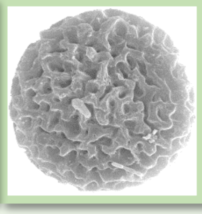
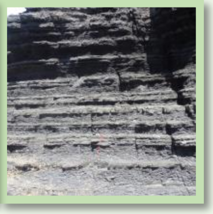
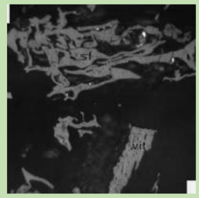
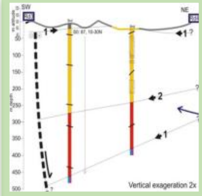
# Cumberland Basin Lower Carboniferous Source Rock Project

Cobequid Fault. Image credits: Mikenorton, Wikimedia










ChronoSurveys Lda www.chronosurveys.com

May 2017 Prepared for Nova Scotia Department of Energy

Final report

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*Prepared for: Nova Scotia Department of Energy*

*Date: May 2017*

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**DISCLAIMER**

The results and technical interpretations presented in this report are the best possible, derived from the data made available to us by the client. The uncertainty associated with the measure and estimation of sub-surface our outcrop parameters does not allow us to guarantee the accuracy or rightness of any of the opinions and interpretation in this report. Therefore, we shall not be responsible or liable for any damages, expenses or losses incurred by anyone or any company/institution resulting from any interpretation made by ChronoSurveys' Lda staff, agents or officers.



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| | | | |

## Table of Contents

## 1. Executive summary

This report describes and interprets the biostratigraphy and source rock potential of grey and black fine-grained sedimentary rocks from the Cobequid Highlands in the Cumberland basin of Nova Scotia.
The contract was awarded to ChronoSurveys Lda by Nova Scotia Department of Energy via the Flextrack system during February 2017.

Twenty samples were sent to ChronoSurveys' office in Almada for analysis. Nineteen of them were considered suitable for palynological processing (including biostratigraphy, palynofacies, vitrinite reflectance, spore colour and fluorescence) and for organic geochemistry (Total Organic Carbon and RockEval).

Palynological processing was conducted in ChronoSurveys partner lab at the University of Algarve, Portugal. The samples were analysed in terms of palynofacies, palynostratigraphy, vitrinite reflectance, fluorescence and spore colour.

Organic geochemistry analyses were conducted in Geo-Data labs in Hannover, Germany.

Eight samples were selected for thin sectioning based on the coarser grain size (even if restricted to thin laminae).

Palynofacies analysis show that all samples were deposited in an aquatic environment, likely lacustrine. There are no direct indicators of marine sedimentation. Most samples are dominated by phytoclasts indicating near lake shore, oxic settings with notable exception of samples 16TMO596 and 16TMO734B which were probably deposited in a more distal, anoxic setting. Samples 11TMO162, 16TMO620b and 15TMO606 were probably deposited in a transitional, suboxic setting.

In terms of hydrocarbon generation potential, the generalized black colour is indicative of inert type IV kerogen, consistent with the geochemical results. Samples 16TM0596, 16TMO622, 16TMO625, 16TMO734B and 16TMO734C are exceptions, with organic matter generally with dark yellow to brown hues, although with some black opaque phytoclasts as well. These samples have kerogen of type II and III with gas generating potential.

The geochemistry analysis show a very poor to negligible hydrocarbon generation potential for most of the samples. Sample 16TMO596 is clearly the one with higher potential as a gas-prone source rock. Other samples such as 15TMO409A, 16TMO625 and 16TMO622 have a poor to fair gas generating potential (TOC > 0,5wt.%). Samples with relatively high TOC – 11TM0162 (2,16 wt.%), 11TM0442B (0,74 wt.%), 15TM0590 (0,82 wt.%), 15TM0606 (1,21 wt.%) – seem to contain essentially inert (type IV) kerogen, a fact that can be explained either by the high thermal maturity.

The thin sections were checked for foraminifera or other bioclasts with stratigraphic relevance, but none of them had observable bioclasts, other than light brown spores that were better observed in palynological preparations

Ten out of the nineteen processed samples provided recognizable spores/pollen which, despite their poor to moderate preservation allowed age determination. These ten samples are assigned to the Mississippian. Of these, samples 16TM0622, 16TM0625, 16TM0734B and 16TM0734C are Tournaisian in age; sample 16TM0596 is Viséan in age and samples 11TM0162, 15TM0408, 15TM0593, 15TM606 and 15TM646 are probably Viséan in age; sample 15TM0590 is Mississippian in age (no refinement possible). Further details are provided in the text and appendixes.

The thermal maturity was assessed by analyzing spore fluorescence, spore colour and vitrinite reflectance with overall consistent results. The analyses show that most of the samples are overmatured in terms of hydrocarbon generation potential. Samples 16TM0622, 16TM0625, and 16TM0734C have much lower maturity in the wet gas window. Samples 16TM0734B and 11TMO162 are within the dry gas window. Sample 16TM0596 is within the oil window.

## 2. Introduction

### 2.1 Geographical location

Samples analyzed in this work were collected by Nova Scotia Department of Energy staff in the Cobequid Highlands, Cumberland county of Nova Scotia. Details of the sampled locations are unknown to the author, but based on the georeferencing of the maps provided, they seem to have been collected along outcrops of river valleys. Approximate location of the sample sites is illustrated in figure 1.

### 2.2 Geological context and previous work

The Cumberland basin is part of a larger group of Late Paleozoic basins in Eastern Canada, collectively called Maritimes basin. They share a Proterozoic to Early Devonian basement over which Famennian to Permian sediments deposited. The infill of the Cumberland basin is dominated by volcanics and continental clastics at its base (Fountain Lake and Horton Groups) followed by evaporitic and carbonate sediments of the Windsor Group. The Mabou and Cumberland Groups represent continental to coastal clastic sediments, including oil shales and coals, deposited during the Late Mississippian to Early Permian, conformably to unconformably on the underlying strata. The basin fill is topped by the continental clastic deposits of the Permian Pictou Group.

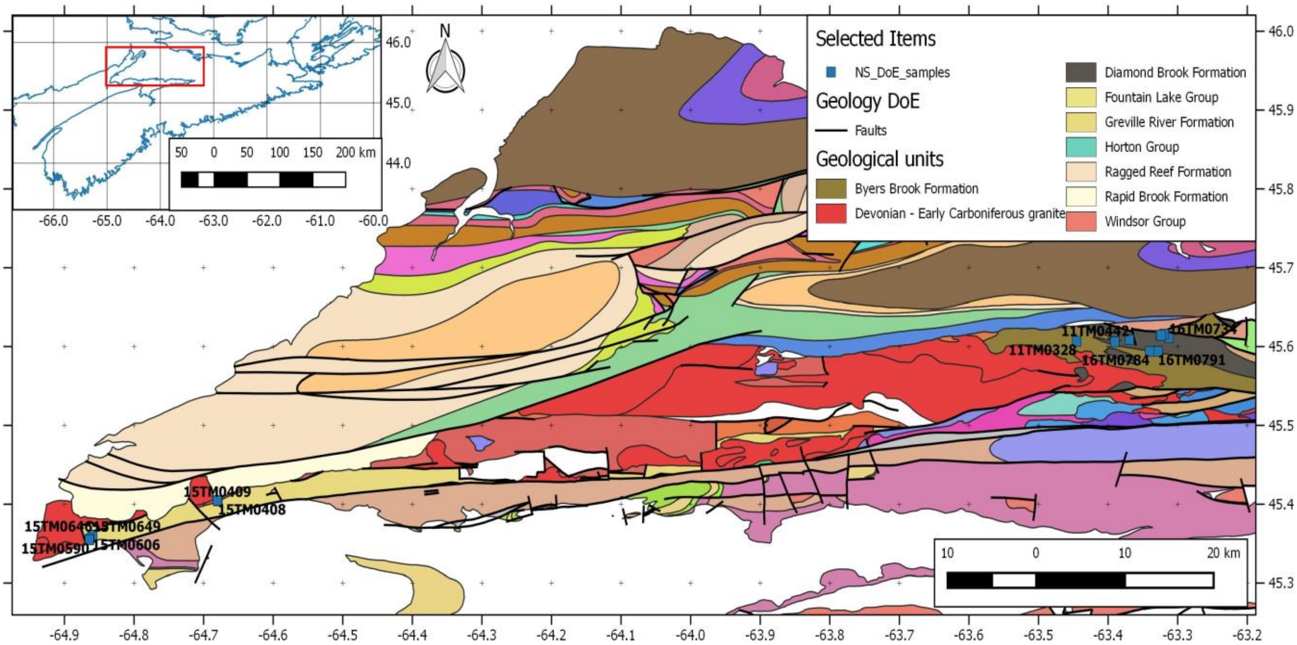


**Figure 1 – Simplified Geological map of the Cumberland County and neighboring areas with samples analyzed in this report. Adapted from NSDoE data.**

#### Biostratigaphy

The biostratigraphy of the basin, along with the neighboring ones, is mostly based on miospores and to a lesser extent, foraminifera and other marine fauna where limestones or other marine sediments occur.

Early palynological work on the Horton Group of Nova Scotia and correlatable units was done by Hacquebard (1957) who described the spore assemblages of two coaly samples from Blue beach and near West Gore. He described numerous species, many of them new, and concludes that the assemblage is Late Devonian or Early Carboniferous in age. Later Playford (1964) studied samples from the Horton Bluff Formation, Cheverie Formation and undifferentiated Horton Group. He concluded that the two Formations have different spore assemblages and are likely Tournaisian in age, although the Horton Bluff Fm. could extend to the Famennian.

Varma (1969) extended the study to the lateral equivalent Albert Formation and found very similar assemblages which were attributed to the Mississippian, although the basal Dawson Settlement Mb. could include Famennian strata.

Utting et al. (1989) revised previous work and studied new sections in Eastern Canada and established the first, and still valid, Mississippian miospore zonation of the Horton Group and lower part of the Windsor Group, largely comparable with the Western Europe zonations. Later Martel et al. (1993), showed the presence of latest Famennian (Strunian) assemblages at the base of the Horton Group in Nova Scotia, although no local biozonation was established for that interval.

| System | Series | Sub-stage | Miospore zones of Western Europe (Clayton et al., 1977) | Miospore zones of Nova Scotia (Utting et al., 1989) | | Nova Scotia Lithostratigraphy |
|---|---|---|---|---|---|---|
| Carboniferous | Viséan | V3 | TS *triradiatus-stephanephorus* | *noctuina-stephanephorus* | | Windsor Gr. |
| | | V1-2 | Pu *pussila* | | | Hiatus / Red beds |
| | Tournaisian | Tn 3 | CM *claviger-macra* | *decorus-claviger* | | Wilkie Brook/ Coldstream Fms. |
| | | | | *pretiosus* | | Cheverie Fm. |
| | | | PC *pretiosus-clavata* | *vallatus* | *cabotii* | Horton Bluff / Diamond Brook / Rights River Fms. |
| | | | | | *abstrusus-distinctus* | |
| | | Tn 2 | BP *balteatus-polyptycha* | | | Hiatus? |
| | | | HD *hibernicus-distinctus* | *rotatus - explanatus* | | Undiff. Horton Gr. |
| | | Tn 1b | VI *verrucosus-inchohatus* | | | |
| Devon. | Famenn. | | LN *lepidophyta-nitidus* | | | |

**Table 1 – Latest Devonian and Mississippian miospore biozonations and Nova Scotia's lithostratigraphy. Based on Clayton et al. (1977), Martel et al. (1993) and Utting et al. (1989).**

## Organic geochemistry and thermal maturity

Hamblin (1989) on his thesis studied Cape Breton Island Horton Group's potential source rocks in terms of maturity, TOC and Rock Eval. He concludes that type I source rocks are the most abundant (based on the presence of *Botryococcus* and other algal material), although likely restricted to the main depocenters. The thermal maturity and kerogen typing of the Horton Group in a wider area has been addressed by Utting and Hamblin (1991) based on the Thermal Alteration Index (TAI) of the palynological preparations from this Group. They conclude that the thermal maturity is mostly dependent on the burial depth, varying considerably (TAI 2 to 4 or possibly 5 – oil window to overmature) depending on the position on the half grabens where the Group was deposited and on post-Tournaisian sedimentation. The thermal influence of granitic plutons seems to be limited. The kerogen types are mostly type II and type III, more rarely of type I where algal amorphous material is common. The kerogen types and thermal maturity data point to a potential for dry gas generation although locally the high maturity reduces the generation potential of any hydrocarbons (Utting and Hamblin, 1991).

Mossman (1992) reviewed the Carboniferous source rocks of the Maritimes basin and concluded that the Horton Group, particularly the oil shales of the Albert Formation are excellent oil-prone source rocks, although the span of TOC, S1 and S2 values (using data from Mossman et al., 1987) also point to the presence of good, fair and poor source rocks.

A publicly available consultant report (Global Geoenergy Research, 2004) studied the source rock potential of Carboniferous rocks of Cape Breton, reviewing previous work and adding new samples and analyses. The main conclusions are that Horton Group's source rocks have oil generating potential in the northern part of the Mabou-Ainslie sub-basin (based on the geochemistry and thermal maturity) while the southern parts of the basin have more gas-prone source rocks, partly due to their higher thermal maturity. Also noteworthy is that the oil seeps in the area were typed to Horton Group source rocks, with minor to no contribution from source rocks of the Windsor Group.

It seems clear that the Horton Group rocks have a significant source rock potential, but the oil- or gas-prone nature of the rocks varies considerably between sub-basins and even within each sub-basin. Similarly, the thermal history of these source rocks seems to be quite varied, depending on their original position in the basin (closer or away from depocenters), post-depositional burial history and tectonic deformation. This variability reinforces the need and value of multidisciplinary source rocks studies: organic geochemistry, biostratigraphy, palynofacies and thermal maturity.

# 3. Materials and methods

## 3.1 Material

The sample lithologies and the analyses performed are summarized in the following table:

| Sample# | Sample ref | Lithology | Analyses performed |
|---|---|---|---|
| 1 | 11TM0162 | Laminated black marl | Paly, maturity, geochem |
| 2 | 11TM0328 | Laminated black marl | Paly, maturity, geochem, TS |
| 3 | 11TM0442B | Massive micritic black limestone | Paly, maturity, geochem |
| 4 | 15TM0408 | Laminated dark grey shale/siltstone | Paly, maturity, geochem |
| 5 | 15TM0409A | Massive black shale/siltstone | Paly, maturity, geochem |
| 6 | 15TM0590 | Laminated dark grey siltstone | Paly, maturity, geochem, TS |
| 7 | 15TM0593 | Micritic rippled laminated marl | Paly, maturity, geochem |
| 8 | 15TM0606 | Laminated dark grey shale/siltstone | Paly, maturity, geochem |
| 9 | 15TM0646 | Laminated dark grey shale/siltstone | Paly, maturity, geochem, TS |
| 10 | 15TM0649 | Massive dark grey shale/siltstone | Paly, maturity, geochem |
| 11 | 16TM0596 | Micritic massive Black limestone (pyritic) | Paly, maturity, geochem |
| 12 | 16TM0620A | Coarse bioclastic grey limestone | TS |
| 13 | 16TM0620b | Micritic black massive limestone (cherty?) | Paly, maturity, geochem |
| 14 | 16TM0622 | Micritic laminated black limestone | Paly, maturity, geochem |
| 15 | 16TM0625 | Coarse massive black limestone | Paly, maturity, geochem, TS |
| 16 | 16TM0734B | Micritic Black limestone | Paly, maturity, geochem, TS |
| 17 | 16TM0734C | Micritic dark grey limestone (laminated?) | Paly, maturity, geochem, TS |
| 18 | 16TM0784A | Micritic laminated black limestone | Paly, maturity, geochem |
| 18 | 16TM0790 | Coarse massive grey limestone | Paly, maturity, geochem, TS |
| 20 | 16TM0791 | Marly micritic black limestone | Paly, maturity, geochem, TS |

**Table 2 – Sample reference, location and analyses performed. Paly: Palynostratigraphy, palynofacies; Maturity: vitrinite reflectance, spore colour, fluorescence; TS: thin section and foraminifera.**

## 3.2 Methodology

### Sample preparation

All samples were observed in cut sections to obtain a general lithological description. They were also tested for carbonate content using 10% hydrochloric acid. The colour, grain size and weathering condition were used as criteria for the selection of samples – non-oxidized, black or grey colour, fine grained – for organic geochemical analyses (TOC and RockEval) and for palynological processing (biostratigraphy, palynofacies, thermal maturity). Grain size and lithology were used as criteria for thin sectioning and subsequent foraminifera studies – observable sand-sized grains (even if restricted to thin laminae) and preferably with carbonate content.

Samples suitable for thin sections were cut perpendicular to bedding in areas where sand-sized grains were observable. The resulting blocks were glued to glass slides and cut and polished to 30 µm thick. Cover slips were applied.

Samples suitable for palynology and organic geochemistry were trimmed, ensuring the removal of visibly weathered portions of the samples. The resulting pieces were then crushed using a hammer to 1-4mm sized particles for palynology processing (30 to 50g).

For geochemical analyses, ca. 10g of each sample were dried at 105°C for > 4h and milled using a ball mill. For determination of total organic carbon (TOC, wt%) the carbonate in the samples was removed by treatment with 10% hydrochloric acid and dried overnight.

### Palynology

Samples were processed for palynology using a standard cold hydrochloric acid (30% HCl) followed by cold hydrofluoric acid (40% HF) technique and finally hot hydrochloric acid (10% HCl) to remove resistant mineral particles. The resulting unsieved palynological (organic) residue of each sample was mounted in glass slides for palynofacies analysis/kerogen typing, representing full particulate organic matter contained in the rock. The remaining palynological residues were sieved using a 15µm mesh and two or more slides were produced.

Fifteen of the nineteen samples required oxidation to render palynomorphs translucent. This was attempted by using Schulze's solution (60% nitric acid supersaturated with potassium chlorate).

Taxonomic work was conducted under a biological transmitted light microscope coupled with a dedicated camera for the samples with translucent organic matter. For samples with dark opaque organic matter a reflected light microscope coupled with a dedicated camera was used, following the methodology of Machado and Flores (2015). Age determination was based on the published material for Nova Scotia and neighbouring regions (e.g. Utting, 1989) and regional biozonation schemes applicable to Nova Scotia, notably of Western Europe (Table 1; Clayton et al., 1977; Higgs et al., 1988).

### Palynofacies

The term palynofacies was introduced by Combaz (1964) and the concept has been successfully used for palaeoenvironmental interpretations and source rock assessment since then. Palynofacies is based on the study, usually quantified, of particulate organic matter (or palynological matter) obtained by maceration of sedimentary rocks (Tyson, 1993), as observed under transmitted light microscopy. The relative and absolute percentages of land- and marine-derived palynomorphs provide valuable information for the determination of sedimentary facies. Similarly, the quantification of oil- and gas-prone organic particles allows a rapid and semi-quantitative assessment of source rocks.

Palynological residues contain organic matter derived from terrestrial and aquatic sources. Several inshore, marine or terrestrial indexes exist in the literature, based on the proportions of the several types of organic matter. In the case of the Cumberland basin samples there are no direct evidences of marine sedimentation. Amorphous Organic Matter (AOM) is formed in aquatic (but not necessarily marine) anoxic/dysoxic conditions. The rare prasinophytes found (very small grey rounded specimens) may also exist in fresh water environments, although they are more typical of near shore marine environments. Thus, an adapted Terrestrial/Aquatic Index TA (analogous to Terrestrial/Marine Index) was used:

TA = sum of terrestrial particles / (sum of terrestrial particles + sum of aquatic particles)

where terrestrial particles are all phytoclasts, spores/pollen and reworked organic matter and aquatic particles are all AOM, prasinophytes and zooclasts. Samples with TA close to 1 will be near shore or terrestrial while samples with low TA deposited in deeper parts of the lake.

For palynofacies analysis, 300 particles were counted on each non-sieved slide, in random fields of view with the 40X objective under a transmitted light biological microscope. The area occupied by each particle was weighted as visual estimates. These values were transferred to an Excel sheet and proportions of the several components calculated to use them in ternary diagrams (such as the Tyson diagram) and calculate relevant indexes. The types of particles considered were the following: AOM, spore, pollen, prasinophyte, acritarch, plant cuticle, dark phytoclast, light phytoclast, foraminifera lining, grey tissues (possible zooclasts), reworked acritarch, reworked spore.

The results from the 19 samples processed for palynology were analyzed using the total particulate organic matter content analysis as observed on slides made from a non-sieved residue. The following table summarizes the categories considered for the Tyson diagram plotting:

| Category | Palaeonvironmental significance | Source rock |
|---|---|---|
| Amorphous Organic Matter (AOM) | Stratified water column or deep basin. Anoxic-suboxic conditions | Oil-prone (type I) |
| Phytoclasts (light and dark) | Exclusively land-derived. proxy for shore proximity | Gas-prone (type III) |
| Palynomorphs (spore/pollen, acritarchs, prasinophytes) | Variable | Oil-prone (type I or II) |

**Table 3 - Summary table of the selected categories used for the palynofacies analysis on non-sieved slides and plotting on Tyson diagram. Compiled from Tyson (1987, 1993) and Batten (1996a, b).**

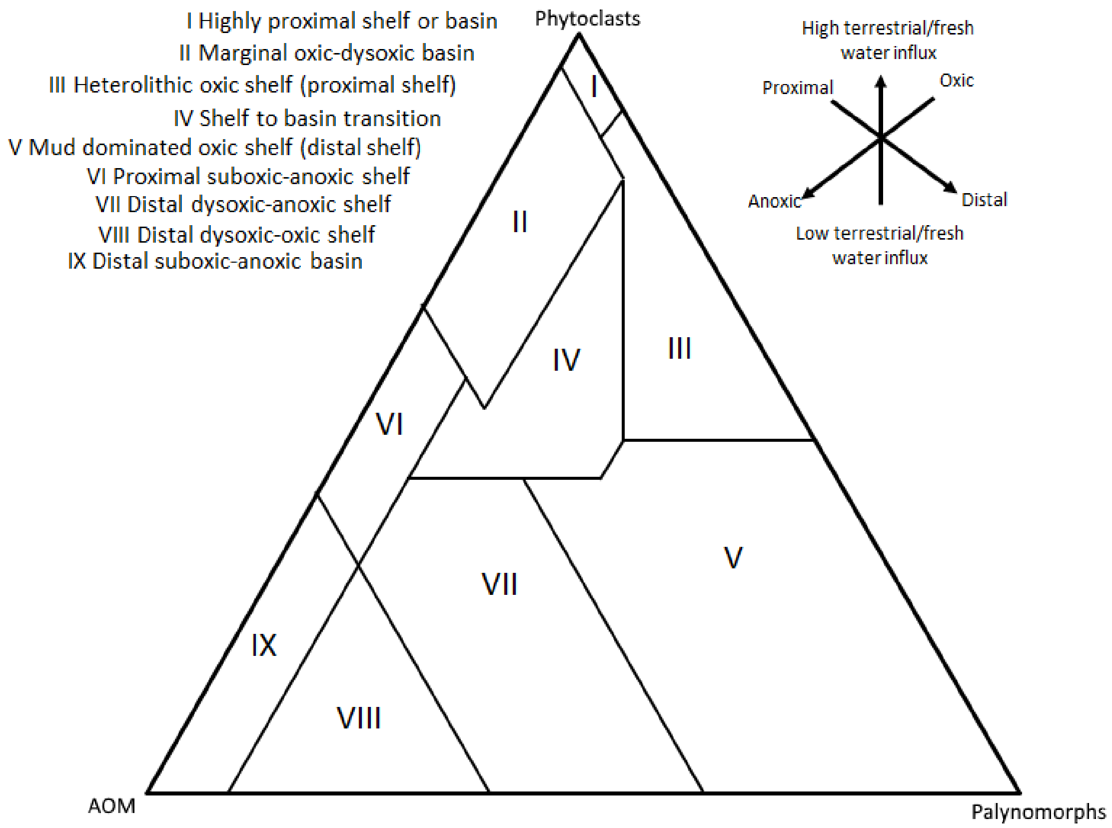


**Figure 2 – Example of Tyson diagram used to determine general sedimentation/oxidation environments. (Adapted from Tyson 1987).**

For more refined paleoenvironmental/kerogen typing interpretations, the categories in the following table were considered:

| Category | Origin | Palaeonvironmental significance | Source rock |
|---|---|---|---|
| Spores | Terrestrial | Exclusively land-derived, proxy for shore proximity | Oil-prone (type II) |
| Phytoclasts | | Exclusively land-derived, proxy for shore proximity | Gas-prone (type III) |
| Zooclasts | | Benthic marine arthropods, but also land derived debris | Inert (type IV) |
| Chitinozoans | Marine | Exclusively marine, relatively deep environments. | ? |
| Acritarchs | | Exclusively marine, proxy for organic productivity under “normal” marine conditions | Oil-prone (type I or II) |
| Prasinophytes and other algae | Aquatic | Dominant in abnormal marine or lacustrine conditions (salinity, temperature, oxygenation, etc.) | Highly Oil-prone (type I) |
| Reworked particles | varied | Erosion of older sedimentary units | Inert (type IV) |

**Table 4 - Summary table of the selected categories used for the palynofacies analysis on non-sieved slides. Compiled from Tyson 1987, 1993; Miller, 1996 and Batten 1996a, b.**

### Vitrinite reflectance, spore colour and fluorescence

Several methods to estimate thermal maturity of sedimentary rocks exist. Many of them are based on the alteration of chemical and optical properties of organic matter as it is heated over geological time scales. The most widely used and the industry standard is vitrinite reflectance. Its usage allows to accurately estimate paleo-peak temperatures attained by sedimentary rocks, from immature to post-mature hydrocarbon generation stages (and into low temperature metamorphism) in rocks from Devonian (first widespread vascular plants) to recent sediments. The method is standardized internationally and tried and tested for decades. This method is based on the measurement of the reflected light from woody fragments (vitrinite), smoothly polished from palynological residues or coaly particles under reflected light microscopes.

Other methods, mostly qualitative or semi-quantitative exist, which are good calibration points for vitrinite reflectance.

Optically, woody fragments, spores and most particulate organic matter darkens progressively with increasing temperature in an irreversible way. Several types of palynomorphs can be used to estimate paleotemperatures. Spores are the most commonly used due to their sensitivity to colour change within the range of temperatures of hydrocarbon generation and their widespread occurrence in palynological residues from Silurian to recent sediments. Several semi-quantitative scales have been established and correlated with vitrinite reflectance and other scales – see following figure.

Organic particles were extracted from the rock samples using standard cold hydrochloric and hydrofluoric acids (HF) techniques. The organic residues obtained were then mounted and polished using a method adopted from that described by Hillier & Marshall (1988).

**Mean random vitrinite reflectance** (%*Ro*) was the vitrinite reflectance parameter chosen for maturation assessment of mudstones because the mounting technique used provides non-oriented vitrinite particles and also because %*Ro* is the most widely used organic maturation parameter. Vitrinite measurements of all the samples were made using an Olympus BX 51 microscope equipped with a black and white digital camera. The black and white (8-bit) digital images of vitrinite particles were analysed using a MatLab routine. This routine is a graphical tool that runs within the Mirone suite (Luis, 2007) and calibrates the scale of 256 grey levels with standards of known reflectivity (Fernandes et al., 2010). The reflectance values of the standards used were 0.428, 0.595, 0.897, 1.314, 1.715, 3.15 and 5.37%. VR was measured in incident light with a wavelength of 546 nm and immersion oil with a refractive index of 1.518. Vitrinite reflectance results for individual samples are presented in the form of histograms in appendix 6. The number of vitrinite grains measured, the arithmetic mean reflectance value and the standard deviation are also indicated. All histograms are based on random reflectance determined on kerogen concentrates from the samples. Peak paleotemperature (Tp) in °C is estimated using the formula by Barker and Goldstein (1990) where

$$Tp = (((\mathrm{Ln}(\%Ro) + 1,26) / 0,00811) * 0,965) + 12,1$$

**Fluorescence microscopy** is used to differentiate source rocks from non-source rocks and to estimate the level of maturation from autofluorescence colours and spectra of palynomorphs. Organic maturation causes a gradual shift in fluorescence colours (red shift) from the shorter to the longer wavelengths, that is, blue and green to yellow, orange and finally red. Of all the sub-macerals of the liptinite-exinite group, sporinite is the one that shows the most consistent changes in fluorescence colour spectra and intensity with increasing organic maturation. Despite some differences in fluorescence colours and intensity for different spore taxa, spore fluorescence is an important parameter of organic maturation for low-rank material.

For this study, qualitative spore fluorescence colour analyses of the samples were completed using a Leitz Dialux 20 microscope with Ploemopak 2.4 incident fluorescent tube with a violet and blue +12 filter block, giving a wavelength band of 390 - 490 nm. This system was allowed to stabilise for 30 minutes prior to any observation of the fluorescence properties of the samples. Suitable palynomorph species were subjected to 5 minutes of excitation, after which their autofluorescence colours were recorded.

In this study, spore colours were recorded using the 'Phillips Petroleum Colour Standard', version no.2 (1984). In order to determine true spore colour of a sample, the dominant and palest spore colour was recorded and compared with the Phillips Petroleum Colour chart. The index number from this chart was then attributed to the sample. Results of TAI determinations are presented together with fluorescence colours and vitrinite reflectance values for each sample. Not all spore species are suitable for TAI determinations. When possible, thin walled or delicately ornamented spores were avoided. Thick walled and heavily ornamented spores were also avoided. In the present study, the palynomorph best suited for TAI determinations were acamerate, azonate pollens with a smooth exine of medium thickness.

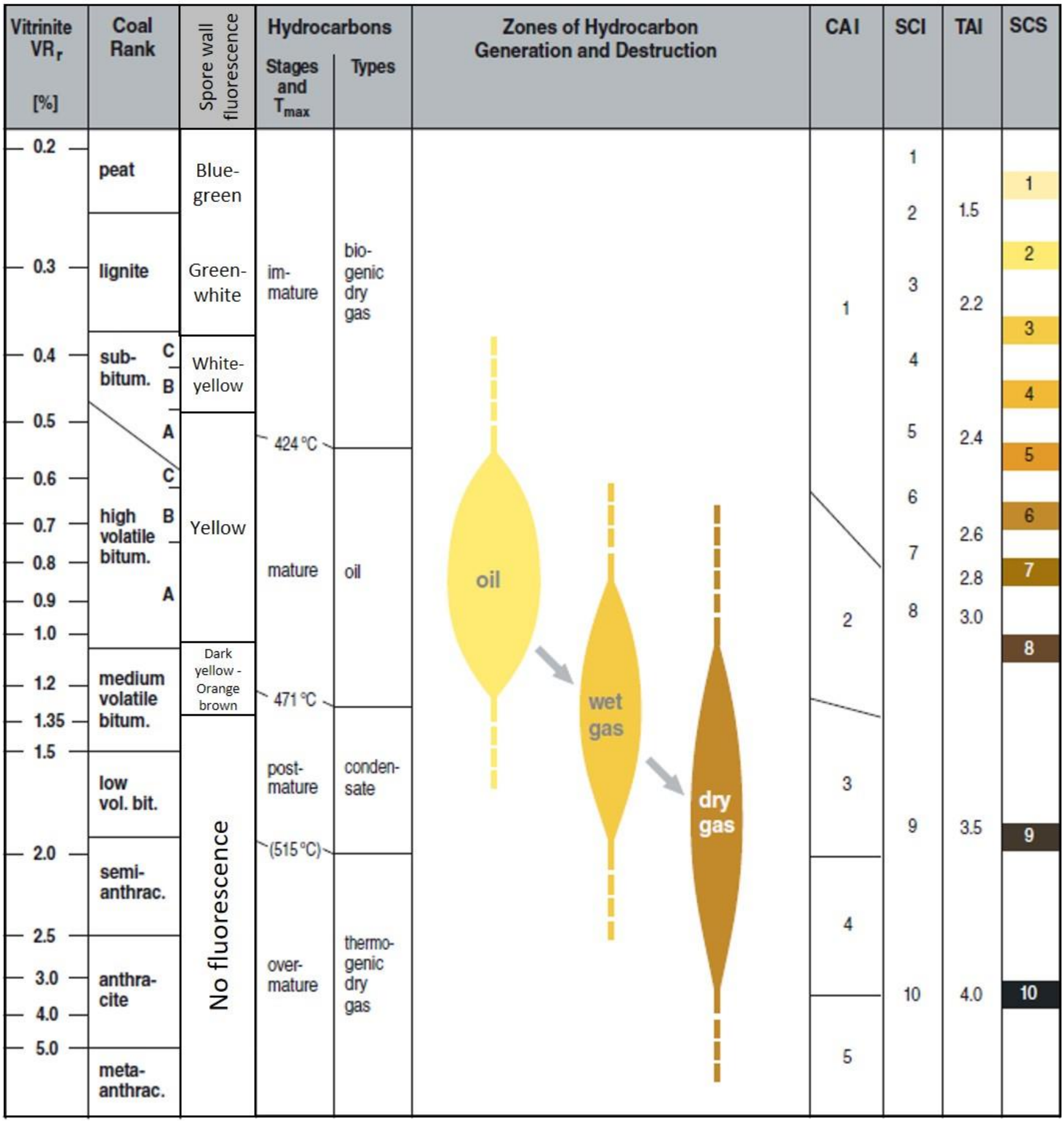


**Figure 3 – Comparison of thermal maturity scales. CAI – Conodont Alteration Index; SCI Spore Colour Index of Fisher et al. (1980), TAI –Thermal Alteration Index (TAI) of Staplin (1969); SCS Pollen/Spore Color "Standard" of Pearson (1990). Adapted from Hartkopf-Fröder et al. (2015)**

## Organic geochemistry (by Geo-Data)

The Total Organic Carbon measurements were carried out on a LECO SC-144 DR carbon/sulfur analyzer. The samples were heated in oxygen current up to 1250 °C to liberate carbon dioxide formed from the remaining organic carbon in the solid phase. The amount of the liberated carbon dioxide was recorded on an infrared (IR) detector. The measurement of the control standard before and during the analysis is used for quality control. Rock-Eval analysis was performed with a Rock-Eval 6 instrument of Vinci Technologies SA. Approximately 100 mg of the powdered rock were pyrolysed in a helium atmosphere in the absence of oxygen. The Rock-Eval analysis is used as an estimation of the petroleum potential of source rocks by pyrolysis according to a programmed temperature pattern. Released hydrocarbons are monitored by a flame-ionization detector (FID), forming at the initial temperature of 300 °C (hold for 3 min) the S1 peak (thermo-vaporized free hydrocarbons, mgHC/g rock) and the S2 peak (hydrocarbons from cracking of the organic matter, mgHC/g rock) during the heating phase with 25 °C/min up to 650 °C. In addition, CO and $CO_2$ released during pyrolysis is recorded by means of an IR cell and quantified as S3 peak (mg$CO_2$/g rock), giving information on the oxidation state of organic matter (Fig. 4). Usually for samples with total organic carbon contents (TOC) above 1% good and reproducible values are obtained with respect to hydrocarbon liberation (S1 and S2 values). The Tmax, heating temperature at which the top of S2 occurs, is detected as Tpeak S2 and calibrated with the Tmax of standard (obtained by the old RE II instrument). All values have been calibrated on an international standard distributed by the Institut Francais du Pétrole (IFP 160000). The analytical conditions of the instrument are: FID He 30ml/min; Splitter: 400°C; pyrolysis: 300°C; Oxidation: 300°C; IR Cell: 0 ppm CO/CO2; H2: 30ml/min; N2: 100ml/min; Split flow: 50ml/min; Air: 300ml/min.

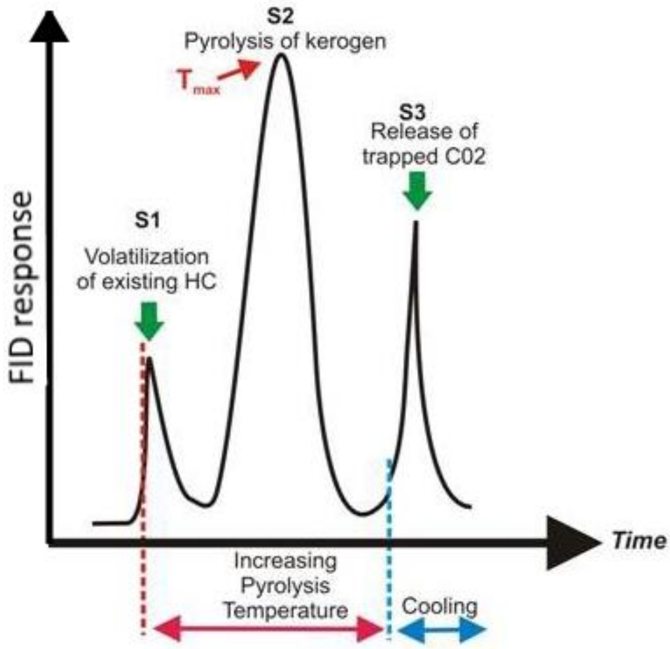


**Figure 4 – Schematic S1, S2 and S3 curve of a pyrolysis analysis. Adapted from Pennsylvania Geological Survey website.**

The main parameters measured and its significance are summarized in the following table:

| Parameter | Detector/Oven | Unit | Interpretation |
|---|---|---|---|
| S1 | FID/Pyrolysis | mg HC/g rock | Free hydrocarbons |
| S2 | FID/Pyrolysis | mg HC/g rock | Remaining hydrocarbon potential |
| Tmax | – | °C | Proxy for thermal maturity |
| S3 | IR/Pyrolysis | mg CO2/g rock | CO2 organic source |
| TOC | DR carbon/sulphur analyser. | % weight rock | Organic content of rock |

**Table 5 - Measured parameters in basic Rock-Eval 6 analysis.**

Several derived parameters were calculated from these main parameters, notably:

Oxygen Index (OI = (S2/TOC)x100)
Hydrogen Index (HI = (S3/TOC)x100) and
Production Index (PI = S1/(S1+S2)).

Full results are presented in appendix 4 and as interpretative graphs, with a discussion of the generation potential of the analyzed samples.

## 4. Results

The results of each discipline are described in detail in the following sections. The following table summarizes the main results.

| Sample 1 | 11TM0162 |
|---|---|
| Particulate organic matter description | Dark grey AOM, black opaque phytoclasts and rare broken black (some dark brown) sporomorphs. Very rare grey leiospheres and tissues. |
| Age determination | Mississippian, probably Viséan |
| Paleoenvironmental interpretation | Lacustrine suboxic environment. TA = 0,51 |
| Thermal maturity | Late dry gas window |
| Hydrocarbon generation potential | None (type IV) to residual gas |

| Sample 2 | 11TM0328 |
|---|---|
| Particulate organic matter description | Black opaque phytoclasts, dark grey AOM and very rare black sporomorphs |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Lacustrine (or fluvial?) very proximal to subaerial oxic environment. TA = 0,94 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| Sample 3 | 11TM0442B |
|---|---|
| Particulate organic matter description | Black opaque phytoclasts, dark grey AOM and rare black sporomorphs. Very rare grey leiospheres |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Lacustrine sedimentation in oxic environment TA = 0,68 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| Sample 4 | 15TM0408 |
|---|---|
| Particulate organic matter description | Black opaque phytoclasts, black sporomorphs and dark grey AOM |
| Age determination | Mississippian, probably Viséan |
| Paleoenvironmental interpretation | Lacustrine (or fluvial?) very proximal to subaerial environment. TA = 0,99 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| Sample 5 | 15TM0409A |
|---|---|
| Particulate organic matter description | Black opaque phytoclasts, very rare black sporomorphs and very rare dark grey AOM |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Lacustrine (or fluvial?) very proximal to subaerial environment. TA = 0,96 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | Poor to none (type IV) |

| | |
|---|---|
| Sample 6 | 15TM0590 |
| Particulate organic matter description | Black opaque phytoclasts, black sporomorphs and dark grey AOM, very rare prasinophytes and grey tissues. |
| Age determination | Mississippian |
| Paleoenvironmental interpretation | Very proximal lacustrine, oxic environment. TA = 0,87 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| | |
|---|---|
| Sample 7 | 15TM0593 |
| Particulate organic matter description | Black opaque phytoclasts, very rare black sporomorphs and very rare dark grey AOM, prasinophytes and grey tissues. |
| Age determination | Mississippian, probably Viséan |
| Paleoenvironmental interpretation | Very proximal lacustrine, oxic environment. TA = 0,93 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| | |
|---|---|
| Sample 8 | 15TM0606 |
| Particulate organic matter description | Black opaque phytoclasts, dark grey AOM and rare black sporomorphs. Very rare grey leiospheres |
| Age determination | Mississippian (possibly Viséan) |
| Paleoenvironmental interpretation | Lacustrine suboxic environment. TA = 0,63 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| | |
|---|---|
| Sample 9 | 15TM0646 |
| Particulate organic matter description | Black opaque phytoclasts, very rare black sporomorphs and very rare dark grey AOM, prasinophytes and grey tissues. |
| Age determination | Mississippian (possibly Viséan) |
| Paleoenvironmental interpretation | Very proximal lacustrine, oxic environment. TA = 0,97 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| | |
|---|---|
| Sample 10 | 15TM0649 |
| Particulate organic matter description | Barren sample |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Indeterminate |
| Thermal maturity | Not determined |
| Hydrocarbon generation potential | None (type IV) |

| | |
|---|---|
| Sample 11 | 16TM0596 |
| Particulate organic matter description | Dark yellow to light brown AOM and spores, brown and black phytoclasts |
| Age determination | Viséan, possibly NS biozone of Eastern Canada. |
| Paleoenvironmental interpretation | Deep lacustrine anoxic environment. TA = 0,17 |
| Thermal maturity | Late oil window |
| Hydrocarbon generation potential | Good gas source rock (type III) |

| | |
|---|---|
| Sample 12 | 16TM0620A |
| Particulate organic matter description | Not processed for palynology |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Lacustrine carbonate setting (?) |
| Thermal maturity | Not determined |
| Hydrocarbon generation potential | Not determined |

| | |
|---|---|
| Sample 13 | 16TM0620B |
| Particulate organic matter description | Dark yellow to light brown AOM, black (and some brown) phytoclasts and rare brown spores |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Lacustrine suboxic-anoxic environment. TA = 0,52 |
| Thermal maturity | Dry gas window |
| Hydrocarbon generation potential | Poor to none (type IV) |

| | |
|---|---|
| Sample 14 | 16TM0622 |
| Particulate organic matter description | Black (and some brown) phytoclasts, brown spores and dark yellow to light brown AOM. |
| Age determination | Tournaisian (Tn3) probably *S. cabotii* subzone |
| Paleoenvironmental interpretation | Lacustrine suboxic environment. TA = 0,86 |
| Thermal maturity | Wet gas window |
| Hydrocarbon generation potential | Poor to fair gas-prone source rock |

| | |
|---|---|
| Sample 15 | 16TM0625 |
| Particulate organic matter description | Black and brown phytoclasts, dark yellow to light brown AOM and brown spores. |
| Age determination | Tournaisian (Tn3) |
| Paleoenvironmental interpretation | Lacustrine suboxic environment. TA = 0,69 |
| Thermal maturity | Wet gas window |
| Hydrocarbon generation potential | Poor to fair gas-prone source rock |

| | |
|---|---|
| Sample 16 | 16TM0734B |
| Particulate organic matter description | Dark yellow to light brown AOM and rare brown and black phytoclasts |
| Age determination | Latest Devonian to Late Tournaisian (Tn1 to Tn3) |
| Paleoenvironmental interpretation | Deep lacustrine anoxic environment. TA = 0,06 |
| Thermal maturity | Dry gas window |
| Hydrocarbon generation potential | Poor to none (type IV) |

| | |
|---|---|
| Sample 17 | 16TM0734C |
| Particulate organic matter description | Brown (and some black) phytoclasts, brown spores/pollen and dark yellow to light brown AOM. |
| Age determination | Tournaisian (Tn3) probably *U. abstrusus – U. distinctus* subzone |
| Paleoenvironmental interpretation | Proximal lacustrine dysoxic environment. TA = 0,90 |
| Thermal maturity | Wet gas window |
| Hydrocarbon generation potential | Poor to none (type IV) |

| | |
|---|---|
| Sample 18 | 16TM0784A |
| Particulate organic matter description | Black phytoclasts, dark grey AOM and rare black spores |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Proximal lacustrine oxic-dysoxic environment. TA = 0,86 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| | |
|---|---|
| Sample 19 | 16TM0790 |
| Particulate organic matter description | Black phytoclasts, dark grey AOM and rare black spores |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Proximal lacustrine oxic-dysoxic environment. TA = 0,85 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

| | |
|---|---|
| Sample 20 | 16TM0791 |
| Particulate organic matter description | Black phytoclasts, rare dark grey AOM and rare black spores |
| Age determination | Indeterminate |
| Paleoenvironmental interpretation | Proximal lacustrine oxic environment. TA = 0,95 |
| Thermal maturity | Overmature |
| Hydrocarbon generation potential | None (type IV) |

**Table 6 – Summary of the results, per sample per discipline**

## 4.1 Palynology (Biostratigraphy and Palynofacies)

All but one (15TM0649) of the nineteen processed samples provided enough organic residue to mount in slides and observe under the microscope. Most of the samples rendered organic residues that were generally black and opaque and did not allow standard biostratigraphic work to be conducted although it did allow palynofacies analysis, with some limitations.

Techniques to render palynomorphs translucent were attempted, using aggressive oxidizing agents such as Schulze solution, but even after 24h the residues did not change their colour or translucency. This technique is usually effective after minutes or a few hours.

### Palynofacies

Palynofacies analysis show that most samples are dominated by phytoclasts with subordinate amounts of AOM and palynomorphs (essentially spores). Notable exceptions are samples 16TMO596 and 16TMO734B which were dominated by AOM. Samples 11TMO162, 16TMO620b and 15TMO606 have AOM and phytoclast proportions close to 50% with minor amounts of palynomorphs. There are no direct indications of marine sedimentation in any of the samples. Acritarchs (even if simple Carboniferous species), foram linings or other marine organic-walled particles would be expected in marine sediments. The presence of very rare, small and grey prasinophytes could indicate marine influence, but these simple, *Leiosphaeridia*-like algae are also present in lacustrine sediments. The dominance of phytoclasts is indicative of very proximal sedimentation environments – likely near lake shore.

In terms of hydrocarbon generation potential, the black colour is an indication of very high thermal maturity. These particles are essentially inert (kerogen type IV), consistent with the geochemical results. Samples 16TM0596, 16TMO622, 16TMO625, 16TMO734B and 16TMO734C are exceptions, with organic matter generally with dark yellow to brown hues, although with some black opaque phytoclasts as well. Of these, samples 16TMO596 and 16TMO734B would suggest oil-prone source rocks (due to the abundance of AOM), although the geochemistry results point to more gas-prone source rocks. The remaining ones would have mixed gas-oil potential (more balanced phytoclast-AOM ratios, corresponding to transitional type II-III), but again the geochemistry results point to more gas-prone or inert kerogen (type III-IV).

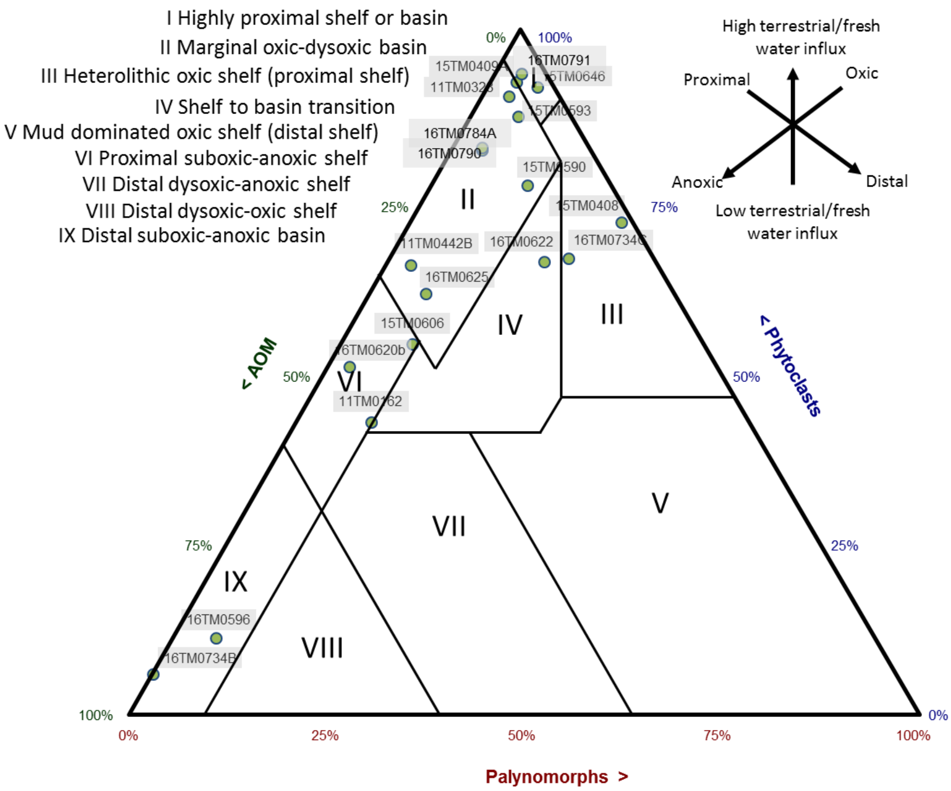


**Figure 5 – Tyson diagram and the plots of the analyzed samples.**

## Palynostratigraphy

Five out of the nineteen processed samples provided easily observable residues with abundant, recognizable spores/pollen which, despite their poor to moderate preservation allowed age determination (16TM0596, 16TM0622, 16TM0625, 16TM0734B and 16TM0734C).

All the remaining samples provided black opaque residues, in many cases with few organic particles. Of these, five were successfully observed under reflected light microscopy and provided enough spores/pollen for identification, frequently in open nomenclature, that allowed crude age determinations (11TM0162, 15TM0408, 15TM0590, 15TM0593 and 15TM606).

The remaining samples provided very few organic particles. Under reflected light the possible spores/pollen (round opaque particles) had no recognizable morphological features, rather a "crystalline" look which, from experience of the author, is indicative of a very high maturation degree.

All attempts to oxidize the residues were unsuccessful.

The following tables summarize, per sample, the main palynostratigraphic results. Appendix 3 details the taxa found per sample and Appendix 5 illustrates the taxa found.

| Sample | 11TM0162 |
|---|---|
| Description | Poorly preserved and poorly diversified assemblage. Presence of *Grandispora* cf. *spinosa* is indicative of Viséan age. Remaining taxa are consistent with the age determination, although several elements are also present in Tournaisian strata. |
| Preservation | Poor (observed under reflected light microscope) |
| Age determination | Mississippian, probably Viséan |

| Sample | 11TM0328 |
|---|---|
| Description | Few organic particles (possibly sporomorphs) not recognizable under transmitted or reflected light microscopy. |
| Preservation | N/A |
| Age determination | Indeterminate |

| Sample | 11TM0442B |
|---|---|
| Description | Very few organic particles. No recognizable sporomorphs or other biostratigraphically useful particles. |
| Preservation | N/A |
| Age determination | Indeterminate |

| Sample | 15TM0408 |
|---|---|
| Description | Poorly preserved and poorly diversified assemblage. Presence of several taxa is indicative of a Mississippian age (*Convolutispora* cf. *vermiformis*, *Rugospora* cf. *minuta*, R. cf. *polyptycha*, *Spelaeotriletes* spp.), but the presence of *Convolutispora* cf. *labyrinthea* suggests a Viséan age. Remaining taxa are consistent with the age determination. |
| Preservation | Poor (observed under reflected light microscope) |
| Age determination | Mississippian, probably Viséan |

| Sample | 15TM0409A |
|---|---|
| Description | Very few organic particles. No recognizable sporomorphs or other biostratigraphically useful particles. |
| Preservation | N/A |
| Age determination | Indeterminate |

| Sample | 15TM0590 |
|---|---|
| Description | Poorly preserved and poorly diversified assemblage. Of the few identified taxa (mostly genus level) the presence of *Rugospora* spp. and *Densosporites* spp. are indicative of a Mississippian age. |
| Preservation | Poor (observed under reflected light microscope) |
| Age determination | Mississippian |

| | |
|---|---|
| Sample | 15TM0593 |
| Description | Poorly preserved and poorly diversified assemblage. Presence of *Densosporites* cf. *columbaris* is indicative of Viséan age. Remaining taxa are consistent with the age determination, although several elements are also present in Tournaisian strata. |
| Preservation | Poor (observed under reflected light microscope) |
| Age determination | Mississippian, probably Viséan |

| | |
|---|---|
| Sample | 15TM0606 |
| Description | Poorly preserved and poorly diversified assemblage. Identified taxa include forms usually restricted to the Viséan, but also to the Tournaisian (reworked?). |
| Preservation | Poor (observed under reflected light microscope) |
| Age determination | Mississippian (possibly Viséan) |

| | |
|---|---|
| Sample | 15TM0646 |
| Description | Very few organic particles and very low amount of residue. No recognizable sporomorphs or other biostratigraphically useful particles. |
| Preservation | N/A |
| Age determination | Indeterminate |

| | |
|---|---|
| Sample | 15TM0649 |
| Description | Very few organic particles and very low amount of residue. No recognizable sporomorphs or other biostratigraphically useful particles. |
| Preservation | N/A |
| Age determination | Indeterminate |

| | |
|---|---|
| Sample | 16TM0596 |
| Description | Dominated (>90%) by simple large pollen assignable to *Florinites* spp. and *Wilsonites* spp. All sporomorphs badly preserved with pitting. Identifications are difficult, but overall the assemblage seems Viséan (e.g. *Spelaeotriletes arenaceus* and *S. windsorensis*), with some (reworked?) Tournaisian elements. |
| Preservation | Poor |
| Age determination | Viséan, possibly NS biozone of Eastern Canada. |

| | |
|---|---|
| Sample | 16TM0620b |
| Description | Very few organic particles and very low amount of residue. No recognizable sporomorphs or other biostratigraphically useful particles. |
| Preservation | N/A |
| Age determination | Indeterminate |

| | |
|---|---|
| Sample | 16TM0622 |
| Description | Sample dominated by *Spelaeotriletes cabotii* and other *Spelaeotriletes* spp., mostly fragmented. Other common taxa include *Verrucosisporites* spp., *Punctatisporites* spp., *Latosporites* spp. Absence of *Umbonatisporites* spp. |
| Preservation | Moderate |
| Age determination | Tournaisian (Tn3) probably *S. cabotii* subzone |

| | |
|---|---|
| Sample | 16TM0625 |
| Description | Dominated by *Punctatisporites* spp. and *Latosporites* spp. Rare *Spaelotriletes* spp. |
| Preservation | Moderate |
| Age determination | Tournaisian (Tn3) |

| | |
|---|---|
| Sample | 16TM0734B |
| Description | Very poor sample, few taxa identified. cf. *Cymbosporites magnificus* is indicative of Latest Devonian to Late Tournaisian (Tn1 to Tn3) |
| Preservation | Poor |
| Age determination | Latest Devonian to Late Tournaisian (Tn1 to Tn3) |

| Sample | 16TM0734C |
|---|---|
| Description | Sample dominated by *Spelaeotriletes cabotii* and other *Spelaeotriletes* spp., mostly fragmented. Other common taxa include *Verrucosisporites* spp, *Punctatisporites* spp., *Latosporites* spp. Presence of *Umbonatisporites* cf. *abstrusus* |
| Preservation | Moderate |
| Age determination | Tournaisian (Tn3) probably *U. abstrusus – U. distinctus* subzone |

| Sample | 16TM0784A |
|---|---|
| Description | Few organic particles (possibly sporomorphs) not recognizable under transmitted or reflected light microscopy. |
| Preservation | N/A |
| Age determination | Indeterminate |

| Sample | 16TM0790 |
|---|---|
| Description | Few organic particles (possibly sporomorphs) not recognizable under transmitted or reflected light microscopy. |
| Preservation | N/A |
| Age determination | Indeterminate |

| Sample | 16TM0791 |
|---|---|
| Description | Very few organic particles. No recognizable sporomorphs or other biostratigraphically useful particles. |
| Preservation | N/A |
| Age determination | Indeterminate |

## 4.2 Foraminifera

The eight thin sections were scanned for foraminifera and other relevant bioclasts. None of the thin sections had bioclasts other than faint unidentifiable structures. A brief description of each thin section is presented below:

| Sample | Brief description |
|---|---|
| 11TM0328 | Millimeter scale interbeds of siltstone (with organic matter) and sandstone. No obvious carbonate particles. Clay and (?)carbonate matrix. Tiny pyrite overgrowths. Phytoclasts visible in coarser lamina and AOM in finer ones. Small shell fragments and disc shaped objects, but no identifiable bioclasts. |
| 15TM0590 | Millimeter scale interbeds of siltstone and sandstone. No obvious carbonate particles. Clay (?)chlorite matrix. Phytoclasts visible. No other identifiable bioclasts. |
| 15TM0646 | Rather uniform fine sandstone. No obvious carbonate particles. Phytoclasts and spores visible. No other identifiable bioclasts. |
| 16TM0620A | Intraclastic grainstone (and oolithic?) heavily recrystallized. Spar cement and (?)chlorite. Faint possibly bioclastic structures as nucleus of ooliths. |
| 16TM0625 | Carbonate cement/matrix with abundant siliciclastic grains. Light brown and black phytoclasts. Light brown spores. No other identifiable bioclasts. |
| 16TM0734B | Carbonate cement/matrix with abundant siliciclastic grains. No identifiable bioclasts. |
| 16TM0790 | Uniform siltstone/sandstone with (?)carbonate cement. Phytoclasts visible. Faint micritic (?)bioclastic objects. |
| 16TM0791 | Rather uniform siltstone/sandstone with tiny phytoclasts and few AOM. No obvious carbonate particles. No identifiable bioclasts. |

**Table 7 – Brief description of the thin sections analyzed in this work.**

## 4.3 Maturity (vitrinite reflectance, fluorescence and spore colour)

### Fluorescence and spore colour

Samples analyzed for spore fluorescence and spore colour show that most samples are overmatured, with no observable fluorescence and TAI above 4 (5 is considered when spores are black and opaque). Notable exceptions are samples 16TM0622, 16TM0625, 16TM0734B and 16TM0734C which show light brown to brown spore colours, corresponding to TAI 3- and slightly darker in sample 16TM0596 (TAI 3/3+). The results are consistent with the fluorescence observations which show dark orange hues. For these samples, the generation range is in the late oil to wet gas window. The results are generally consistent with the geochemistry results – see next section. This maturity range may also explain the gas-prone indication of samples 16TM0596 and 16TM0734B from geochemistry data, opposed to more oil-prone indication of the kerogen typing from palynofacies, i.e., while the original organic matter was more oil-prone, the current maturity of these samples suggests that the remaining hydrocarbon potential is essentially gas.

| Sample | Fluorescence | TAI | Vr (%Ro) | Peak paleo-temperature °C |
|---|---|---|---|---|
| 11TM0162 | No fluorescence | 4-5 | 2.10 | 250,3 |
| 11TM0328 | No fluorescence | 5 | 4.02 | 327,6 |
| 11TM0442B | No fluorescence | 5 | 4.11 | 330,2 |
| 15TM0408 | No fluorescence | 5 | 4.76 | 347,7 |
| 15TM0409A | No fluorescence | 5 | 6.00 | 375,2 |
| 15TM0590 | No fluorescence | 5 | 4.45 | 339,7 |
| 15TM0593 | No fluorescence | 5 | 4.47 | 340,2 |
| 15TM0606 | No fluorescence | 5 | 4.10 | 329,9 |
| 15TM0646 | No fluorescence | 5 | 5.70 | 369,1 |
| 15TM0649 | Barren sample | N/A | N/A | N/A |
| 16TM0596 | Weak to absent dark orange fluorescence. | 3/3+ | 0.96 | 157,2 |
| 16TM0620b | No fluorescence | 5 | 1.73 | 227,2 |
| 16TM0622 | Dark orange fluorescence without positive fading | 3- | 1.29 | 192,3 |
| 16TM0625 | Dark orange fluorescence | 3- | 1.32 | 195,1 |
| 16TM0734B | Dark orange fluorescence without positive fading | 3- | 1.47 | 207,9 |
| 16TM0734C | Dark orange fluorescence without positive fading | 3- | 1.29 | 192,3 |
| 16TM0784A | No fluorescence | 5 | 3.70 | 317,7 |
| 16TM0790 | No fluorescence | 5 | 3.02 | 293,5 |
| 16TM0791 | No fluorescence | 5 | 4.10 | 329,9 |

**Table 8 - Spore fluorescence, Thermal Alteration Index (TAI) and vitrinite reflectance of the analyzed samples. Peak paleo-temperature calculated using Barker and Goldstein (1990).**

### Vitrinite reflectance

The vitrinite reflectance data is generally consistent with the spore colour and fluorescence data, showing that most samples are overmatured in terms of hydrocarbon generation potential (Fig. 3, table 8 and Appendix 6). Notable exceptions are samples 16TM0596 (oil window), 16TM0622, 16TM0625, 16TM0734C (wet gas) and 16TM0734B, 16TM0620b (dry gas). Sample 11TM0162 is in the late dry gas window. Samples with %Ro values above 3% are considered to have exhausted their hydrocarbon generation potential – but may have generated hydrocarbon during their burial before reaching peak paleo-temperature.

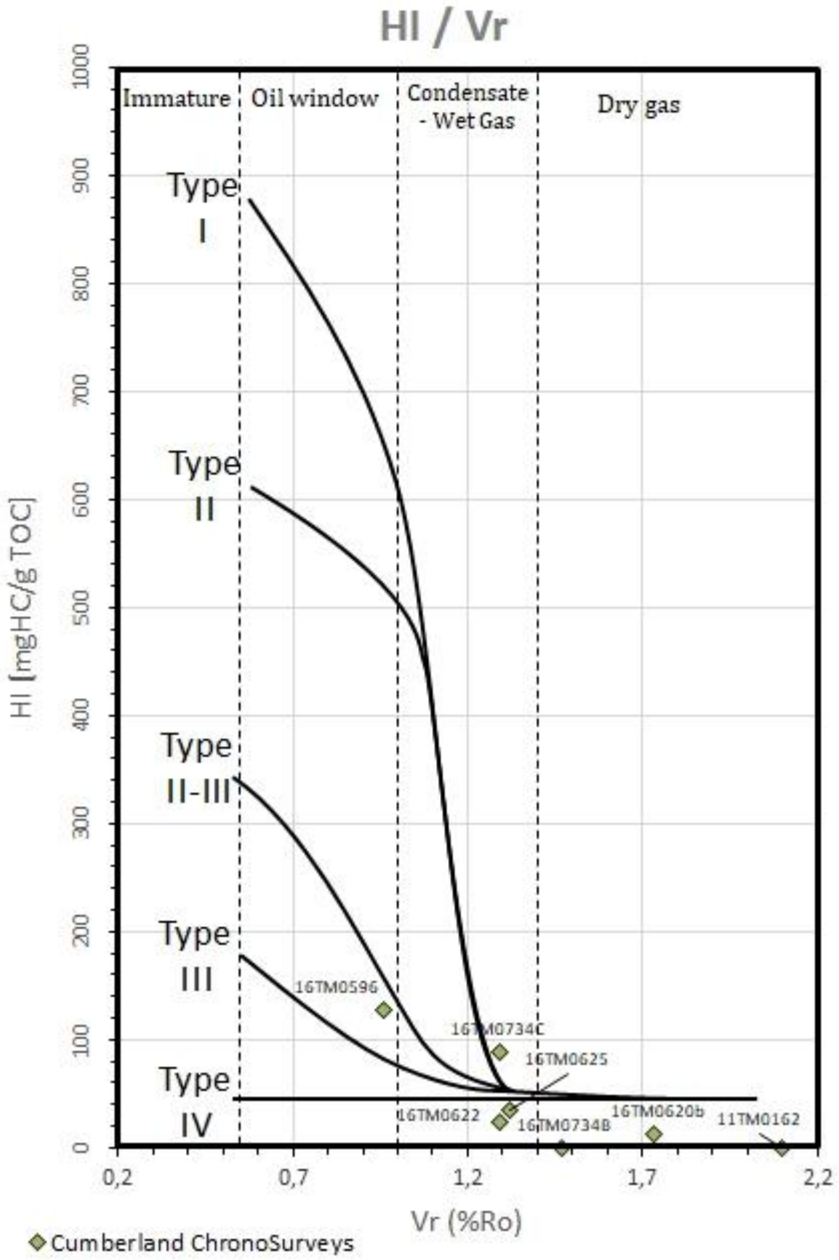


**Figure 6 – Hydrogen Index (HI) Vs Vitrinite Reflectance (%Ro) of the analyzed samples. Samples with Vr > 2,2 %Ro are not plotted.**

The plot above emphasizes the current gas-prone potential of the samples with lower maturity (except for sample 16TMO596). Some of them had originally a more oil-prone potential (as indicated by the palynofacies study), but their current maturity is indicative that the remaining potential is gas. As detailed in the next section the low Hydrogen Index values point to fair to poor source rocks.

## 4.4 Organic Geochemistry (TOC and Rock Eval)

With few exceptions, the TOC values indicate that the samples are organic-lean with TOC values mostly < 1 wt.%. For these samples, proper interpretation of the Rock-Eval data is not possible. Moreover, the somewhat increased S3 peak values relative to S1 and S2 suggest that the organic material is possibly oxidized.

Tmax values are consistent with mature oil generation window (and one sample in late immature).

The following table summarizes the main geochemical parameters:

| Sample | S1 (mgHC/g rock) | S2 (mgHC/g rock) | Tmax (°C) | S3 (mg CO2/g rock) | TOC (wt.%) | HI (mgHC/g TOC) | OI (mg CO2/g TOC) | PI | TIC (wt.%) |
|---|---|---|---|---|---|---|---|---|---|
| 11TM0162 | 0,04 | 0,01 | 451 | 0,27 | 2,16 | 0,5 | 12,5 | 0,8 | 1,7 |
| 11TM0328 | 0,03 | 0,04 | 444 | 0,23 | 0,6 | 6,7 | 38,3 | 0,4 | 0,1 |
| 11TM0442B | 0,02 | 0 | 438 | 0,32 | 0,74 | 0,0 | 43,2 | 1,0 | 1,2 |
| 15TM0408 | 0,01 | 0,01 | 443 | 0,27 | 0,57 | 1,8 | 47,4 | 0,5 | 0,3 |
| 15TM0409A | 0,04 | 0,38 | 394 | 0,45 | 0,67 | 56,7 | 67,2 | 0,1 | 0,1 |
| 15TM0590 | 0,01 | 0 | 437 | 0,11 | 0,82 | 0,0 | 13,4 | 1,0 | 0 |
| 15TM0593 | 0 | 0,05 | 439 | 0,86 | 0,15 | 33,3 | 573,3 | 0,0 | 3,85 |
| 15TM0606 | 0,01 | 0 | 440 | 0,23 | 1,21 | 0,0 | 19,0 | 1,0 | 0,3 |
| 15TM0646 | 0 | 0,01 | 447 | 0,14 | 0,43 | 2,3 | 32,6 | 0,0 | 0,17 |
| 15TM0649 | 0 | 0,02 | 440 | 0 | 0,03 | 66,7 | 0,0 | 0,0 | 0 |
| 16TM0596 | 0,29 | 2,32 | 443 | 0,51 | 1,81 | 128,2 | 28,2 | 0,1 | 5,7 |
| 16TM0620b | 0,01 | 0,02 | 441 | 0,17 | 0,16 | 12,5 | 106,3 | 0,3 | 0,94 |
| 16TM0622 | 0,02 | 0,16 | 443 | 0,41 | 0,68 | 23,5 | 60,3 | 0,1 | 6,9 |
| 16TM0625 | 0,02 | 0,24 | 440 | 0,16 | 0,68 | 35,3 | 23,5 | 0,1 | 5,4 |
| 16TM0734B | 0 | 0 | 441 | 0,25 | 0,15 | 0,0 | 166,7 | 0,0 | 4,15 |
| 16TM0734C | 0,01 | 0,24 | 447 | 0,67 | 0,27 | 88,9 | 248,1 | 0,0 | 7,13 |
| 16TM0784A | 0 | 0 | 0 | 0,17 | 0,37 | 0,0 | 45,9 | 0,0 | 0,43 |
| 16TM0790 | 0 | 0 | 0 | 0,16 | 0,06 | 0,0 | 266,7 | 0,0 | 2,24 |
| 16TM0791 | 0 | 0 | 0 | 0,24 | 0,14 | 0,0 | 171,4 | 0,0 | 1,26 |

**Table 9 – Summary of the calculated and derived geochemical parameters. TIC is total inorganic carbon (proxy for carbonate content).**

In the following paragraphs, several interpretative plots are illustrated. The samples analysed in this report are marked by green color labels and black outline. Published geochemical data of the Horton Group are also included: Hamblin 1989 (red); Global GeoEnergy Resources (blue) and Mossman et al. (1987) (purple crosses).

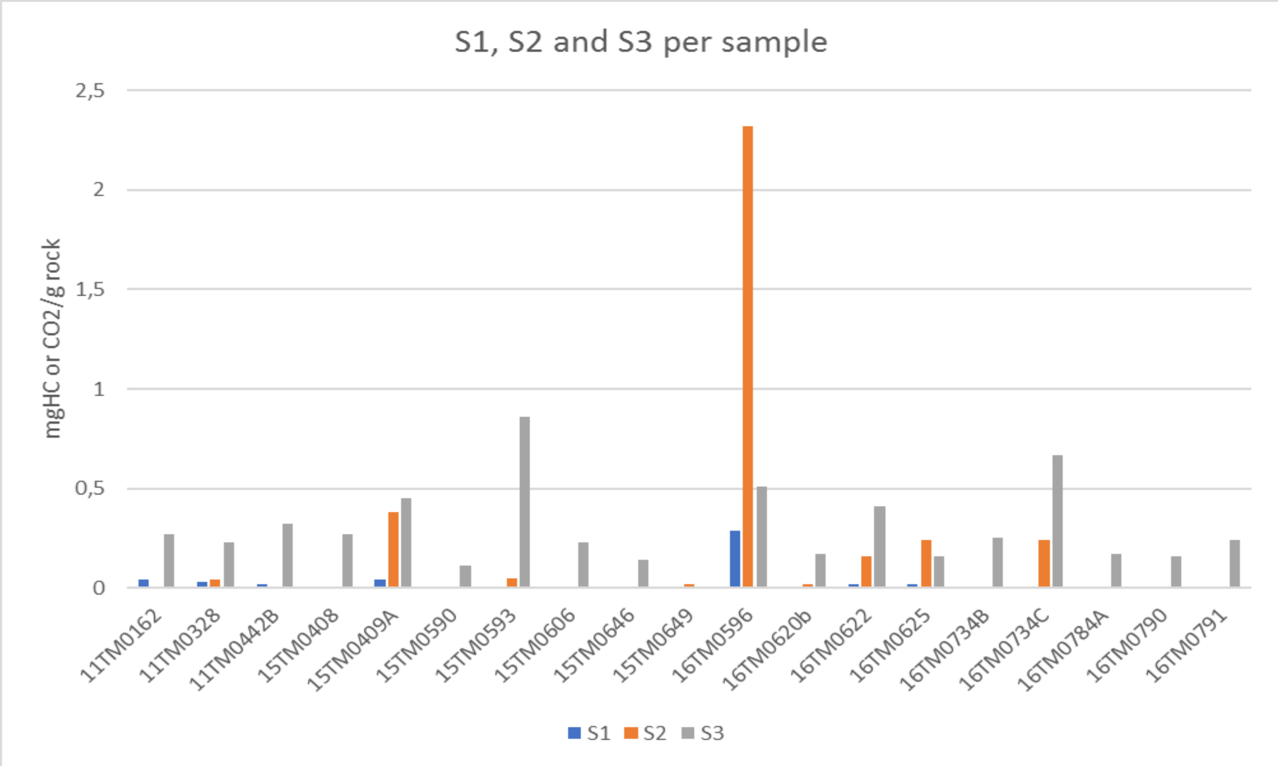


**Figure 7 – S1, S2 and S3 peaks per sample**

The plot above compares the S1 (free hydrocarbons), S2 (remaining hydrocarbon potential) and S3 ($CO_2$) of the analysed samples. Sample 16TMO596 clearly stands out as the one with most potential and samples 15TMO409A, 16TMO622, 16TMO625 and 16TMO734C with poor, but existing potential. Also noteworthy are the relatively high S3 peaks, which are indicative of highly matured source rocks and/or oxidized samples.

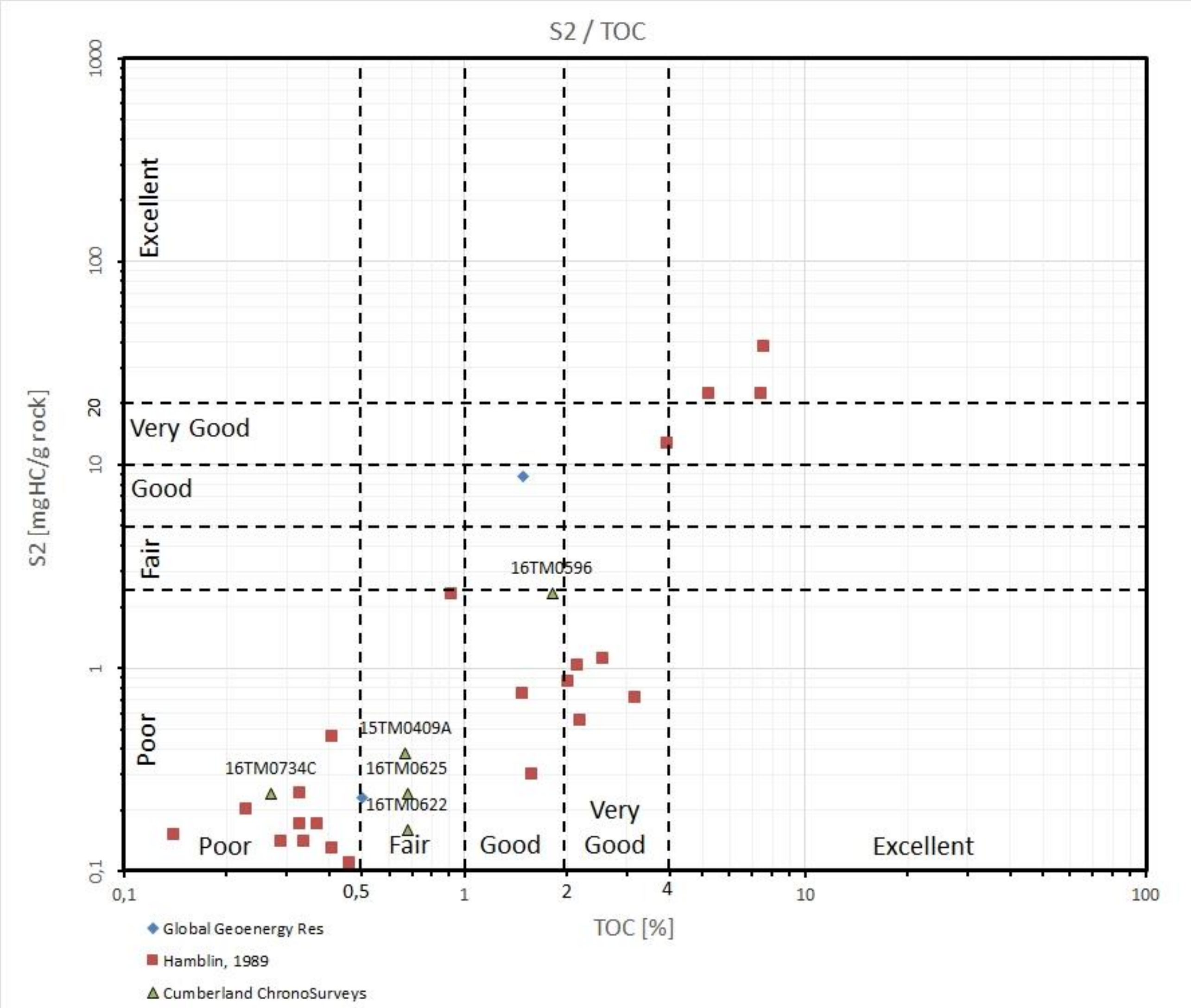


**Figure 8 – S2 Vs TOC plot and general indication of source rock potential**

Generally, source rocks are considered to have good potential when their TOC is above 1%. For the analysed samples, only sample 16TMO596 shows a relatively high TOC (1,81%) and significant S2 values. Sample 11TM0162, at 2,16% %wt TOC does not plot in the graph above as the S2 is very low (<0,1 mgHC/g rock).

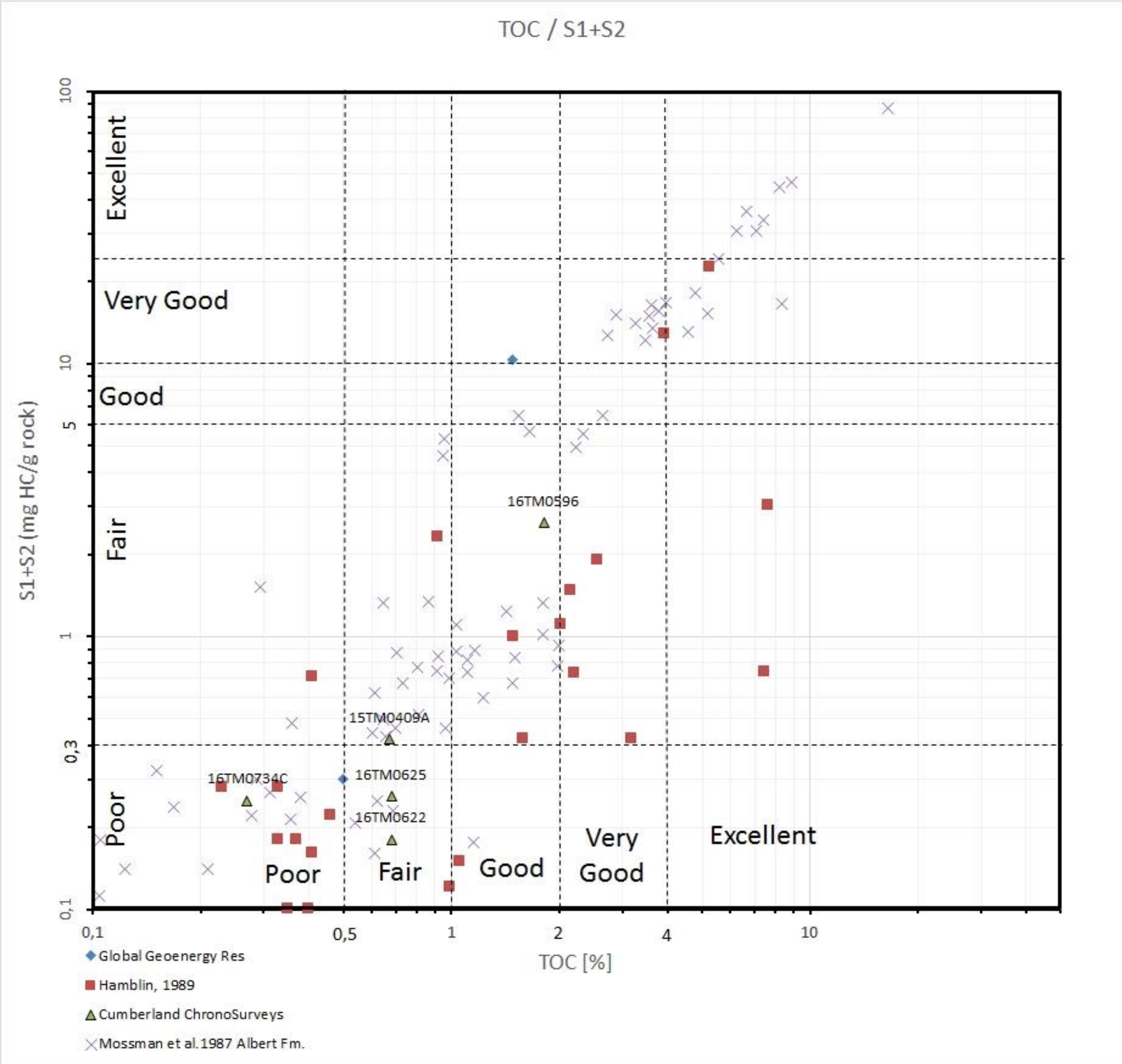


**Figure 9 - S2+S1 Vs TOC plot and general indication of source rock potential**

The plot above is similar to the previous one and again shows the potential of sample 16TMO596 with relatively high TOC and fair S1+S2 content (essentially S2). 15TMO409A has a fair potential (due to TOC higher than 0,5% %wt) and 16TMO625 and 16TMO622 with poor to fair potential (very low S1+S2 content).

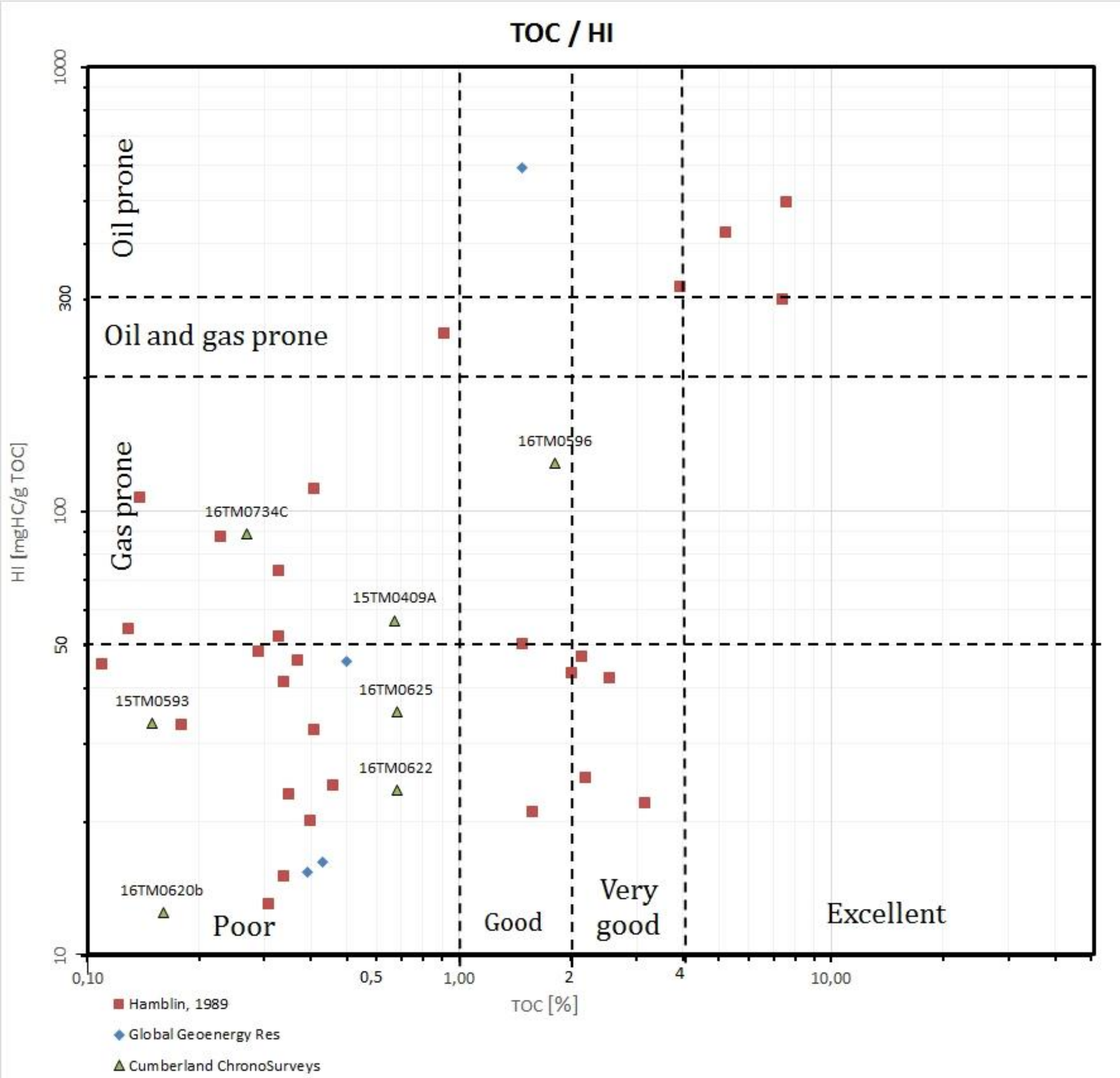


**Figure 10 – Hydrogen Index Vs TOC plot with general indication of source rock potential and type of hydrocarbons.**

The plot above emphasizes the poor source rock potential of the analysed samples, mainly due to their low TOC content. The ones that do have a higher TOC clearly plot as gas-prone source rocks. Sample 16TMO596 stands out as the most interesting and 15TMO409A as having poorer, but existing potential.

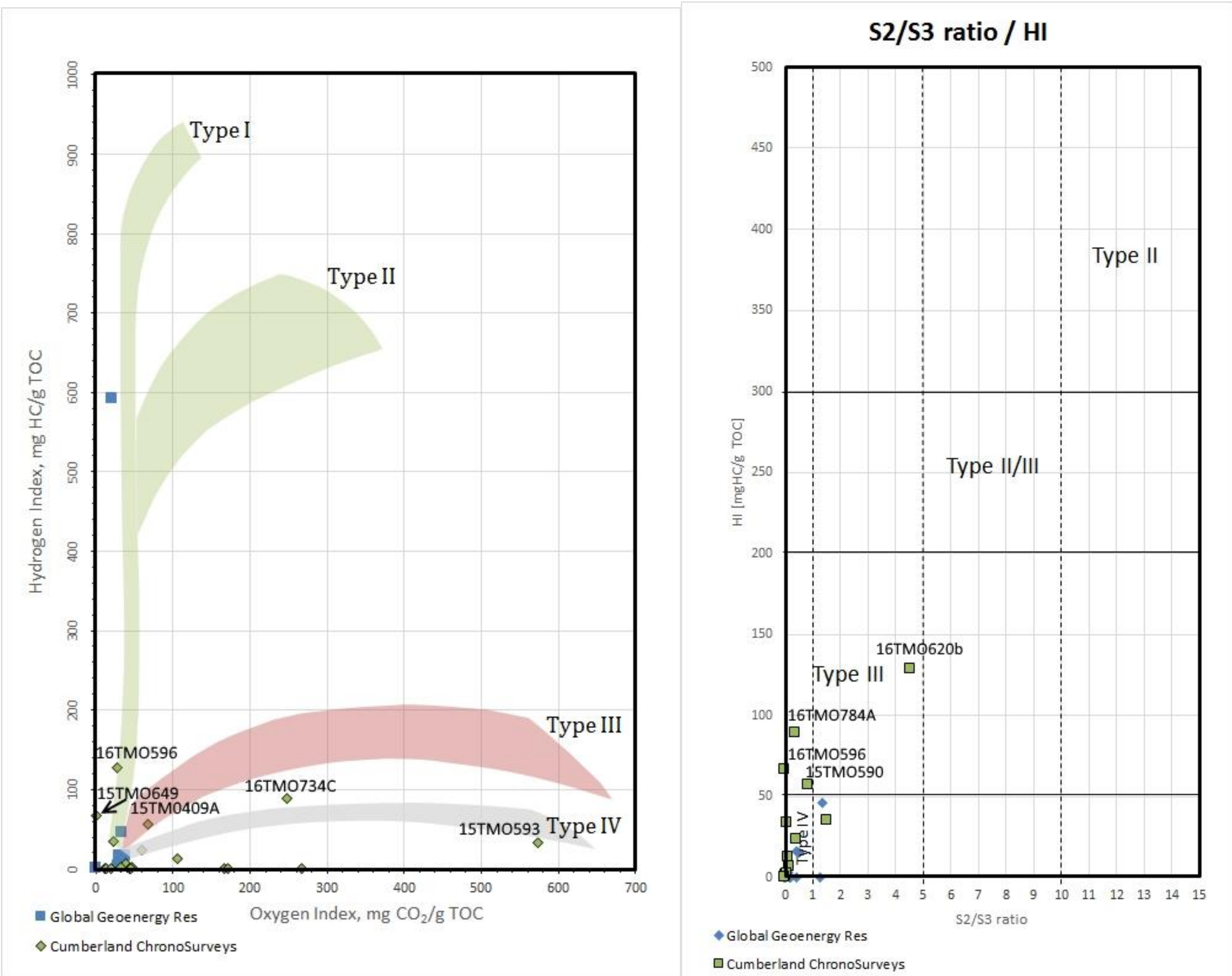


**Figure 11 – Adapted van Krevelen and S2/S3 Vs Hydrogen Index plots with indication of the types of kerogen.**

For samples with low TOC (<1%wt) the plots involving Oxygen and Hydrogen Indexes are not very reliable as usually they plot near to the origin of the plots. In addition, these plots are more appropriate for immature source rocks as they were originally designed to evaluate source rock pre-expulsion characteristics. In the plots above most of samples show a very poor to negligible potential, mostly inert (type IV geochemically) which is consistent with the other results. Samples 16TMO596 and 15TMO649 plot along the type I and II but that is not consistent with the other results and is likely an artifact resulting from the low values of S1 and S2. Similarly, the S2/S3 Vs HI plot shows a cluster in the type IV field with some dispersal into the Type III field. Overall the potential is low to negligible, with some samples having gas potential – notably 16TMO596, as indicated by other parameters.

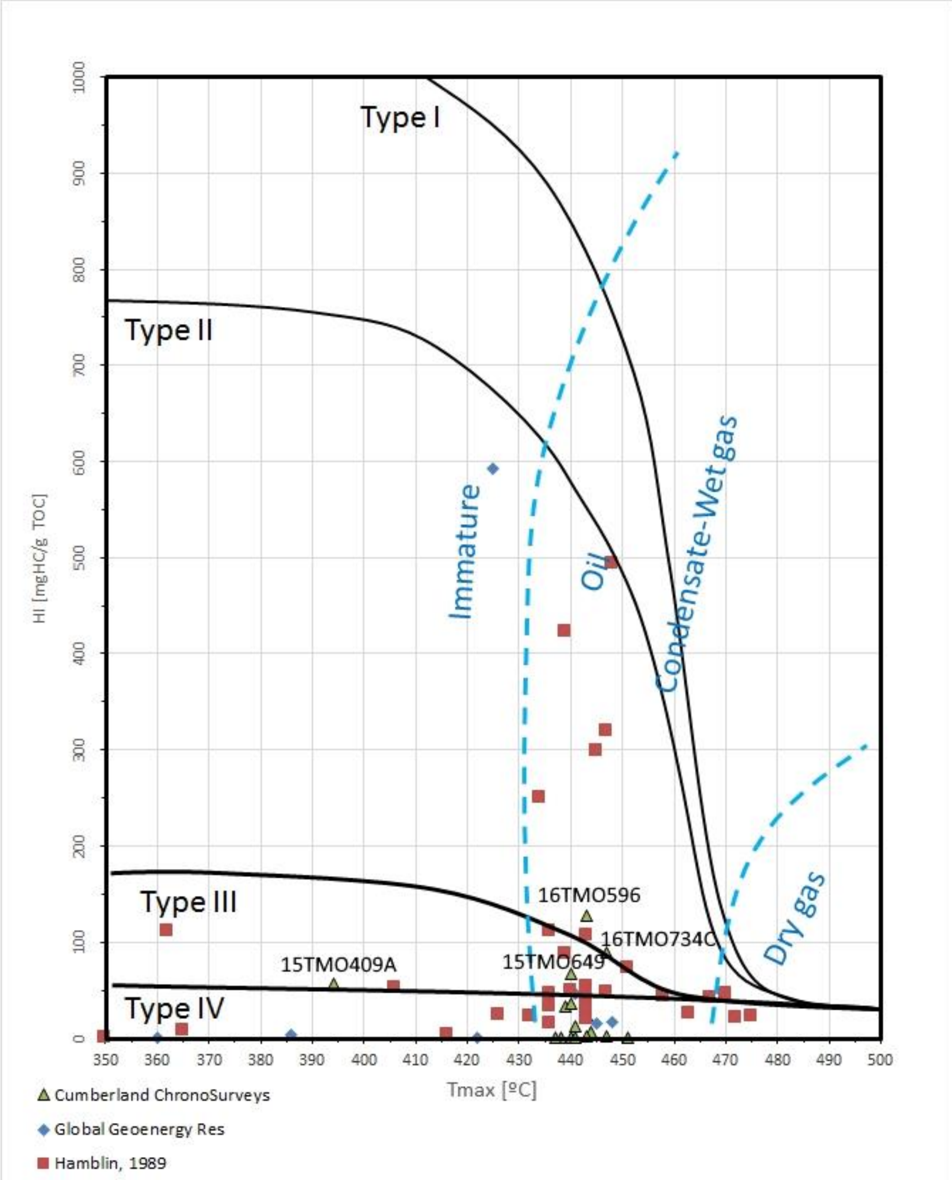


**Figure 12 – Tmax vs Hydrogen Index plot with indication of type of kerogen and overall type of hydrocarbon generated according to maturity.**

The plot above again shows the low source rock potential of the analysed samples, except for sample 16TMO596 which has some gas generation potential. Other samples plot along or close to the Type III line (16TMO734C and 15TMO649) but their low TOC is indicative of negligible gas-generating potential.

## 5. Conclusions

Processing: All nineteen samples were successfully processed for palynology and geochemistry analysis. One sample (15TM0649) contained only very scarce inertinitic organic particles and no quantification or biostratigraphic work was possible. Eighteen samples had enough organic material to perform palynofacies study. Five samples allowed standard taxonomic and biostratigraphic work to be conducted. Thirteen samples were too dark too observe directly and reflected light microscopy was used to observe the organic residues.

Palynology: All the analyzed samples were deposited in an aquatic environment, most likely in a lacustrine setting. Most of the samples show indication of proximal, oxic settings (near lake shore) except for samples 16TMO596 and 16TMO734B which were probably deposited in a more distal anoxic lake setting. Samples 11TMO162, 16TMO620b and 15TMO606 probably deposited in a transitional, suboxic environment.

Most samples have black opaque organic particles indicating inert kerogen (type IV). Samples 16TM0596, 16TMO622, 16TMO625, 16TMO734B and 16TMO734C are the exceptions, showing much lower maturity. Of these, samples 16TMO596 and 16TMO734B have oil-prone kerogen, although the geochemistry results point to more gas-prone source rocks, which can be explained by their maturity in the gas window. Similarly, samples 16TMO622, 16TMO625 and 16TMO734C show mixed and type II-III kerogen, but their maturity puts them in the gas window, as indicated by the geochemistry results.

Biostratigraphy: Foraminifera or other biostratigraphic relevant bioclasts were not found in the analyzed thin sections. Ten out of the nineteen processed samples provided recognizable spores/pollen which, despite their poor to moderate preservation, allowed age determination. These ten samples are assigned to the Mississippian. Of these, four samples are Tournaisian in age - 16TM0622 (Tn3), 16TM0625 (Tn3, *S. cabotii* subzone), 16TM0734B (Tn1-Tn3) and 16TM0734C (Tn3, *abstrusus – distinctus* subzone); sample 16TM0596 is Viséan in age (possibly NS biozone) and samples 11TM0162, 15TM0408, 15TM0593, 15TM606 and 15TM646 are probably Viséan in age; sample 15TM0590 is Mississippian in age (no refinement possible).

Organic geochemistry and thermal maturity: As illustrated above most samples show a very poor to negligible hydrocarbon generation potential. Sample 16TMO596 is clearly the one with higher potential, generally good, with geochemical parameters indicating a gas-prone source rock and within the oil window. Other samples such as 16TMO625 and 16TMO622 have a poor to fair gas generating potential (TOC > 0,5wt.%) and are within the gas window. Sample 15TMO409A has a relatively high TOC, but is clearly post-mature in terms of hydrocarbon generation potential.

An important aspect to note is that other samples with relatively high TOC such as 11TM0162 (2,16 wt.%), 11TM0442B (0,74 wt.%), 15TM0590 (0,82 wt.%), 15TM0606 (1,21 wt.%) which would be, in theory, fair to good source rocks, plot as containing inert (type IV) kerogen, essentially due to the high S3 values. The fact that these are outcrop samples and some of the them showed obvious signs of weathering (despite the removal of visually identifiable weathered pieces of rock for analyses) may be an indication that the true hydrocarbon generation potential of the rock units from where the samples were taken from is greater than estimated here. This may be particularly true for sample 11TM0162 which shows a maturity level within the dry gas window.

Future work: The hydrocarbon potential of the analysed samples is generally poor to negligible essentially due to their high thermal maturity and in some cases low TOC. Nevertheless, several of the samples are less mature and have remaining hydrocarbon potential, mostly gas-prone.

We suggest the analysis of further samples, using the same methods, located in areas outside the influence of granitic plutons, for example lateral equivalents of the same units that may have lower thermal maturity, or in areas that were subject to shallower burial. In addition, samples that can be associated with deeper lake facies seem to have more hydrocarbon generation potential (kerogen preserved in anoxic conditions) than proximal ones.

A wider study of the hydrocarbon prospectivity of the Cumberland basin is proposed, including the results obtained in this work, previous geochemical and biostratigraphic data from shallower levels (e.g. Windsor and Pictou Groups) coupled with seismic, well and other relevant data to properly assess the potential of this area.

## References


Barker, C.E. and Goldstein, R.H., 1990. Fluid-inclusion technique for determining maximum temperature in calcite and its comparison to vitrinite reflectance geothermometer. Geology 18: 1003–1006.

Batten, D., J., 1996a. Chapter 26A - Palynofacies and Palaenvironmental interpretation. In: Jansonius, J. and McGregor, D. C. (eds), Palynology: principles and applications. American Association of Stratigraphic Palynologists Foundation 3: 1011- 1064.

Batten, D., J., 1996b. Chapter 26B - Palynofacies and Petroleum potential. In: Jansonius, J. and McGregor, D. C. (eds), Palynology: principles and applications. American Association of Stratigraphic Palynologists Foundation 3: 1065-1084.

Combaz, A. 1964. Les palynofacies. Revue de Micropaleontologie 7: 205-218.

Fernandes, P., Luís, J., Rodrigues, B., Marques, M., Valentim, B. and Flores, D., 2010. The measurement of vitrinite reflectance with MatLab. In Oliwkiewicz-Miklasinka, M., Stempien-Salek M., and Laptas A. (eds), CIMP Poland General Meeting: 11– 13.

Fisher, M.J., Barnard, P.C., Cooper, B.S., 1980. Organic maturity and hydrocarbon generation in the Mesozoic sediments of the Sverdrup Basin, Arctic Canada. Proceedings 4th International Palynological Conference 2: 581–588.

Global Geoenergy Research, 2004. Evaluation of the Petroleum potential of the Devonian-Carboniferous rocks from Cape Breton Island, onshore Nova Scotia. Contract Number: 60122058 of March 31, 2004: Global Geoenergy Research Ltd. Final Report: 92pp.

Hacquebard, P. A. 1957. Plant Spores in Coal from the Horton Group (Mississippian) of Nova Scotia. Micropaleontology 3 (4): 301-324.

Hamblin, A. P. 1989. Sedimentology, tectonic control and resource potential of the Upper Devonian – Lower Carboniferous Horton Group. Cape Breton Island, Nova Scotia, Ph.D. Thesis, University of Ottawa: 300pp.

Hartkopf-Fröder, C., Königshof, P., Littke, R., Schwarzbauer, J., 2015. Optical thermal maturity parameters and organic geochemical alteration at low grade diagenesis to anchimetamorphism: A Review. International Journal of Coal Geology 150-151: 74-119.

Higgs, K., Clayton, G., Keegan, J. B. 1988. Stratigraphic and systematic palynology of the Tournaisian rocks of Ireland. Geological Survey of Ireland, Special Paper 7: 93pp.

Hillier, S. and Marshall, J. 1988. A rapid technique to make polished thin sections of sedimentary organic matter concentrates. Journal of Sedimentary Petrology 58: 754–5.

Luís, J. 2007. Mirone: a multi-purpose tool for exploring grid data. Computers and Geosciences, 33: 31–41.

Machado, G. and Flores, F. 2015. An effective method for the observation and documentation of highly mature palynomorphs using reflected light microscopy. Palynology 39 (3): 345-349.

Martel, T.A., McGregor, D. C., and Utting, J. 1993. Stratigraphic significance of Upper Devonian and Lower Carboniferous miospores from the type area of the Horton Group, Nova Scotia. Canadian Journal of Earth Sciences 30: 1091 -1098.

Miller, M. A., 1996. Chitinozoa. In: Jansonius, J. and McGregor, D. C., (eds) Palynology: principles and applications. American Association of Stratigraphic Palynologists Foundation 1: 307-336.

Mossman, D. J. 1992. Carboniferous source rocks of the Canadian Atlantic margin. In Parnell L, J. (ed.), Basins on the Atlantic Seaboard: Petroleum Geology, Sedimentology and Basin Evolution. Geological Society Special Publication, 62: 25-34.

Mossman, D. J., Macey, J. F. and Lemmon, P. D. 1987. Diagenesis in the lacustrine facies of the Albert Formation, New Brunswick, Canada: a geochemical evaluation. Bulletin of Canadian Petroleum Geology 35: 239-250.

Pearson, D.L. 1984. Pollen/Spore Color —Standard, Version 2. Phillips Petroleum Company.

Playford, G. 1964. Miospores from the Mississippian Horton Group, Eastern Canada. Geological Survey of Canada Bulletin 107: 47pp.

Staplin, F.L. 1969. Sedimentary organic matter, organic metamorphism, and oil and gas occurrence. Bulletin of Canadian Petroleum Geology 17: 47–66.

Tyson, R. V. 1987. The genesis and palynofacies characteristics of marine petroleum source rocks. Geological Society London, Special Publications 26 (1): 47-67.

Tyson, R. V. 1993. Palynofacies analysis. In: Jenkins, D. G. (ed). Applied micropaleontology. Kluwer Academic Publishers, Dordrecht. The Netherlands: 153–191.

Utting, J., Keppie, J.D., and Giles. P.S. 1989. Palynology and stratigraphy of the Lower Carboniferous Horton Group, Nova Scotia. In Contributions to Canadian Paleontology, Geological Survey of Canada Bulletin 396: 117-143.

Utting, J; Hamblin, A P. 1991. Thermal Maturity of the Lower Carboniferous Horton Group, Nova Scotia. In Kalkreuth, W., Bustin, R. M., Cameron, A. R. (eds). Recent Advances in Organic Petrology and Geochemistry: a Symposium Honoring Dr. P. Hacquebard; International Journal of Coal Geology 19: 439-456.

Varma, C. P. 1969. Lower Carboniferous Miospores from the Albert Oil Shales (Horton Group) of NewBrunswick, Canada. Micropaleontology 5 (3): 301-324.