to 3–10% of the total organic carbon. Hydrocarbon contamination of the core sample surfaces was minimal and not detectable in the interior of the samples.

#### Lithologic and petrographic analysis

Fifty-five organic-rich (mostly >0.50% TOC) samples were selected for lithologic and petrographic analyses. Macroscopic characterization resulted in several lithology categories, whereas incident white light (bright field) and reflected blue light fluorescent microscopy enabled the detection of organic constituents within the rocks. The data were used to ascertain the relationship between organic carbon content and the depositional environment interpretations of Elmore (1981) and Milavec (1986) and between kerogen pyrolysate composition and visual petrographic constituents.

#### Kerogen isolation

The nine kerogen isolates selected for PY/GC/MS analyses were prepared as follows. Coarse pieces of rock (~1 cm) were sonicated (30 min) four times in fresh, distilled CH<sub>2</sub>Cl<sub>2</sub>. The clean rock fragments were crushed with a mortar and pestle to pass 20 mesh and the above CH<sub>2</sub>Cl<sub>2</sub> extraction process with frequent vortexing was repeated. The rock was then treated with a 10% HCl solution followed by concentrated HF (48–52%), with several distilled water rinsings after each step. Neoformed fluorides (e.g. reported by Durand and Nicaise, 1980) were removed by treatment with hot 10% HCl (~100°C) with

subsequent distilled water washings. Density separation using filtered (0.45  $\mu\text{m}$ )  $\text{ZnBr}_2$  solution (specific gravity, 1.9) was done in several steps, with the float portion removed each time. The float material was filtered by vacuum aspiration through a 2  $\mu\text{m}$  stainless steel frit. Material remaining on the filter was rinsed, accompanied with agitation by stirring, with approximately 50 ml distilled water, 50 ml distilled methanol and 100 ml  $\text{CH}_2\text{Cl}_2$ , with complete drying between each step.

#### PY/GC/MS analyses

A PYRAN fused quartz pyrolysis system (RUSKA Laboratories, Inc., Houston, Tex.) coupled to a Finnigan Ion Trap Detector mass spectrometer was used to thermally degrade the kerogens and assess pyrolysate compositions. One to three mg of kerogen isolates were heated from 30 to 600°C at 30°C/min in a He flow of 30 ml/min. Pyrolysates were cryogenically trapped on a 30 m  $\times$  0.32 mm i.d. DB-1 (J&W Scientific, Rancho Cordova, Calif.) fused silica column at -35°C, which was subsequently ramped to 320°C at 10°C/min. The Ion Trap Detector was scanned from 47 to 400 amu once every second during the gas chromatographic separation. Mass chromatograms characteristic of aliphatic ( $m/z$  55, 57, 69, 71, 83, 85), aromatic ( $m/z$  92, 104, 106, 120, 128, etc.) and phenolic ( $m/z$  94, 108) pyrolysates and resulting fragmentogram area intensities were used to compare relative abundances and ratios of particular pyrolysates from the various samples.

### RESULTS AND DISCUSSION

#### Distribution of organic carbon

Total organic carbon (TOC) values for the 183 outcrop and core samples ranged from essentially zero to greater than 2.5%. It is evident that the majority of the higher TOC values are from the core samples, in particular those from the vicinity of the Porcupine Mountains, Michigan (PI-2 and WPB series). The apparent discrepancy in organic carbon content between outcrop and core samples in this area may simply reflect the ease with which organic-rich intervals in cores are identified relative to those in outcrops or perhaps, to a lesser extent, weathering effects.

The upper range of TOC values reported here are higher than those previously reported (e.g. the high range of values was listed in a compilation by Hunt, 1979 as 0.8–1.2% TOC). This is not doubt the result of limited sampling in the past, which appears to be exclusively from the cupriferous zone (White and Wright, 1954) occupying the basal several meters of the Nonesuch Formation in the White Pine Mine.

Organic carbon distribution in the Nonesuch Formation appears to be dictated by depositional environment. Figure 2 shows the relationship between TOC and independently-determined facies assemblages (Milavec, 1986). The Lacustrine Assemblage,

in particular its Shale Facies constituent, contains organic-rich deposits throughout the study area. Organic-rich zones also occur in the Mudstone Facies constituent (not shown) of the Marginal Lacustrine Assemblage, but only in the Michigan portion of the study area. Silstones and mudstones within the Fluvial Lacustrine Assemblage occasionally exceed 1.5% TOC.

#### Organic petrography

Microscopic analysis by incident white light and reflected blue light fluorescence of 55 selected samples revealed a complex array of organic constituents. Two prevalent "organic petrographies" were evident (Figs 2 and 3).

Organic Petrography 1 is recognized by the occurrence of orange-yellow to bright yellow fluorescing, filamentous material [Fig. 3(b)] that is often associated with an amorphous groundmass. Individual strands of this material, typically 10–50  $\mu\text{m}$  long and 1–2  $\mu\text{m}$  wide, usually occur in aggregates that occasionally intertwine to form 100–250  $\mu\text{m}$  thick organic-rich laminae. This material, when viewed in incident white light, is orange with distinct dark orange boundaries [Fig. 3(a)].

A distinction of two varieties of the filamentous material is made on the basis of size and clarity of boundaries. Most prevalent are those that have the larger of the above listed dimensions and ill-defined boundaries. The presence of the second variety, which appears to be gradational with the first, may be a manifestation of size or orientation. Should this distinction be real, the larger filamentous material strongly resembles the anastomosing "threads" of Barghoorn *et al.* (1965), interpreted as fungal or "actinomycete mattes" by Moore *et al.* (1969). The smaller filamentous material may correspond to the smaller "sporangia" of Moore *et al.* (1969).

The absence of unequivocal occurrences of either variety of filamentous material in blue light fluorescence defines Organic Petrography 2. Little or no fluorescence, other than that of minerals and sparse occurrences of dark orange-green fluorescing organic groundmass, was observed [Fig. 3(d)]. Incident white light, however, reveals an extensive network of diffuse dark orange or orange-red material that is similar in distribution and morphology to that seen in the Organic Petrography 1 samples [Fig. 3(c)]. A black, granular material, similar in appearance to bituminite (Sherwood, 1984), occurs in discontinuous laminae up to 150  $\mu\text{m}$  thick. Bituminite has been described as a possible algal degradation product (Teichmüller, 1982). This material occasionally grades into the dark orange filamentous material, possibly suggesting selective microbial degradation.

The geographic distribution of samples exhibiting the two organic petrographies is readily apparent (Figs 1 and 2). All of the 21 western samples examined, with the exception of a single WC-25 core sample (WC-25 B), are classified as Organic

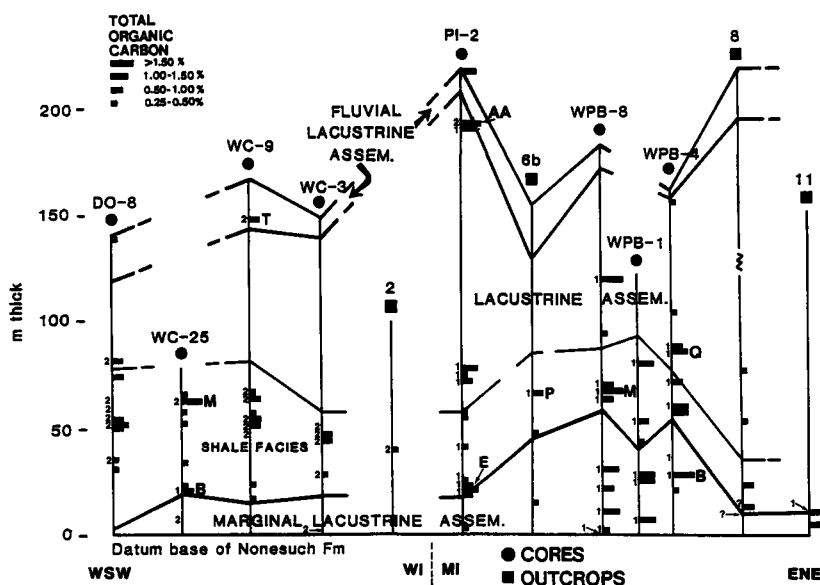


Fig. 2. Fence diagram showing the depositional environment interpretations of Milavec (1986). Total organic carbon values are indicated by the legend. Organic petrographies 1 and 2 are designated by the numbers 1 and 2, respectively. Kerogens analysed by PY/GC/MS are identified by letters. The datum is the base of the Nonesuch Formation. Although the sections are arranged from WSW to ENE, no horizontal scale is implied.

Petrography 2. Organic Petrography 1 is observed in sample WC-25 B as well as in 30 of the 34 eastern samples that were examined. Of the eastern samples not exhibiting Organic Petrography 1, one is from the Fluvial-Lacustrine Assemblage (PI-2 AA) and is an example of Organic Petrography 2. The remaining samples are not dissimilar to Organic Petrography 1 but appear to be organic lean other than groundmass and some pyrobitumen occurrences.

The task of explaining the distribution of the two organic petrographies is complicated by possible combined depositional environment and maturity effects. Rocks in the eastern and western study areas have been established by Milavec (1986) to be largely equivalent with respect to lithologies and depositional environment. It is concluded from the results of the present study that organic carbon distribution between the study areas is comparable and that similar, if not identical, filamentous material is present in eastern and western samples when observed in incident white light. This material shows little or no fluorescence in any of the western samples, with the exception of WC-25 B. Milavec (1986) has speculated that core WC-25 represents deposition on the northern flank of the basin rather than in the depocenter, where the other western samples were located. In incident white light, the same material appears orange in the eastern samples but dark orange-red in the western samples. Such a light to dark color change is thought by palynologists to be indicative of increasing maturity (e.g. Staplin, 1969). This evidence would appear to indicate that the western rocks, with the exception of the WC-25 core, are more thermally mature than the eastern rocks. Such an interpretation,

however, is not consistent with the occurrence of the Organic Petrography 2 sample in the eastern area. Alternatively, differential preservation of the same material may account for discrepancies in the bright field and fluorescent properties of organic matter comprising the two organic petrographies. The results of the pyrolytic analyses performed on kerogens representing both organic petrographies from the two study areas is presented below. The PY/GC/MS data are used to establish source or preservation differences and maturity-related trends in the Nonesuch Formation.

#### PY/GC/MS

Reconstructed ion chromatograms (RIC) from the PY/GC/MS analyses of nine Nonesuch Formation kerogens are presented in Fig. 4 (see Fig. 2 for location of samples analysed). Table 1 gives pertinent geologic information, TOC determinations and petrographic and lithologic data for the kerogens. The kerogens are readily divisible into three groups. The kerogen RIC traces shown in Figs 4(a)–4(f) are typical of those produced from Type I and II kerogens (e.g. Larter, 1984). Two of the remaining chromatograms [Figs 4(g) and 4(h)] show more aromatic and less aliphatic character. These two chromatograms are similar in overall appearance to the Group 2 kerogens examined by Philp and van de Meent (1983), which include the Fig Tree and Moodies (Swaziland Sequence, South Africa), the Soudan graphitic lens (northeastern Minnesota, U.S.A.) and the Nonesuch Formation, although the dominant aliphatic species in the Group 2 kerogens are methyl branched alkenes, possibly resulting

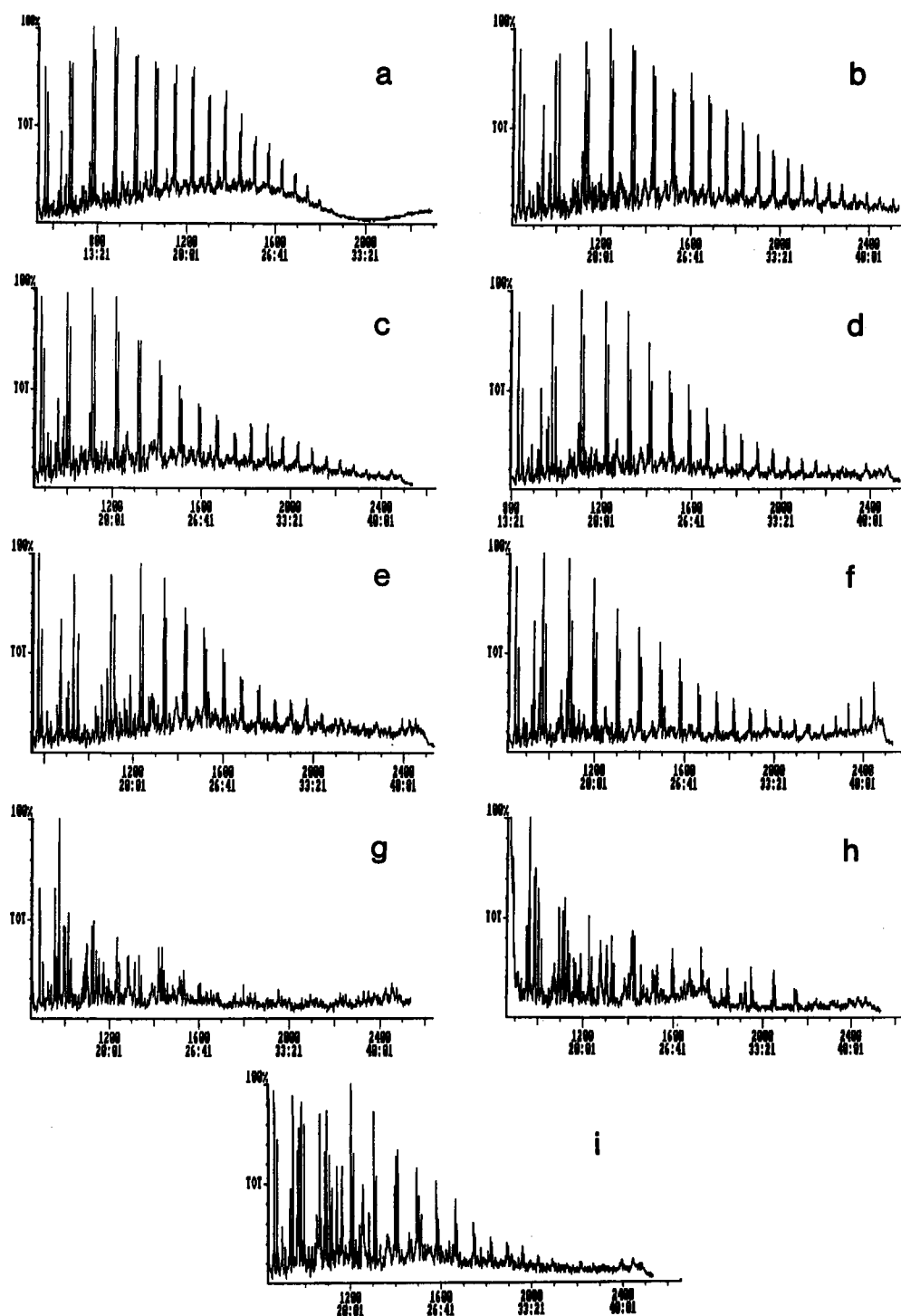


Fig. 4. Reconstructed ion chromatogram traces for each of the nine kerogens analysed by PY/GC/MS. The first *n*-alkene/*n*-alkane couplet shown in each chromatogram is  $C_8$ . Classification of the kerogen pyrolysates is described in the text. Kerogen identities are listed as follows: (a) 6b P; (b) WPB-8 M; (c) WPB-4 B; (d) WC-25 B; (e) PI-2 E; (f) WPB-4 Q; (g) PI-2 AA; (h) WC-9 T; (i) WC-25 M.

from pyrolysis conditions. The remaining kerogen [Fig. 4(i)] exhibits significant phenolic character that is atypical of Precambrian kerogens.

In addition to abundant normal *n*-alkanes and

1-alkenes and lesser quantities of alkyldienes, the following pyrolysate constituents were identified by retention times and comparison with standard mass spectra: simple alkyl-substituted benzenes,

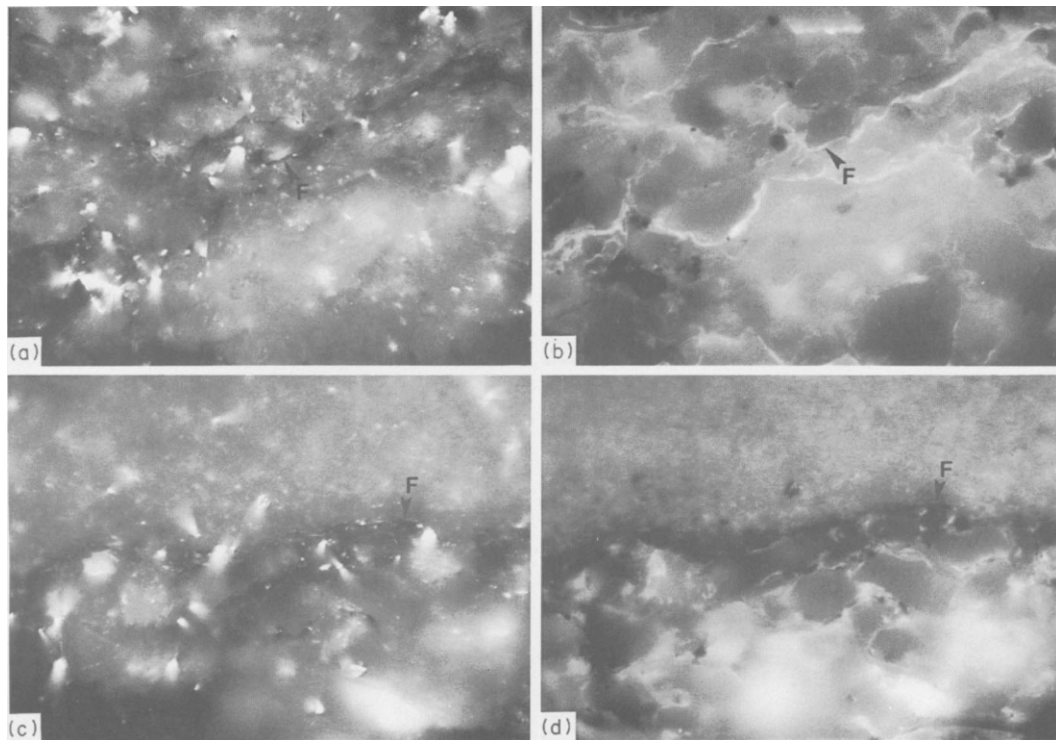


Fig. 3. Incident white light and blue light fluorescence photomicrographs representative of Organic Petrographies 1 and 2. Orange to dark orange filamentous material (F) is depicted in incident white light for Organic Petrographies 1 and 2 [(a) and (c), respectively]. Corresponding fluorescent photomicrographs reveal that this material fluoresces moderate to bright yellow orange in Organic Petrography 1 (b). The same material present in Organic Petrography 2 (d) either does not fluoresce or exhibits a dull, diffuse dark green-orange fluorescence. Field of view equals 250  $\mu\text{m}$ .

Table 1. General geological information for the kerogens selected for analysis by PY/GC/MS

Kerogen I.D. <sup>a</sup>	Study area <sup>b</sup>	Lithology	Facies Assemblage <sup>c</sup>	% TOC	% C <sub>CaCO3</sub>	Organic Petrography <sup>b</sup>
WPB-8 M	eastern	laminated siltstone	Lacustrine <sup>d</sup>	2.75	11.3	1
WPB-4 B	eastern	carbonate laminite	Marginal Lacustrine	1.55	35.4	1
WPB-4 Q	eastern	muddy-siltstone	Lacustrine <sup>d</sup>	1.24	10.8	1
PI-2 E	eastern	laminated siltstone	Lacustrine <sup>d</sup>	0.70	16.0	1
6b P	eastern	laminated siltstone	Lacustrine <sup>d</sup>	0.57	11.0	1
WC-25 B	western	carbonate laminite	Lacustrine <sup>d</sup>	0.98	42.8	1
PI-2 AA	eastern	silty-mudstone	Lacustrine	1.58	9.4	2
WC-9 T	western	mudstone	Fluvial Lacustrine	0.98	8.4	2
WC-25 M	western	laminated siltstone	Lacustrine <sup>d</sup>	1.84	8.6	2

<sup>a</sup>See Fig. 2 for sample locations.<sup>b</sup>See text for explanation.<sup>c</sup>After Milavec (1986).<sup>d</sup>Shale Facies of the Lacustrine Assemblage.

Table 2. Maturity-related parameters derived from kerogen pyrolysates

Kerogen I.D.	PYRAN Level I: $T_{max}$ <sup>a</sup>	$R_c$ <sup>b</sup>	Aromatic "complex" <sup>c</sup>	$n-C_8$ : alkene + alkane
			Aliphatic "complex"	$n-C_{20}$ : alkene + alkane
WPB-8 M	463	— <sup>d</sup>	0.06	4.3
WPB-4 B	449	— <sup>d</sup>	0.09	4.8
WPB-4 Q	451	0.67	0.14	3.7
PI-2 E	452	0.69	0.11	5.6
6b P	450	— <sup>d</sup>	0.04	4.5
WC-25 B	460	0.72	0.07	0.6
PI-2 AA	~410	0.98	0.64	14.2
WC-9 T	448	0.67	0.67	8.4
WC-25 M	446	0.65	0.39	13.3

<sup>a</sup>Proportional to but not numerically identical to Rock-Eval:  $T_{max}$  (Espitalié, 1977).<sup>b</sup>Calculated vitrinite reflectance equivalent (Radke *et al.*, 1982; Radke and Welte, 1983).<sup>c</sup>Aliphatic "complex" =  $n-C_8$ – $n-C_{25}$  (alkenes + alkanes); Aromatic "complex" = naphthalene + two methyl naphthalene isomers + phenanthrene + 1,2,3,9 methylphenanthrene isomers + anthracene.<sup>d</sup>All constituents necessary for determination not detected.

Table 3. Source-related parameters derived from kerogen pyrolysates

Kerogen I.D.	$\delta^{13}C_{PDB}$ kerogen (%)	Alkene + alkane: (first/second peaks)	Normalized abundances (%) <sup>a</sup>			Carbon Preference Index ( $n-C_{12-22}$ ) <sup>b</sup>		
			n-Octene	<i>m</i> + <i>p</i> Xylenes	Phenol	Alkenes	Alkanes	$\Sigma$
WPB-8 M	–33.45	8/10	49.4	28.7	21.9	0.89	0.92	0.90
WPB-4 B	–33.66	8/11	38.9	37.6	23.6	1.06	1.07	1.07
WPB-4 Q	–32.68	11/10	29.7	40.2	30.1	0.94	0.94	0.94
PI-2 E	–33.44	8/11	27.0	34.8	33.9	1.02	1.07	1.04
6b P	–33.29	8/10-11	65.0	33.3	1.7	1.03	1.01	1.02
WC-25 B	–34.08	8/11	44.7	39.1	16.2	1.02	1.03	1.02
PI-2 AA	–32.84	8/-	15.8	42.1	42.1	1.15	1.02	1.08
WC-9 T	–30.83	8/-	13.4	43.9	42.7	0.72	1.05	0.84
WC-25 M	–33.12	8/-	15.8	26.0	58.2	1.01	1.11	1.05

<sup>a</sup>After Larter (1984).<sup>b</sup>After McKirdy and Hahn (1982).

phenol and methyl phenols, small multi-ring aromatics including naphthalene, phenanthrene, methyl substituted phenanthrenes, anthracene, and varying quantities of styrene and methyl styrene, indane, indene and methyl indene. Tricyclic and pentacyclic terpane compounds and sterane compounds were not found. The identities of isoprenoid compounds and thiophene derivatives are, at present, inconclusive. An additional, unusual peak appeared in the 700–800 scan range (not shown) of some of the kerogens (in particular PI-2AA). Mass spectral analysis indicates that it may be a contribution from HBr remaining from the ZnBr<sub>2</sub> density separation step employed in the kerogen isolation procedure. Core treatment prior to sampling or other laboratory contamination appears unlikely, as all of the samples were

thoroughly solvent extracted and otherwise treated in an identical manner.

Ratios and values derived from the pyrolytic analyses were calculated (Tables 2 and 3) for each of the kerogens to ascertain if the initial distinction among RIC traces and petrographic observations is valid and, if so, whether maturity or source-related factors best explain the differences. As previously noted, all of the cores in the western portion of the study area (with the exception of WC-25) appear to be essentially devoid of fluorescent organic matter (i.e. Organic Petrography 2). Given that lithologies and depositional environment interpretations for the eastern and western cores largely correspond, it seems logical to invoke a thermal maturity explanation to account for the discrepancy. Such a hypothesis, how-



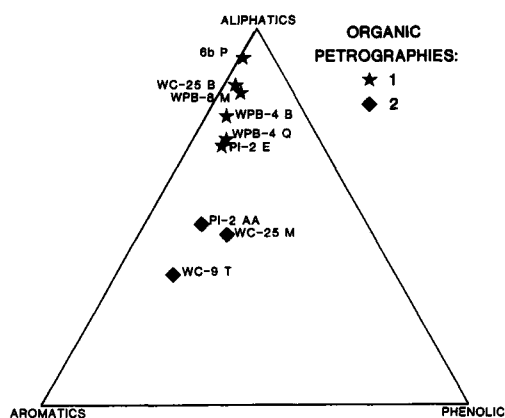


Fig. 5. Ternary diagram showing the relationship between chemical composition of kerogen pyrolysates and organic petrographies established for each sample (see text for explanation). The parameters listed at each vertex were obtained by summing ion concentrations of the following compounds: Aliphatics: normal alkenes and alkanes ( $C_8$ – $C_{25}$ ); Aromatics: toluene, ethyl benzene,  $m + p$  and  $o$ -xylenes and styrene; Phenolic: phenol and two methyl phenol isomers.

ever, is difficult to confirm using pyrolysis techniques, as few reliable parameters are presently available for maturity assessment (Larter, 1984). In addition, even small levels of differential source input may negate the influence of relatively small maturity differences.

Whereas the Organic Petrography 1 (aliphatic) and Organic Petrography 2 (aromatic or aromatic/phenolic) kerogens are distinct with respect to two maturity parameters that will be discussed below, it is interesting to note that, with the exception of sample PI-2 AA, the  $T_{max}$  and  $R_c$  values for the Organic Petrography 1 and 2 kerogens are similar. Whereas absolute maturity values are not implied here, Pyran Level I:  $T_{max}$ , analogous to the Rock-Eval:  $T_{max}$  (Espitalié, 1977), indicates that sample PI-2 AA is less mature than all of the other samples studied. The  $R_c$  value [calculated vitrinite reflectance equivalent derived by Radke *et al.* (1982) and Radke and Welte (1983)] using rock bitumens, however, shows kerogen PI-2 AA to be more mature than the others. It should be noted, however, that the application of the calculated  $R_c$  value to kerogen pyrolysates has not been established, and that  $T_{max}$  and  $R_c$  values are also source dependent.

Aromaticity, assessed by the Aromatic complex/Aliphatic complex parameter (see Table 2 for explanation), is high for the Organic Petrography 2 kerogens (PI-2 AA, WC-9 T and WC-25 M). As has been shown in recent studies (e.g. van Graas *et al.*, 1980, 1981; van de Meent *et al.*, 1980; Eglinton *et al.*, 1988), however, aromaticity of kerogen pyrolysates may not be as indicative of kerogen maturity as conventional views have implied (i.e. kerogen aromatizes with increasing maturity and, therefore, the pyrolysates from such a kerogen should be increasingly aromatic in character). A final parameter,  $(n-C_8 \text{ alkane} + \text{alkene})/(n-C_{20} \text{ alkane} + \text{alkene})$ , is

based on the concept that shorter-chain normal hydrocarbons are more likely to survive the effects of maturity than their longer chain counterparts. The Organic Petrography 2 kerogens show high ratios for this parameter relative to the other kerogens.

The apparent discrepancies between maturity-related parameters and the results of the petrographic analyses suggest different kerogen compositions, perhaps only partially related to maturity effects (e.g. differential preservation, as discussed below). The similarity in composition and chromatogram appearance between kerogens WC-9 T and PI-2 AA provides further evidence for this viewpoint as sample PI-2 E, from the same core as PI-2 AA, contains fluorescent entities and possesses maturity-related values similar to the majority of the kerogens. This is not to conclude, however, that the western cores are not, in general, more mature than the eastern cores. The lack of fluorescence in the western samples (exclusive of WC-25 B) of the presumably equivalent filamentous material (observed in incident white light), suggests the possibility of a detectable maturity difference.

Analysis of likely source-related parameters, in conjunction with petrographic data and the RIC traces (Fig. 4), reveals several distinctions amongst the kerogens. Selected parameters, listed in Table 3 and plotted on the ternary diagram in Fig. 5, show

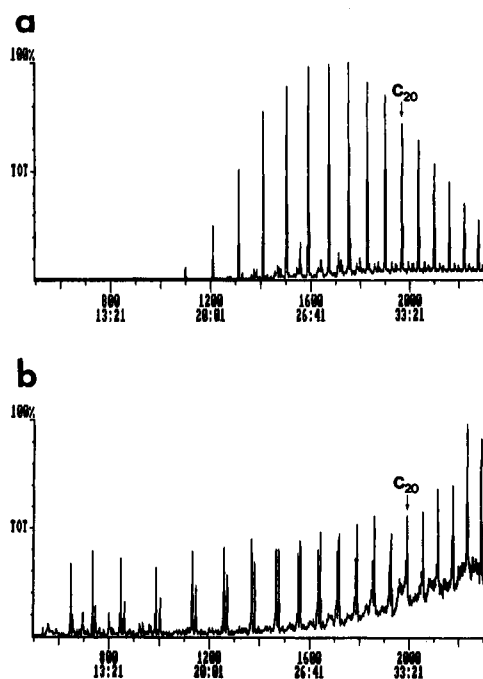


Fig. 6. PY/GC/MS analysis in two stages of a bitumen extracted from a solid-hydrocarbon-impregnated sandstone taken from the White Pine Copper Mine. The low temperature pyrolysis (30–330°C) represents the thermal extract (a). Aliphatic constituents are predominant and consist mainly of saturated compounds. The high temperature pyrolysis (330–600°C) released predominantly saturated and unsaturated compounds (b), probably resulting from thermal destruction of the asphaltene fraction.

a strong correlation to the petrographic constituents observed using incident white light and reflected blue light fluorescence. Most readily discernible is the aliphatic-rich character of kerogens from Organic Petrography 1 rocks. The remaining kerogens, aromatic and aromatic/phenolic-rich, represent samples with Organic Petrography 2. Further, tentative distinctions can be made between Organic Petrography 1 and 2 kerogens. Organic Petrography 1 kerogens appear to be slightly depleted in  $^{13}\text{C}$  relative to Organic Petrography 2 kerogens (Table 3). Organic Petrography 2 kerogens have a unimodal  $n$ -alkene +  $n$ -alkane maxima (8/-), whereas Organic Petrography 1 kerogens typically have slight but detectable 8/10 or 11 bimodalities. Relatively large discrepancies are apparent between  $n$ -alkene and  $n$ -alkane carbon preference indices for Organic Petrography 2. Petrographic variations in the relative abundances of the larger and smaller varieties of fluorescing, filamentous organic materials were observed in Organic Petrography 1 samples. However, little consistent chemical expression of these differences was observed, indicating that the materials are essentially identical in origin, or at least in composition. The dominant aliphatic nature of the pyrolysates derived from the Organic Petrography 1 kerogens indicates a likely algal (Type I) origin rather than the fungal origin suggested by Moore *et al.* (1969).

The RIC traces (Fig. 4) and the ternary plot of aliphatic, aromatic and phenolic components (Fig. 5) suggests three categories of kerogens: aliphatic (6b P, WPB-8 M, WPB-4 B, WC-25 B, PI-2 E and WPB-4 Q), aromatic (PI-2 AA and WC-9 T) and aromatic/phenolic (WC-25 M). Although petrographic data confirms the distinction between the aliphatic and the aromatic and aromatic/phenolic categories, no such distinction can be made between the latter two categories. The categories of kerogens proposed here are believed to result from kerogen type or preservation differences superimposed over possible maturity differences.

It is interesting to note that, based on the  $m + p$  xylene,  $n$ -octene and phenol compositions (Table 3), the three Organic Petrography 2 kerogens (WC-9 T, PI-2 AA and WC-25 M) are consistent with a Type III kerogen assignment according to the ternary plot proposed by Larter (1984) to estimate kerogen composition. It should be noted, however, that a comparison of the results of the present study with those reported by Larter (1984) are tentative, as different analytical techniques were employed, i.e. PY/GC (FID; Larter, 1984) versus PY/GC/MS (ion abundances; present study). Type III kerogens, according to the classic scheme of Tissot *et al.* (1974), are distinguished by their high O/C atomic ratios. High oxygen contents are typically described as being derived from terrestrial plant debris, an obvious impossibility for pre-Silurian rocks such as the Nonesuch Formation. It has been noted by McKirdy and

Hahn (1982, and references therein), however, that amorphous, "microbial" kerogens similar to vitrinite in elemental composition do exist. Such kerogens have been reported (McKirdy, 1976) to occur in Proterozoic to mid-Paleozoic carbonate and chert stromatolite deposits and are believed to originate from algal and pectic tissue (McKirdy *et al.*, 1980). Recent incorporation of terrestrially-derived bitumen, or contaminants of similar composition, into the WC-25 M kerogen is considered unlikely as methoxyphenol compounds, typically interpreted as lignin-derived (Sigleo, 1978; van de Meent *et al.*, 1980) were found to occur in extremely low concentrations. It is suggested here that the black, granular material (possibly bituminite), that is evident in samples exhibiting Organic Petrography 2, may result in the higher phenol contents. This material may be the result of degradation of algal material, which is a proposed origin of the maceral bituminite (e.g. Teichmüller, 1982).

A tentative relationship between lithology and phytoclast composition and, consequently, pyrolysate composition is apparent in this study. Aromatic dominated, Organic Petrography 2 samples WC-9 T and PI-2 AA are dark mudstones with small to moderate silt contents, respectively. Samples WC-25 B and WPB-4 B, both similar in pyrolysate composition, represent a "carbonate laminite" lithology (42.8 and 35.4%  $\text{CaCO}_3$ , respectively; Table 1). The remaining samples are described as fine to very finely-laminated siltstones, with the exception of WPB-4 Q, which has a significant clay component. It is of further interest to note that the two aromatic-dominated and  $^{12}\text{C}$ -depleted kerogens, WC-9 T and PI-2 AA, were sampled from portions of the formation interpreted as having fluvial-lacustrine and upper lacustrine (not in the Shale Facies; Fig. 2) depositional environments, respectively, as opposed to a marginal lacustrine or shale facies lacustrine environment that was interpreted for the remaining samples (Milavec, 1986). It was speculated by Milavec (1986) that organic-rich sediments associated with the former depositional environments may have been deposited in ponded areas on fluvial floodplains.

#### *Bitumen from the White Pine Mine*

Bitumen isolated from the White Pine Mine solid hydrocarbon-impregnated sandstone was analyzed in two stages. The low temperature pyrolysis i.e. thermal extract [30–330°C; Fig. 6(a)] yields almost exclusively  $n$ -alkanes, with a distribution very similar to those previously obtained by gas chromatographic analysis of oil from seeps and shale extracts from the same mine (Barghoorn *et al.*, 1965; Eglinton *et al.*, 1966; Johns *et al.*, 1966; Hoering, 1976). The high temperature pyrolysis [330–600°C; Fig. 6(b)], which is likely to represent the pyrolytic destruction of the asphaltene fraction, is more difficult to interpret. It shows little similarity to the kerogen pyrolysates, although this may be the result of a simultaneous-

release of loosely-bound lower molecular weight normal alkanes and tightly-held higher molecular weight normal alkanes from the asphaltenes (i.e.  $n\text{-C}_{17}$  and  $n\text{-C}_{25}$ ,  $n\text{-alkane} + n\text{-alkene}$  bimodalities, respectively). The stable carbon isotopic composition of the bitumen ( $-31.74\%$ ) indicates that kerogen WC-9 T ( $-30.83\%$ ) might reflect the composition of a possible source, as bitumens are typically depleted in  $^{13}\text{C}$  relative to their source kerogens (Stahl, 1977). It is apparent, however, based on PY/GC/MS data, that filamentous-dominated kerogens, predominantly aliphatic in nature, represent a more likely source. Clearly, it is premature to conclude, based on this limited data set (Table 3), which kerogen is the best candidate as a source for the bitumen isolated from the mine sample. Additional PY/GC/MS and stable carbon isotope analyses are planned to resolve this question.

#### SUMMARY

The Nonesuch Formation represents an unusual regional occurrence of a Precambrian sedimentary rock with organic carbon levels approaching those of many analogous Phanerozoic rocks, i.e. rift settings, but without the accompanying high maturity levels. Organic carbon values frequently exceed 1.0% throughout much of the formation and occasionally approach 3.0% in the Shale Facies of the Lacustrine Assemblage.

Two organic assemblages, or organic petrographies, were defined for the Nonesuch Formation using incident white light and blue light fluorescence. Organic Petrography 1, predominating in the eastern study area, is defined by the occurrence of an orange, filamentous network of organic matter (incident white light) that fluoresces. Organic matter, apparently similar to this in the western area, appears dark orange or orange-red with diffuse boundaries in incident white light but exhibits little or no fluorescence. This and the occurrence of black, granular material resembling bituminite defines Organic Petrography 2.

A combined organic petrographic and analytical pyrolysis approach was employed to determine whether source or maturity factors can account for the geographic and stratigraphic distributions of the petrographies and their constituent organic materials. It is concluded that the orange to dark orange filamentous material (white light) appearing in both organic petrographies is likely of the same origin but is better preserved in Organic Petrography 1 samples (in general, the eastern samples). It is, at present, uncertain whether microbial degradation, for example, results in the loss of fluorescent properties, although bituminite (material corresponding to descriptions of bituminite is prevalent in Organic Petrography 2 samples) has been cited as an algal degradation product (e.g. Teichmüller, 1982). A thermal maturity trend increasing to the west probably

exists, although it has not been firmly established by this study. The possibility of such a trend is supported by the presence of thermally post-mature Oronto Group equivalents in southeastern Minnesota (Hatch and Morey, 1985) and a satisfactory structural explanation for the occurrence of an Organic Petrography 1 sample in the western area. The clear distinction in pyrolysate composition between Organic Petrographies 1 and 2 is, therefore, very likely the result of differential preservation superimposed on postulated maturity influences. The occurrence of at least one Organic Petrography 2 sample in the eastern area supports this assessment. Based on PY/GC/MS data, the bitumen extracted from an asphalt-impregnated sandstone from the White Pine Mine may have possibly been sourced by a rock bearing aliphatic-rich kerogen similar to Organic Petrography 1.

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