

SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE
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THE ORGANIC GEOCHEMISTRY OF THE ORDOVICIAN WHITBY FORMATION -
A POSSIBLE ONTARIO SHALE

By

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INTRODUCTION

Historically, shale oil was produced in Ontario from a plant near Collingwood, on Lake Huron. In 1859, rock of the Ordovician Whitby Formation was retorted to produce fuel and lubricants. In 1863, this operation became uneconomic in the fact of the newly discovered conventional crude oil near Oil Springs, Ontario. Existing data suggested three units were sufficiently organic to warrant an updated assessment -- the Ordovician Whitby and the Devonian Kettle Point and Marcellus Formations. The initial phase of the project involved shallow sampling of the Whitby Formation by diamond drilling at 20 locations stretching from Manitoulin Island to Toronto (see Figure 1) and to Ottawa, where the stratigraphic equivalent Billings Formation is present. Lithological and geophysical logs for these boreholes and preliminary geochemical results are in press (1).

GEOLOGY

The Whitby Formation (Upper Ordovician) overlies the Lindsay Formation - a limestone with interbedded shaley units. The character of the contact with the overlying Whitby Formation is variable and may be an important control over the organic content of the lower part of the Whitby Formation. The Whitby Formation has been subdivided into Upper, Middle and Lower (Collingwood) members. The Upper member is generally a greenish-grey fissile shale between 36 and 52 m thick in the study area. The Middle member is a brownish-grey fissile shale between 5 and 26 m thick. The Lower member or Collingwood is a dark brownish-grey, sometimes highly fossiliferous marl with black shale interbeds and is 1.5 to 7 m thick. The Whitby Formation is overlain by interbedded limestone and shale of the Upper Ordovician Georgian Bay Formation.

The most organic-rich zone of the Whitby is the calcareous Lower (Collingwood) member which occurs in a transition from carbonates of the Lindsay Formation to shales of the Whitby Formation. Hutt, et al (2) suggest the Whitby Formation was deposited under reducing conditions, perhaps in a stagnant, non-aerated basin. Initially, however, restricted circulation with little input of clay and silt produced organic-rich marls (Collingwood member). Increased supply of terrigenous mud diluted the organic matter and produced the less-organic-rich shales of the Middle and Upper members. The Upper and Middle members rarely contain more than 2.5% total organic carbon (TOC) while the Collingwood member often includes intervals of 2 to 5 m with more than 3% TOC. Clearly, the major economic potential lies in the Collingwood member.

OIL YIELDS

The available Fischer Assay (FA) oil yields are less than 40 litres/ton. This oil has a specific gravity in the range 0.895 to 0.942 and the oil yields correlate reasonably well with TOC as shown in Figure 2. For the Whitby samples, the relationship between TOC and Fischer Assay oil yield is:

$$FA(1/t) = 7.7 \text{ TOC } (\%) - 8.8$$

1)

with a correlation coefficient of 0.847. The Whitby Formation samples averaged about 6.8 litres/ton per 1% organic carbon. The non-zero intercept on the TOC axis is consistent with the common observation that the oil yield from oil shales is not limited by organic carbon but rather by hydrogen. Some carbon residual remains after pyrolysis since there is insufficient hydrogen to combine to form hydrocarbons.

GEOCHEMISTRY

Besides evaluating the amount of organic matter present and the yield of hydrocarbons upon pyrolysis, this study examines the nature of the organic matter in the Whitby Formation. Basically, two questions are being addressed. What is the maturation state of the organic matter and what is the chemical nature and origin of the organic matter?

The thermal history of kerogen is usually discussed relative to the optimum time-temperature conditions for hydrocarbon generation. Immature kerogen has not been heated sufficiently to produce oil. At perhaps 40-80°C maximum paleotemperature, the kerogen should have been sufficiently matured to produce oil as well as natural gas. At higher paleotemperatures, 120-160°C, only hydrocarbon gases should be present as liquid hydrocarbons are no longer stable. The associated kerogen is considered overmature. Only kerogen which is immature to perhaps marginally mature can be expected to produce oil upon commercial pyrolysis. In fact, commercial retorting or pyrolysis can be viewed as a much more rapid version of natural oil generation in which the mature and overmature maturation levels are reached in the retort.

Standard petroleum geochemical studies have been undertaken to define the maturation level attained by the Whitby Formation. Preliminary assessment indicates an average vitrinite reflectance in the range 0.44% to 0.57%, corresponding to immature or marginally mature kerogen. Billings Formation shale from the Ottawa area is apparently overmature with reflectance of 1.38%. The thermal alteration index, T. A. I. (3), based on kerogen particle color changes with increased temperature, indicates a mature to overmature level for Ottawa and Manitoulin samples. The conodont alteration index (C. A. I.), values based on microfossil color changes with increased maturation, range from 1.5 to 2.0 at Manitoulin and Collingwood, from 2.0 to 2.5 in the Toronto area and are about 3.0 for the Billings Formation near Ottawa (4). These values correspond to immature or marginally maturation levels except for the overmature level for the Billings shale.

Although maturation studies are continuing, it would appear that the Billings shale in the Ottawa area is not a potential oil shale because of its overmature nature. On the other hand, the immature to marginally mature nature of the Whitby Formation in Ontario is encouraging. In fact, it may be advantageous to explore for less mature areas in order to obtain higher pyrolysis yields per unit of organic matter. Perhaps the high TOC sections in the Manitoulin Island-Collingwood area of the Whitby subcrop should be emphasized in further assessment.

CHEMICAL NATURE OF KEROGEN

Oil generation potential is not only dependent upon the amount and thermal history of organic matter, but also upon its chemical nature. This is controlled by the nature of the source material and by biological and/or chemical transformations upon burial. The classification of kerogen has been made on a number of bases (5). A very useful system for potential oil shales involves the recognition of essentially three "types" of kerogen -- types I, II and III. Type I kerogen is composed of marine or lacustrine organic material. It has the highest H/C of the kerogen types and has a high capacity to generate liquid hydrocarbons. Structurally, kerogen particles are dominantly algal (alginate) or amorphous. Type II kerogen may have a significant component of terrestrial as well as marine material. Its H/C is lower than type I kerogen and its O/C is slightly higher. Exinuous (cutinite, resinite), vitrinous and fusinuous materials are more common relative to amorphous material. Type III kerogen is dominantly terrestrial in origin with higher O/C and lower H/C values than the other types reflecting the increased proportions of polycyclic aromatics and oxygen-containing functional groups. Vitrinous and fusinuous materials dominate over exinuous and amorphous materials.

All known oil shales are types I or II kerogen. Type III kerogen tends to produce mainly gas upon pyrolysis. In this study, kerogen type is being assessed by visual examination under the transmitted light microscope and by geochemical means including atomic H/C determinations and pyrolysate types (6).

Initial visual assessments of Whitby shales along the subcrop indicated a dominance of amorphous organic matter in the NW and a dominance of exinuous material in the SE. Less than 10% vitrinous and fusinuous material was found. H/C values ranged from 1.2 to 1.6. Both methods indicate the dominance of type I and type II kerogens in the Whitby Formation.

Generally, there is an increase in the ratio of aromatic to aliphatic hydrocarbon types in the sequence from type I, through type II to type III kerogen. The products of kerogen pyrolysis

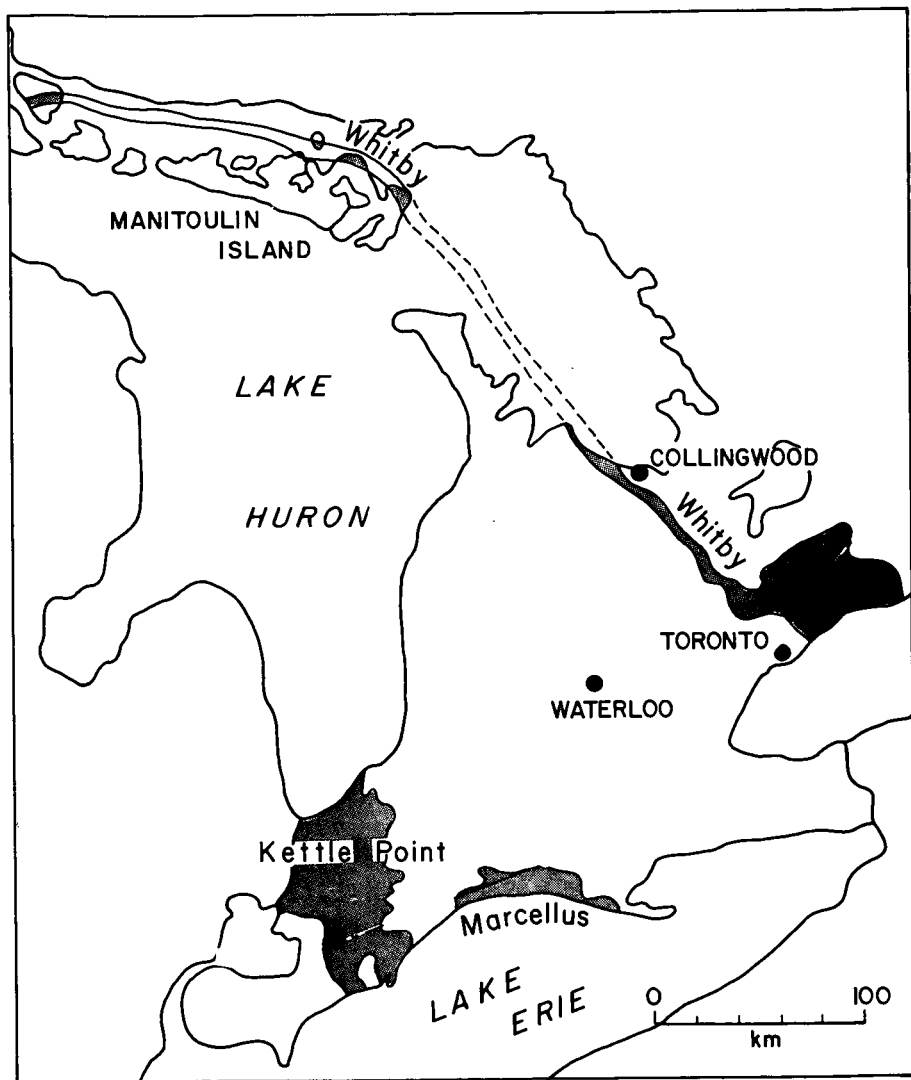


Figure 1. Outcrop and subcrop locations of the Whitby, Kettle Point and Marcellus shales in southern Ontario.

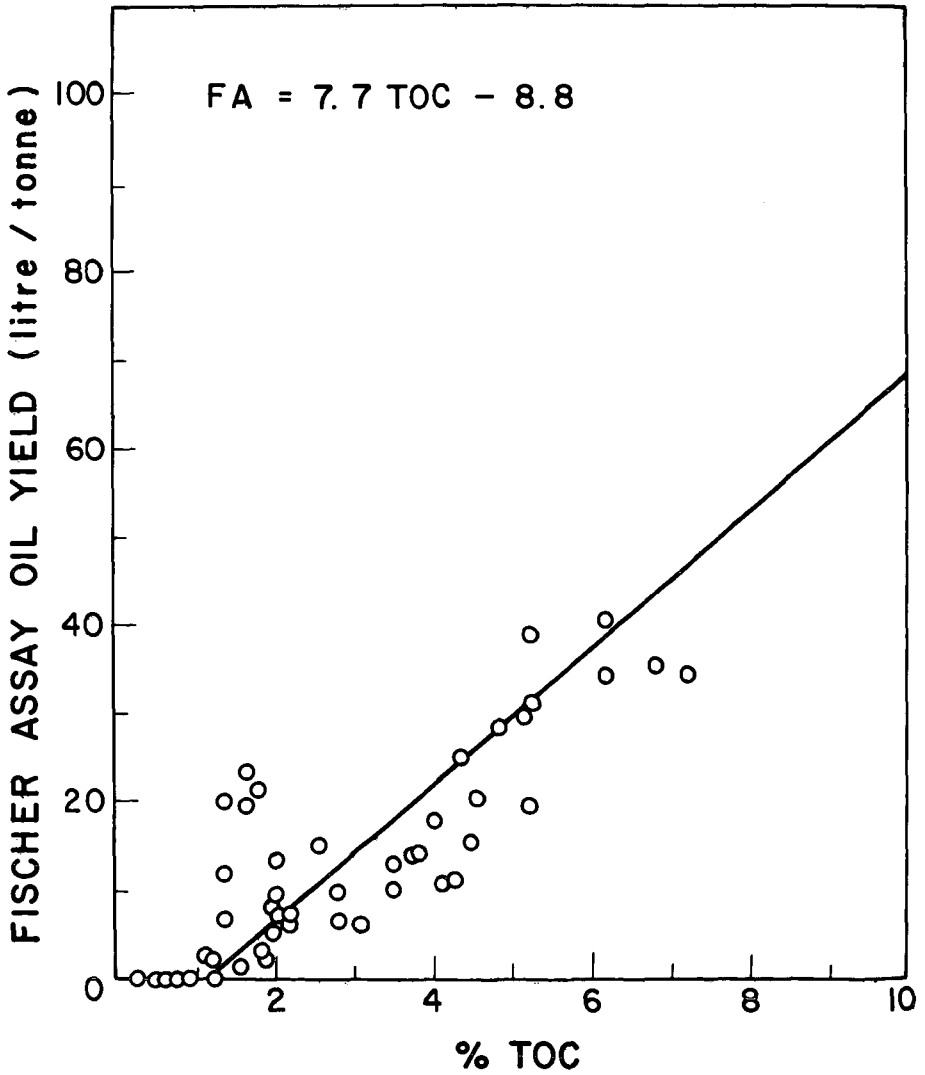


Figure 2. Relationship between oil yield by Fischer Assay and TOC for Whitby Formation samples.

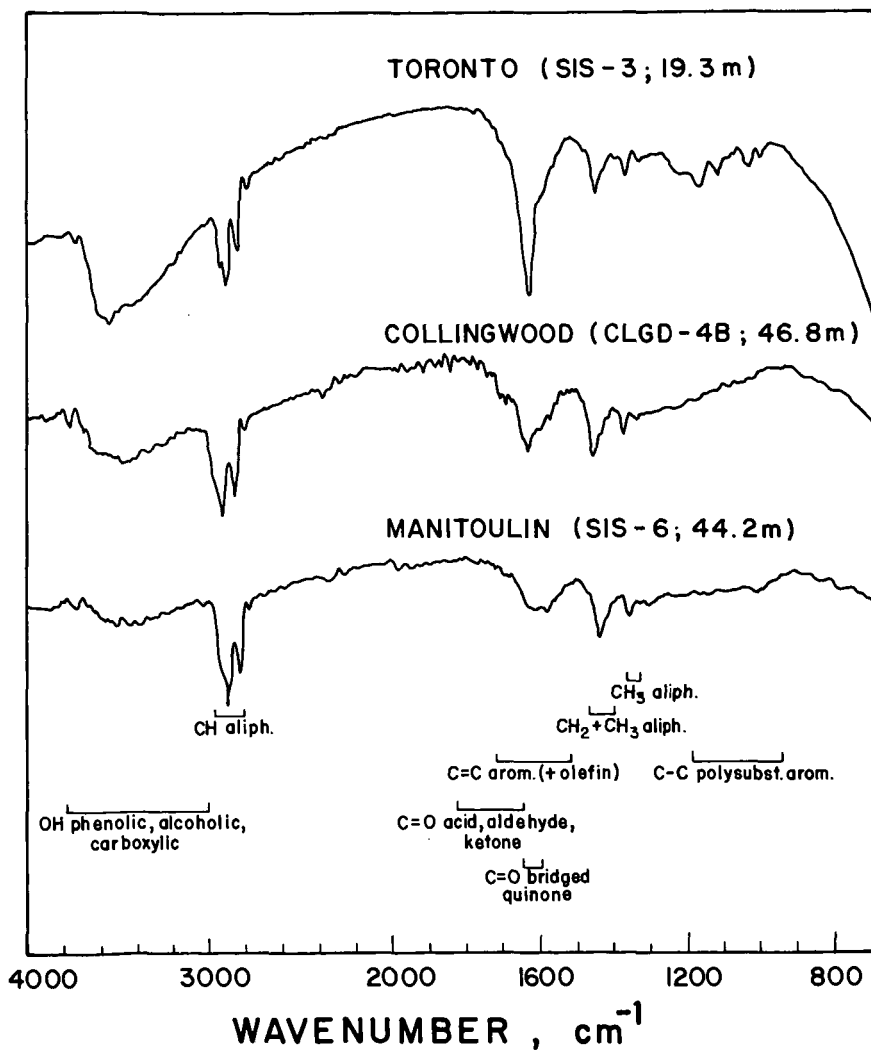


Figure 3. Typical I.R. spectra of kerogen isolated from the Whitby Formation.

also show this trend. Larter and Douglas (6) made use of this fact to establish a kerogen type index (R), which is the ratio of a selected aromatic (m- and p-xylene) to a selected aliphatic (n-octene) pyrolysis product. Type I kerogen has $R < 0.4$; type II has $0.4 < R < 1.3$; and type III has $R > 1.3$. Samples of Whitby shale and isolated kerogen have R values ranging from 0.28 to 0.7, again indicative of type I and type II kerogens.

Infrared (I. R.) spectra provide a qualitative indication of the types of organic structures present in the kerogen and their variation between samples (see Figure 3). In general, I. R. spectra from Manitoulin Island samples of Whitby shales are dominated by aromatic and aliphatic adsorption bands with a minor OH band. Shales from the Collingwood area also have only a minor OH band, but often have relatively larger C=C aromatic adsorption relative to aliphatic adsorption than Manitoulin samples. Many samples from the Toronto area show strong OH adsorption, C=O quinone adsorption and, perhaps, a more aromatic than aliphatic nature.

It seems that the Collingwood area shales are more aliphatic than the Manitoulin or Toronto area counterparts. This is reflected in higher H/C and higher FA/TOC for samples from Collingwood. The more aliphatic nature of Collingwood area spectra is also consistent with their greater proportion of amorphous organic matter. Clearly, more samples must be examined to assess the controls of the organic matter types and richness.

Isolated kerogen pyrolysates have been characterized by gas chromatography and mass spectrometry for clues as to the structural components of the kerogen itself. Horsfield and Douglas (7) found that mineral matrices increased the relative yield of low molecular weight pyrolysis products relative to high molecular weight products and also increased the proportion of aromatic to aliphatic pyrolysis products. Such secondary reactions were minimized by isolation from mineral catalysts. The gas chromatograms of kerogen pyrolysate are dominated by alkene-alkane pairs up to at least C₁₅ imposed on a background of polysubstituted benzenes. Above C₁₅, mono-substituted n-alkyl benzenes dominate.

The general view of kerogen structure presented by Tissot and Welte (5) is nuclei of stacked polyaromatic rings with some heterocycles containing O, N and S. Attached to these nuclei are alkyl chains, naphthenic rings and some oxygen-containing functional groups (hydroxyl, carboxyl, etc.). Bridges between nuclei include aliphatic chains and oxygen- and sulfur-containing groups such as ketones, esters and quinone. Almost all of these structural groups are indicated in the I. R. spectra. The pyrolysates clearly show the alkane-alkene chains, some of which may be breakdown products of the nuclei. The nuclei remnants are evident as higher molecular weight alkyl-substituted aromatics and as the lower molecular weight polysubstituted benzenes. No evidence of oxygen- or sulfur-containing heterocycles or bridges is found; however, CO₂ and H₂S are significant products of kerogen pyrolysis and could represent these components.

SUMMARY

In summary, the Upper Ordovician Whitby Formation represents an episode of deposition of fine-grained material on a shallow carbonate shelf. The Lower member - the Collingwood member - has the most potential for shale oil production, with TOC values ranging up to 9.2%. Fischer Assay oil yields of 40 l/t have been found. Yields up to 60 l/t can be expected for high TOC intervals.

These kerogen-rich rocks are immature to marginally mature with considerable oil generation potential remaining. Amorphous and exinous kerogen material dominate. Geochemical parameters point to a type II - minor type I kerogen which has favorable implications for shale oil potential. Kerogen pyrolysates are dominantly alkene-alkane chains of less than C₁₈ with numerous substituted benzenes including large molecular weight n-alkyl benzenes. Both pyrolysis products and I. R. spectra support current concepts of kerogen structure.

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