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C. Jiang¹, D. Lavoie², and C. Rivard²

¹ Geological Survey of Canada, Calgary, Alberta

² Geological Survey of Canada, Québec, Quebec

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ABSTRACT

Water wells were drilled in November 2015 over the McCully gas field in southern New Brunswick as part of the Geological Survey of Canada (GSC) Environmental Geoscience program. Drill cuttings were collected and immediately put in Isojars at the well sites. Cuttings samples from PO-01 to PO-06 wells have been submitted to the Organic Geochemistry and Petrology Laboratories at the GSC-Calgary for Rock-Eval and hydrocarbon compositional analyses to evaluate their hydrocarbon potential, hydrocarbon property and source rock characteristics. Cuttings from one well (PO-06) have generated results indicative of presence of organic matter and hydrocarbons in the rock although no dissolved hydrocarbons were detected in groundwater at the well site. New Rock-Eval analyses were carried out on the cuttings as well as organic extracts and detailed geochemistry to further address the issue of either *in situ* hydrocarbon production or external hydrocarbon charge into the sediments.

INTRODUCTION

Environmental Geoscience Program Research in Southern New Brunswick

The Geological Survey of Canada Environmental Geoscience Program is actively carrying out environmental research projects in southern New Brunswick where shale gas activities are taking place. A local seismograph dense network (6 stations) has been deployed since 2013, in the McCully gas field area of the Moncton sub-basin to monitor natural and fracking-induced seismicity in the area (Lamontagne et al., 2015; Lamontagne and Lavoie, 2015). In 2015, the Geological Survey of Canada initiated a 2 year groundwater – cap rock integrity research project in the McCully area, following a similar project carried out in southern Quebec between 2012 and 2016 (Rivard et al. 2014; Lavoie et al., 2014, 2016). This contribution presents preliminary data and interpretation on organic geochemistry of the shallow bedrock geological units in the McCully gas field area.

Geological Setting

The project research area, the McCully gas field, occurs in the Moncton Sub-basin in southern New Brunswick, and is hosted by Carboniferous sandstones and shales. The Carboniferous-Permian Maritimes Basin unconformably overlies diverse Appalachian crustal zones of varying age and composition, deformed during the Middle to Late Ordovician Taconian and Early to Mid-Devonian Acadian orogenies (Calder, 1998). In Late Devonian, small fault-bounded basins opened from the continued oblique convergence of Gondwana following the Middle Devonian Acadian Orogeny (Gibling et al., 2008). These basins, collectively known as the Maritimes Basin, were either isolated or initially poorly connected. With time, these small continental basins became larger and recorded one major marine incursion but sedimentation was largely continental to marginal marine (Gibling et al., 2008). The Maritimes Basin covers a total area of 250,000 km2, with about 75% of the basin area being offshore.

Regional Tectonic and Stratigraphic Settings

The tectonic history of the Maritimes Basin included extensional and strike-slip settings in the Late Devonian to Mississippian and a wrench-foreland basin setting in the Pennsylvanian to early Permian (Bradley, 1982; Durling and Marillier,1993; Rehill, 1996). Regional strike-slip faults were active through most of the basin's development, resulting in local development of pull-apart basins and subsequent basin inversions and deformation. The present day Maritimes Basin is an erosional remnant of a formerly much more extensive cover of Upper Paleozoic strata (Fig.1).

The Maritimes Basin contains Upper Devonian to Lower Permian continental and shallow marine strata, with a maximum known thickness of approximately 12,000 meters in the east-central Magdalen Basin (eastern Gulf of St. Lawrence, Dietrich et al., 2011). In this contribution, the stratigraphic framework of the Moncton sub-basin, illustrated in Figures 2 and 3 will be used.

The earliest record of post-Acadian sedimentation in the Moncton sub-basin is the Upper Devonian to lower Mississippian Horton Group, a thick succession dominated by coarse-grained sandstone and conglomerate near the faulted margins of individual half-graben basins (Hamblin and Rust, 1989). Away from the faulted margins, interbedded fluvial (lithic sandstone) and lacustrine (organic matter rich shale) facies were deposited (Hamblin, 1992). Local unconformities typical of terrestrial settings are present at the top of the Horton Group (Lavoie et al., 2009).

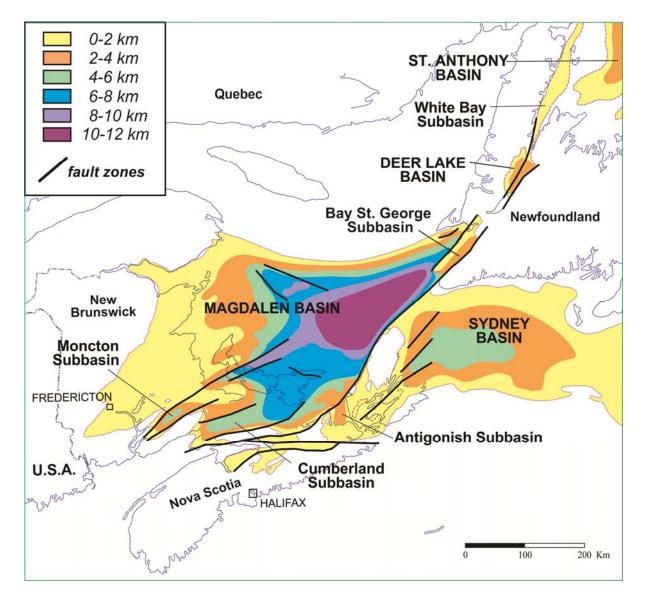


Figure 1. Isopach map of the latest Devonian – Permian basins in eastern Canada. The Maritimes Basin is the regional designation of the regrouped local basins and sub-basins. The Moncton sub-basin is the fault-bounded depocenter in southern New Brunswick. Modified from Lavoie et al. (2009).

In the Moncton sub-basin, the Horton Group is unconformably overlain by the lower Mississippian (end-Tournaisian) Sussex Group (St. Peter and Johnson, 2009) whereas elsewhere, it is abruptly unconformably overlain by the middle Mississippian (Visean) Windsor Group (Giles, 1981; Gibling et al., 2008). The Sussex Group comprises a complex succession of proximal coarse to distal fine-grained continental and evaporite facies. At the sub-basin scale, the succession consists of two coarse grained intervals separated by a fine-grained dominated one (St. Peter and Johnson, 2009).

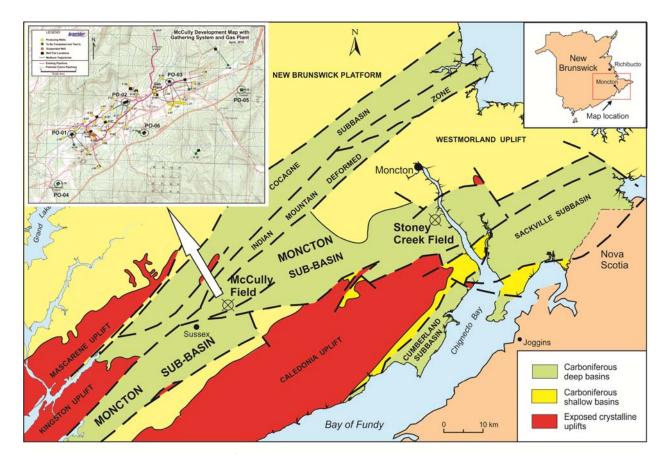


Figure 2. Location of the McCully and Stoney Creek gas and oil fields respectively. The top left inset, modified from Corridor Resources, locates drilling pads and wells drilled by Corridor Resources and Potash Corporation in the gas field. The circles locate the drilling pads where the GSC shallow hydrogeological wells (PO-01 to PO-06) were drilled. Figure modified from St. Peter and Johnson (2009).

The base of the Windsor Group records a significant marine flooding event and the establishment of shallow marine metazoan-algal-microbial reefs on the shoulders of pre-Upper Devonian palaeotectonic highs (Gays River Formation) and coeval organic matter rich deeper marine argillaceous calcilutites (Macumber Formation) (Lavoie and Sami, 1998). The Gays River – Macumber basal marine assemblage is overlain by a thick succession of deep-marine sulfates (gypsum and anhydrite) and salt (halite). The upper part of the Windsor Group consists of

alternating nearshore to continental fine-grained clastic successions and subordinate shallow marine carbonates with local small metazoan reefs (Giles, 1981).

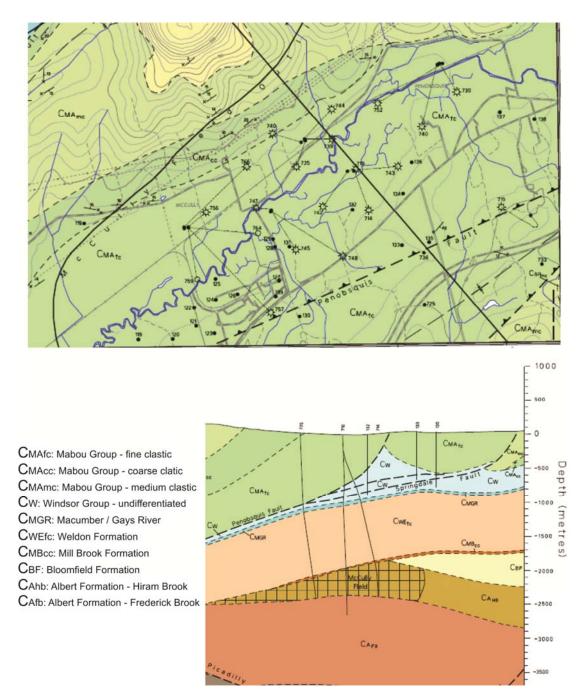


Figure 3. Surface geological map of the area of the McCully gas field (upper) and cross-section (lower) through the central part of the producing gas field. Modified from Hinds (2009).

The Windsor Group is conformably overlain by the upper Lower Mississippian Mabou Group. The Mabou Group consists of nearshore to marginal marine fine-grained clastics with some local coals and rare small limestone intervals (St. Peter and Johnson, 2009). The Mabou Group is unconformably overlain by the end Mississippian to Pennsylvanian Cumberland Group. The Cumberland Group is dominated by more fine- and coarse-grained clastic continental deposits with abundant coal measures with significant hydrocarbon generating potential (Dietrich et al., 2011).

Finally, Lower Permian continental clastics to eolian sandstones of the Pictou Group occur at the top of the stratigraphy, these eolian sandstones are nicely exposed on the Magdalen Islands in the central part of the Gulf of St. Lawrence.

Local stratigraphy and structural geology

The McCully gas field occurs in the Moncton sub-basin (Fig. 2). The local bedrock geology consists of informally divided clastic facies of the Mabou Group, where fine-, medium- and coarse-grained clastics are mapped. The dominant lithology consists of red-colored mudstone, siltstone and sandstone with rare conglomerate. Overall, the area in the immediate vicinity of the gas field is poorly outcropping and is dominated by friable sandstone with secondary fine-grained mudstones beds. The stratigraphic framework of the area follows the regional nomenclature presented in St. Peter and Johnson (2009).

The understanding of the shallow and deep sub-surface geological architecture relies on the large number of wells drilled in the gas field (Fig. 3). The kilometer-thick Mabou Group is involved in two local synclines that are separated by the Penobsquis Fault. Below the Mabou Group, the Lower Carboniferous (Viséan) Windsor Group is either in fault contact (through the Penobsquis Fault) or unconformably underlies it. In the McCully area, the Windsor Group consists of a basal limestone succession, the laterally equivalent Macumber / Gays River formations overlain by a thick (hundreds of meters thick diapir) to thin (tens of meters) potash-rich evaporite unit. The inverse Springdale Fault cuts through the Windsor Group evaporites and connects with the Penobsquis fault at depth. The Macumber Formation consists of a thin, fine-grained laminar limestone; this unit in Nova Scotia is rich in organic matter and is considered as a fair hydrocarbon source rock (Lavoie et al., 2009). The basal Windsor Group unconformably overlies the kilometer-thick lowermost Carboniferous (Tournaisian) red mudstone and shale of the Sussex Group with a basal conglomerate (Mill Brook Formation) draping a major angular

unconformity at the top Horton Group. The lowermost Carboniferous (Tournaisian) Horton Group is the host of the McCully gas field (see below). The Horton Group consists downwards of the fine to coarse grained clastics of the Bloomfield Formation, underlain by the Albert Formation with the hydrocarbon produced from interbedded tight sandstones and kerogen-rich mudstones of the 500- 700 meters thick Hiram Brook Member underlain by the kerogen veryrich and potential shale gas and tight oil target, kilometer-thick Frederick Brook Member (Hamblin, 2006; Lavoie et al., 2009). The coarse-grained clastics of the Dawson Settlement Member are found at the base of the Albert Formation. The red sandstone and sub-ordinate mudstone of the McQuade Formation (Horton Group) is the deepest unit known in the McCully gas field area. Overall, the known Carboniferous succession in the study area is up to 4 km thick with the producing gas interval between 2 and 2.6 km depth.

Tectonism in the eastern Moncton sub-basin has been recently analyzed and discussed by St. Peter and Johnson (2009). The tectonic setting of the Horton and Sussex groups is regionally characterized by a fold/thrust belt. The end-Horton and end-Sussex inversion events in the fold/thrust belt were accomplished by NW-dipping reverse or thrust faults assisted by NW-striking sidewall ramps or tear faults (St. Peter and Johnson, 2009). However, locally the inversion occurs via oblique dextral transgression (St. Peter and Johnson, 2009).

Historical hydrocarbon exploration and unconventional shale gas

The up to 12km thick Maritimes Basin has numerous potential and proven hydrocarbon systems (Lavoie et al., 2009; Dietrich et al., 2011). New Brunswick is one of the oldest oil-producing provinces in Canada. In 1859, one of the first oil wells in North America was drilled just outside of Moncton, near the village of Dover (St. Peter, 2000). Historic oil production from the Stoney Creek Field (Dover area) was from shallow wells that were drilled into the Lower Carboniferous lacustrine sandstones of the Albert Formation of the Horton Group. Most oil and gas development in New Brunswick has focused on the Albert Formation of the Moncton sub-basin.

Corridor Resources has drilled 39 wells in the McCully field (Sussex area) and currently produce dry gas primarily from tight sandstones of the Hiram Brook Member (Albert Formation), although four wells have been drilled to the Frederick Brook shale Member (Albert Formation). These wells are considered unconventional because the Hiram Brook sandstone and the Frederick Brook shale at the McCully field require fracking stimulation to promote economic production. The production at McCully field is from vertical or inclined wells that were subjected to few stages – low water volume fracking operations, although propane gel was recently used as proppant carrying fluid.

SAMPLES AND METHODS

Samples

In November 2015, six shallow wells, PO-01 to PO-06, (50 m total vertical depth; TVD) were drilled in the McCully gas field area. The wells were drilled on Corridor Resources drill pads (Fig. 2). The location of the wells was based on the interpreted presence or lack of faults reaching or close to the surface in this area devoid of significant outcrops. No coring program was performed, and cuttings were immediately collected and stored in Isojars at the drilling sites and sent for geochemical analysis. Samples were collected 1) immediately below the unconsolidated sediment/bedrock interface; 2) at an intermediate depth between 30 - 35 metres; and 3) at the bottom, about 1 m above TVD.

The shallow groundwater wells were drilled using water, and thus no mud or oil contamination is expected. The intercepted succession at PO-06 well which has been subjected to detailed geochemical analysis (see below) consists of 2.7 m of man-made backfill followed by 11.7 m of unconsolidated sediments with red clay, sand and gravel. Bedrock started at 14.3 m and drilling stopped at 50.3 m. Based on cuttings, the succession consists of alternating fine- to medium-grained grey sandstone with red siltstone and dark mudstones. Black viscous oil was reported between 14.3 to 46.6 m from PO-06 well, but unfortunately was not collected for laboratory analysis.

Cuttings samples from the Isojars were dried in air before being powdered for Rock-Eval analysis. Based on the Rock-Eval results, samples from PO-06 well at the depths of 20.57, 34.29 and 49.53 meters have been selected for detailed geochemical analysis via solvent extraction, column chromatography separation followed by gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS) analyses.

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Rock-Eval/TOC Analysis

At the GSC-Calgary, typical Rock-Eval analysis of core and drilling cuttings samples is performed on a Rock-Eval 6 Turbo device. Aliquots of about 70 mg of powdered samples are used in single Rock-Eval analysis. Initially samples are heated at 300°C for 3 minutes to volatilize any free hydrocarbons (HC) and these are represented by the Rock-Eval S1 peaks from the FID-pyrograms. Ideally, the area under the S1 pyrolysis curve (mg HC/g of initial rock) represents hydrocarbons naturally generated *in situ* over geologic time, but sample impregnation by migrated hydrocarbons, expulsion and loss of hydrocarbons, and organic drilling contaminants (e.g. oil-based drilling mud) can also affect the S1 values (Jarvie and Baker, 1984; Bordenave et al., 1993; Jarvie, 2012; Jiang et al., 2015, 2016). Following this isothermal heating step, samples are heated linearly from 300°C to 650°C at a rate of 25°C/minute, yielding an S2 peak that represents thermal decomposition products from solid sedimentary organic matter, the kerogen. Under ideal conditions, the area under S2 curve (mg HC/g of initial rock) represents the remaining hydrocarbon potential of the rock sample at increased thermal maturity or deeper burial depths; however, the results can also be affected by the presence of heavy bitumen or oil impregnation due to oil migration and accumulation (Snowdon, 1984 and 1995; Peters, 1986; Delvaux et al., 1990). The temperature at the maximum of S2 peak (TpS2) varies with the thermal maturity of the sedimentary organic matter, and is converted to Tmax (°C), the widely accepted thermal maturity parameter established on the older Rock-Eval 2 model. Similar to S2 peak value, the Tmax and TpS2 can also be affected by the presence of heavy hydrocarbons that often appear as a front shoulder (S2' peak) to the S2 peak.

The S3 curve corresponds to the amount of CO_2 (mg CO_2/g of initial rock) generated from organic matter during the initial isothermal heating step and the programmed heating phase up to 400°C. CO_2 generated between 400°C and 650°C is from the thermal decomposition of carbonate minerals. The Rock-Eval 6 instrument also records the amount of CO generated during pyrolysis and attributes various proportions to organic carbon and mineral sources depending on sample temperature (Behar *et al.*, 2001 for details). The amount of pyrolysable or productive organic carbon (PC) is determined by combining the S1, S2, S3 contributions according to a predefined formula (Behar *et al.*, 2001). Pyrolysis mineral carbon is determined from the high temperature portions of the CO and CO₂ pyrolysis curves.

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Following pyrolysis, samples are transferred to an oxidation furnace of the Rock-Eval 6 instrument where they are linearly heated from 300° C to 850° C under air flow to determine the amount of residual organic carbon (RC) and oxidation mineral carbon from CO and CO₂ generated during oxidation. The total organic carbon (TOC) is the sum of the productive and residual organic carbon. Similarly, mineral carbon (MinC) is the sum of the pyrolysis and oxidation mineral carbon.

Solvent Extraction

About 20 gram of each powdered rock sample was subjected to Soxhlet extraction for 72 hours using dichloromethane (DCM) as solvent. Activated copper grains were added to the extract content at the end of extraction or during solvent removal to remove any elemental sulfur. After removing most of solvent using a rotary evaporator, the extract content was filtered to remove copper, copper sulfide and any inorganic salts that were extracted by the solvent. The residue was retained and weighed as extract after removal of the remaining solvent using a gentle stream of nitrogen.

Column Chromatography Fractionation

Rock extracts were de-asphaltened with *n*-pentane and then separated into aliphatic, aromatic and polar fractions by column chromatography using the mixture of silica gel (28-200 mesh) and alumina (80-200 mesh) (1:3 by weight) as support. Activated support (400°C overnight) in the amount of 1 g per 10 mg of de-asphaltened extract was added slowly into a glass column filled with *n*-pentane while tapping the column to release the air bubbles and to settle the support material. *n*-Pentane (3.5 mL per gram of support) was used to elute the aliphatic fraction, followed by *n*-pentane/dichloromethane (1:1 by volume and 4 mL per gram of support) to isolate the aromatic fraction. Methanol (4 mL per gram of support) and chloroform (6 mL per gram of support) were finally used to obtain the polar fraction. All fractions were weighed after removal of solvent using rotary flash evaporator followed by slow stream of nitrogen.

A mixture of admantane-d16, naphthalene-d8, phenanthrene-d10, dibenzothiophene-d8 and 1,1binaphthyl was added to the aromatic fractions, and cholestane-d4 added to the saturated fractions of the extracts in appropriate amounts as internal standards before GC and GC-MS analyses. The purpose of the use of internal standards is to compare the concentrations of selected compounds among samples but not for absolute quantification.

GC and GC-MS of C_{12}^+ hydrocarbon fractions

GC analysis of saturated fractions was done on a Varian 3700 GC equipped with a FID. A 30 m×0.25mm×0.25µm DB-1 fused silica capillary column was used with helium as carrier gas. The samples were injected using a split injector heated at 320°C. The temperature program was as follows: 60°C (@6°C/min) \rightarrow 300°C (30min). The FID detector temperature was maintained at 320°C.

GC-MS analysis of aliphatic fractions was carried out on an Agilent GC-Q-TOF system in full scan mode. Split injection (1:10) was employed into a HP5MS UI 30m×0.25mm×0.25µm capillary column with helium as carrier gas at a flow rate of 1.2mL/min. Mass spectrometer ion source was operated at 70 eV ionization voltage.

GC-MS analysis of the aromatic fractions was performed on an Agilent 6890 series GC coupled to a 5973 series Mass Selective Detector (MSD) operating in both full scan and selected ion monitoring (SIM) modes. Split injection was employed into a J&W DB-5 $30m\times0.32mm\times0.25\mu m$ capillary column at 300°C temperature. Helium was used as carrier gas at a flow rate of 1.2mL/min. The GC oven temperature was programmed as follows: 40°C (@4°C/min) \rightarrow 325°C (15min).

RESULTS AND INTERPRETATION

Rock-Eval Analysis

Table 1 presents the Rock-Eval results for all the cuttings samples collected from the water wells at the McCully gas field. The Carboniferous Mabou Group sediments at PO-06 well are the most organic-rich among the samples from the six wells. While the samples from PO-01 to 05 wells have their Rock-Eval organic richness parameters (i.e. TOC, S1 and S2) close to zero, PO-06 samples display TOC contents ranging from 0.19% to 0.40%, S1 peaks in the range of 0.01 to

0.28 mg HC/g rock, and S2 peaks between 0.59 and 1.98 mg HC/g rock. This difference likely relates to a lithological change. The cuttings from PO-01 to 05 wells are red-colored sandstone and mudstone that were likely deposited in an oxidizing environment, and thus contain little

Sample ID	Well	Depth (m)	Depth (ft)	S1	S2	S3	Tmax (°C)	тос (%)	MINC%	н	OI	PC (%)	RC (%)
C-601698	PO-01	11.43	37.5	0.00	0.01	0.02	341	0.03	1.0	33	67	0.00	0.03
C-601699		31.24	102.5	0.00	0.00	0.01	425	0.00	0.9	0		0.00	0.00
C-601700		49.53	162.5	0.00	0.00	0.01	400	0.00	0.9	0		0.00	0.00
C-601701		25.15	82.5	0.00	0.00	0.04	397	0.04	2.1	0	100	0.00	0.04
C-601702	PO-02	37.34	122.5	0.00	0.00	0.00	338	0.03	1.1	0	0	0.00	0.03
C-601703		49.53	162.5	0.00	0.00	0.00	341	0.03	0.9	0	0	0.00	0.03
C-601704		19.05	62.5	0.00	0.00	0.01	341	0.00	0.0	0		0.00	0.00
C-601705	PO-03	34.29	112.5	0.00	0.00	0.02	344	0.00	0.0	0		0.00	0.00
C-601706		49.53	162.5	0.00	0.00	0.03	321	0.00	1.5	0		0.00	0.00
C-601707		6.86	22.5	0.00	0.01	0.08	340	0.06	1.9	17	133	0.01	0.05
C-601708	PO-04	31.24	102.5	0.00	0.00	0.02	-45	0.00	2.9	0		0.00	0.00
C-601709		49.53	162.5	0.00	0.00	0.02	-45	0.04	2.5	0	50	0.00	0.04
C-601710		6.86	22.5	0.00	0.00	0.01	338	0.00	0.0	0		0.00	0.00
C-601711	PO-05	31.24	102.5	0.00	0.00	0.00	-45	0.00	0.0	0		0.00	0.00
C-601712		49.53	162.5	0.00	0.00	0.01	337	0.00	0.0	0		0.00	0.00
C-601713		20.57	67.5	0.01	0.59	0.07	437	0.19	0.2	311	37	0.05	0.14
C-601714	PO-06	34.29	112.5	0.28	1.98	0.02	435	0.33	0.6	600	6	0.19	0.14
C-601715	r 0-00	49.53	162.5	0.08	1.35	0.04	432	0.28	0.1	482	14	0.12	0.16
C-601716		49.53	162.5	0.05	0.99	0.07	432	0.24	0.1	412	29	0.09	0.15
C-601713*		20.57	67.5	0.03	1.11	0.15	436	0.31	0.1	357	48.5	0.10	0.21
C-601714*	PO-06	34.29	112.5	0.13	1.17	0.14	437	0.22	0.4	530	63.5	0.12	0.11
C-601715*	PO-00	49.53	162.5	0.09	1.38	0.17	436	0.36	0.1	389	46	0.13	0.23
C-601716*		49.53	162.5	0.11	1.55	0.19	433	0.40	0.2	388	48	0.15	0.25
C-601713*X	PO-06	20.57	67.5	0.02	0.92	0.14	435	0.30	0.1	307	47	0.08	0.22
C-601714*X		34.29	112.5	0.02	0.77	0.18	438	0.17	0.4	453	106	0.07	0.10
C-601715*X		49.53	162.5	0.02	1.05	0.21	436	0.32	0.1	328	66	0.10	0.22
C-601716*X	CALL ACTION)	49.53	162.5	0.03	1.12	0.23	435	0.33	0.1	339	70	0.10	0.23

Table 1. Rock-Eval results for the Carboniferous Mabou Group cuttings samples from the water wells drilled at the McCully gas field, southern New Brunswick

Note: C-601715 and C-601716 are cuttings collected from the same depth interval, with the former un-washed and the latter washed. After Rock-Eval analyses, samples C-601713 to C-601716 from PO-06 well were selected for geochemical analyses, and thus a larger aliquots of the cuttings were powdered and labelled as C-601713* to C-601716* for additional Rock-Eval analyses before (light green in table) and after (light brown in table) solvent extraction.

preserved organic matter. In contrast, cuttings from PO-06 well are mixtures of sandstone, siltstone and mudstone of light grey to dark grey color. The PO-06 mudstones cuttings appear to be of darker color than the sandstone, and are likely deposited in more reducing environments and therefore may contain certain amount of preserved organic matter. It seems that if handpicking had been carried out on the PO-06 cuttings samples to separate mudstone from the sandstone and siltstone, a higher content of organic matter and values including S1, S2 and TOC would have been detected in the mudstone samples.

The pre-solvent extraction PO-06 samples have a calculated hydrogen index (HI) between 311 and 600, and an oxygen index (OI) less than 64, suggesting a Type II organic matter in terms of their hydrocarbon generation potential. The Rock-Eval S2 peaks are well formed and near-symmetric for the PO-06 samples (Fig. 4), and the resulting Tmax values of 432 to 437°C place the PO-06 Mabou Group samples at the onset of hydrocarbon generation. However, this may slightly under-estimate the true thermal maturity of the Mabou Group mudstones at PO-06 well, as there is a significant presence of heavy hydrocarbons (see below) that can result in reduced Tmax values. Rock-Eval Tmax values for Mabou Group sediments from PO-01 to 05 wells are not considered reliable as their S2 peaks cannot be resolved given the low contents of organic matter resulting in an erratic pattern.

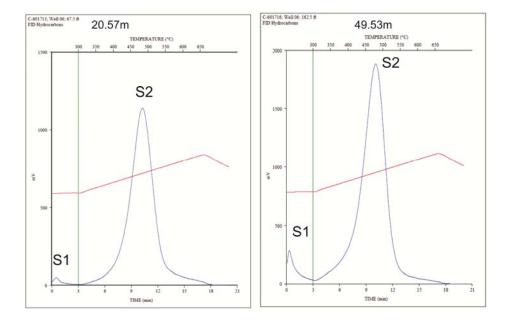


Figure 4. Typical Rock-Eval pyrograms of selected Mabou Group cuttings samples from the PO-06well.

By comparing the Rock-Eval S1 peaks with the solvent extraction results for PO-06 samples (Table 2), one can see that the amounts of free oil represented by Rock-Eval S1 peaks are far less than the corresponding solvent extracts, meaning that there is a relatively large amount of heavy hydrocarbons or bitumen that was not thermally liberated and recorded by the S1 peaks at 300°C during the analysis but was released into the Rock-Eval S2 peaks during pyrolysis stage. This is supported by the fact that the S2 peaks obtained on solvent-extracted samples are smaller than the corresponding S2 peaks obtained on the original samples (Tables 1 and 2). The solvent extraction results show that 21 to 38% of organic matter in the cuttings samples are soluble organic matter that was either generated in situ from kerogen in the Mabou Group sediments or migrated from source rocks elsewhere. The presence of heavy hydrocarbons in the Mabou Group sediments from McCully PO-06 well have only slightly lowered Tmax values by about 1°C on average as shown in Table 1 (light green vs light brown shaded area). This effect has been reported previously by Snowdon (1984 and 1995), Peters (1986) and Delvaux et al. (1990) in other sedimentary basins.

Sample	Depth (m)	TOC (% Rock)	mg free	Oil/g Rock	mg free	Oil/g TOC	RE S2 (mg	HC (%) in	
Lab ID			RE (S1)	Extraction	RE (S1)	Extraction	original	Extracted	Extract
X11801	20.57	0.31	0.03	0.40	9.7	211.7	1.11	0.92	73.9
X11802	34.29	0.22	0.13	0.73	56.8	221.5	1.17	0.77	85.4
X11803	49.53	0.36	0.09	0.79	25.4	283.3	1.38	1.05	78.9
X11804*	49.53	0.40	0.11	0.92	27.5	382.4	1.55	1.12	66.8

Table 2. Comparions of free oil/hydrocarbon content obtained from Rock-Eval analysis and solvent extraction

Note: RE: Rock-Eval; S1: S1 peak of Rock-Eval; S2: S2 peak of Rock-Eval; Sample X11804 is the same as X11803 but has been washed with water; HC% in Extrcat: % of hydrocarbons in the solvent extracts.

Organic Geochemical Analysis

Considering their low organic matter content and low maturity, the Mabou Group samples from the PO-06 well cannot be considered as either an effective (potential) hydrocarbon source rock unit or a reservoir unit. Nevertheless, molecular organic geochemical analyses have been carried out on the cuttings samples from PO-06 in an attempt to characterize the type of hydrocarbons, their source rock depositional environment, organic input and thermal maturation.

Biodegraded Oil or Low Maturity Crude?

Results from column chromatographic separation show that hydrocarbons (i.e. saturated plus aromatic fractions) account for 73.9 to 85.4% of the solvent extracts from the Mabou Group sediments from the McCully PO-06 well (Table 2). The GC analysis clearly indicates a lack of light to medium (<C20) hydrocarbons in the PO-06 Mabou Group cuttings that seem to contain mainly heavy crude even though in minor amounts (Fig. 5). This confirms the above comparison of Rock-Eval S1 peaks with the amounts of solvent extracts (Table 2). More specifically, their saturated fractions are characterized by a low abundance of normal alkanes (n-alkanes) and a predominance of steranes and hopanes, as evidenced from the GC-FID traces of the saturated fractions (Fig 5). β-carotane, identified by comparison of its GC retention time and mass spectrum (Fig. 6), is also found to be a prominent compound (Fig. 5). Considering that the well had been drilled only a few months prior to these analyses and that the cuttings had been stored in Isojars and thus immersed in demineralized water, evaporative loss associated with sample handling and storage cannot be a major factor for the scarcity of <C₂₀ components and the enrichment of heavy hydrocarbons in the sediments. Moreover, no dissolved light hydrocarbons $(C_1 \text{ to } C_5)$ were detected in the groundwater sampled from the shallow PO-06 well. Hence, extractable hydrocarbons in the Mabou Group at the PO-06 well likely correspond to heavy oil. This is also supported by the observation of black viscous oil during drilling of the PO-06 well.

The above observed geochemical signatures can be either a result of oil biodegradation or a characteristic of immature to low maturity crude oils and source rocks, or both (Peters et al., 2005). Mature crude oils are typically dominated by n-alkanes. Their biodegradation will preferentially remove n-alkanes followed by acyclic alkanes and different rings and isomers of aromatic compounds, resulting in the enrichment of the relatively more resistant components such as steranes and hopanes (Peters et al., 2005). As such, the saturated fraction GC traces of biodegraded oils usually display certain degree of absence/presence of n-alkanes seated atop UCM (unresolved complex mixture) humps height of which depends on the degree of biodegradation. The lack of an apparent UCM hump or the presence of minor UCM humps under the n-alkane distributions for the PO-06 samples appears to exclude biodegradation as the only cause or the main cause for the enrichment of biomarkers (Fig. 5).

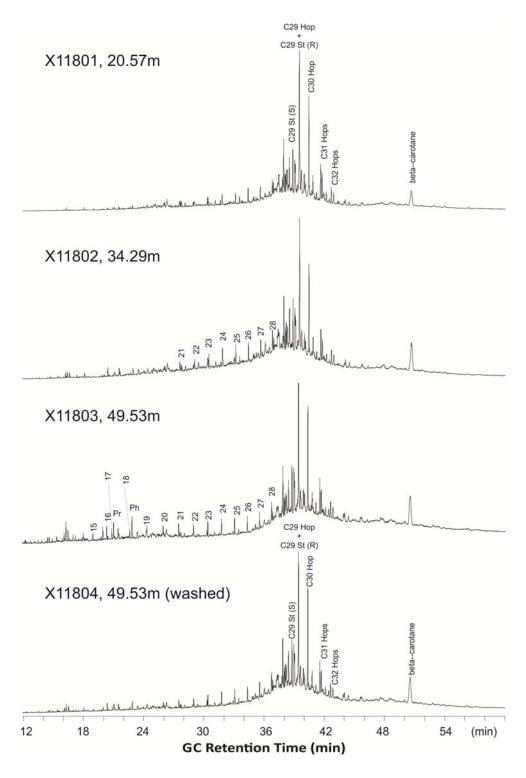


Figure 5. GC traces of saturated fractions for Mabou Group cuttings samples from the PO-06 well at the McCully gas field. C29 St: C29 ααα steranes; Hop: Hopanes; beta-carotane: β-carotane; Pr: pristane; Ph: phytane; numbers are carbon numbers for the corresponding n-alkanes.

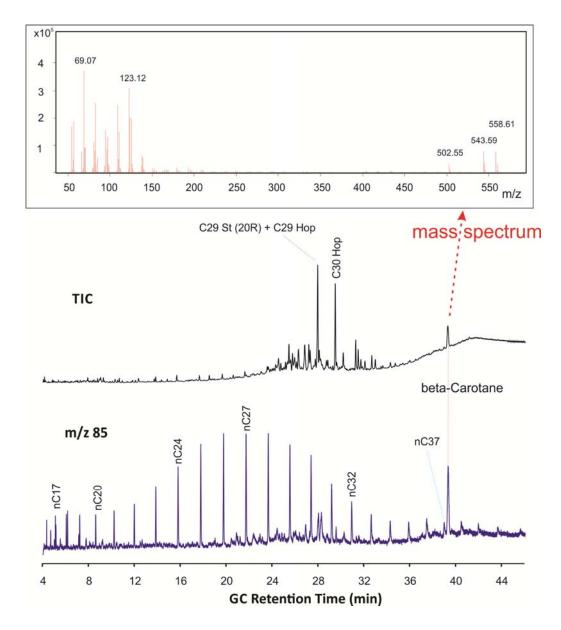


Figure 6. Total ion chromatogram (TIC) and m/z 85 mass chromatograms from GC-MS analysis of sample X11803 showing the distribution of n-alkanes and hopanes, as well as the mass spectrum of the carotenoid compound. C29 St (20R): C₂₉ ααα 20R sterane; C29 Hop: C₂₉ hopane; C30 Hop: C₃₀ hopane; nC17: C₁₇ n-alkane, and same with other labels on m/z 85.

It is well known that branched and cyclic hydrocarbons including pristane, phytane, steranes and terpanes are generated from their precursors in kerogen earlier during oil generation than n-alkanes (Larter, 1990; Li et al., 1994; Durand, 1993; Jiang and Li, 2002; Wilhelms and Larter, 2004; Peters et al., 2005). Thus, the dominance of steranes and hopanes in the PO-06 extracts may also suggest that the hydrocarbons or a portion of the hydrocarbons are products from an

immature or early mature source rock such as the mudstone interbedded in the Mabou Group sandstones and siltstones. The grey-colored mudstone in the Mabou Group cuttings at the PO-06 well has just entered oil generation window based on their Tmax values as discussed above, thus capable of producing low maturity oil.

The distributions of steranes and hopanes do suggest that bitumen in the PO-06 samples were generated during early oil window (Figs. 7 and 8; Table 3). The C₃₁ and C₃₂ homohopanes usually have their 22R \rightarrow 22S isomerisation reach equilibrium (i.e. 60% of 22S) around the onset of oil generation and the C₂₉ $\alpha\alpha\alpha$ steranes reach their 20R \rightarrow 20S equilibrium (i.e. 55% of 20S) just before peak oil generation (Peters et al., 2005). The PO-06 samples in this study have their C_{32} hopane 22S/(22S+22R) ratios between 0.60 and 0.63, and their C_{29} sterane 20S/(20S+20R) ratios ranging from 0.40 to 0.42 (Table 3), indicating a low maturity for the hydrocarbons. Furthermore, the dominance of 17α -trisnorhopane (Tm) over 18α -trisnorhopane (Ts) on mass chromatogram m/z 191 (Fig. 8 and Table 3) also suggests a low thermal maturity for hydrocarbons in the PO-06 Mabou Group cuttings. The thermal maturity estimate based on the biomarker composition of soluble bitumen seems to be slightly higher than the Rock-Eval Tmax maturity (i.e. 432 to 438°C, Table 1) that is based on the thermal decomposition of solid organic matter. The maturity discrepancy between soluble and solid organic matter may indicate that the hydrocarbons extracted from the PO-06 cuttings are a mixture of locally sourced low maturity oil in the mudstone facies and some oil generated from other deeper source rock units which after some unknown migration distance and time of post-expulsion and migration, has accumulated and experienced some degree of biodegradation in the Mabou Group sandstone and siltstones.

Figure 9 presents the distributions of tetramethyl naphthalenes (TeMN) and methyl phenanthrenes (MP). They are dominated by the 1,2,5,6-TeMN and 9-MP respectively. These distribution patterns have been reported in some biodegraded Athabasca oil sand (Bennet and Larter, 2008) and some biodegraded heavy oil from the Liaohe Basin, China (Bao and Zhu, 2009). On the other hand, these two isomers are thermo-dynamically unstable, and a high concentration of these aromatic compounds is often associated with immature and early mature oils and source rocks (Peters et al., 2005).

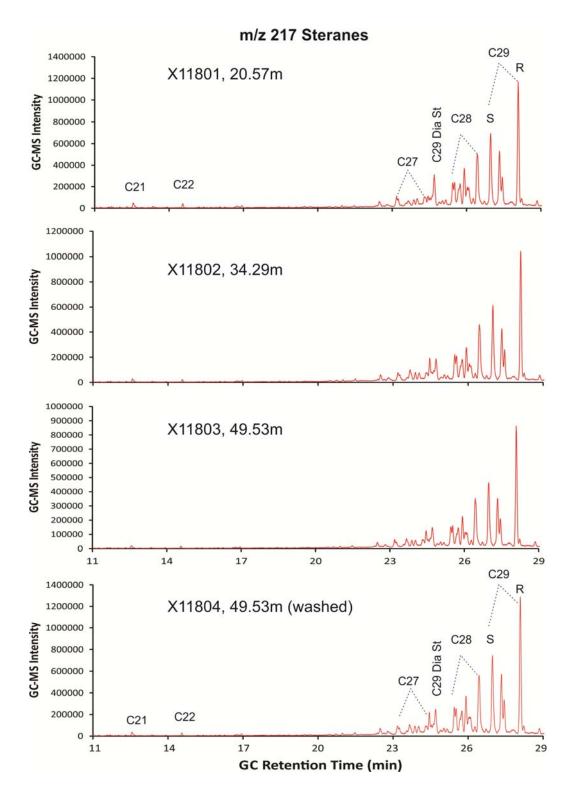


Figure 7. Mass chromatograms m/z 217showing the distributions of steranes in Carboniferous Mabou Group cuttings samples from PO-06 well at the McCully gas field. The carbon numbers of steranes are marked.

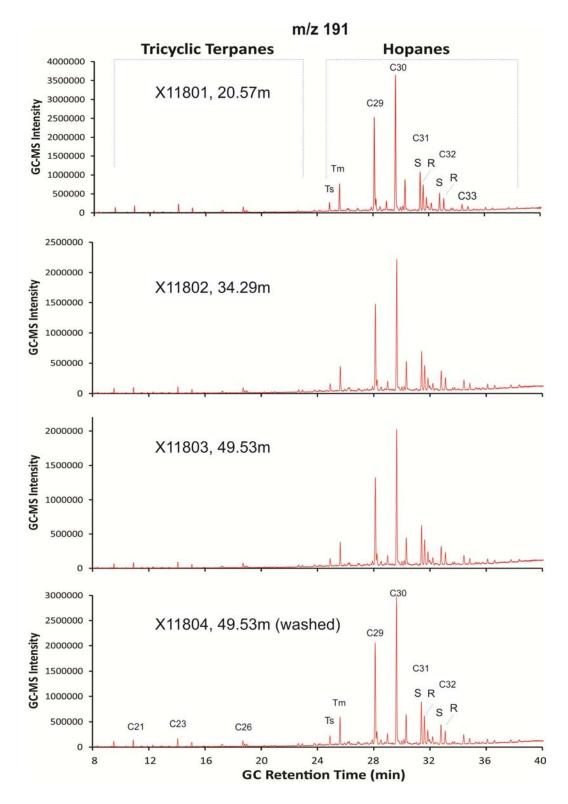


Figure 8. Mass chromatograms m/z 191 showing the distributions of tricyclic and pentacyclic terpanes (hopanes) in Mabou Group cuttings from the PO-06 well. The carbon numbers of tricyclic terpanes and hopanes are marked. Ts and Tm are $18\alpha(H)$ – and $17\alpha(H)$ -trisnorhopanes.

Sample Lab ID	Pr/Ph	C ₂₉ ααα St.	C ₃₁ Hop S/(S+R)	C ₃₂ Hop S/(S+R)	Ts/Tm	C ₂₇ -C ₂₈ -C ₂₉ %			
		S/(S+R)			15/111	C ₂₇	C ₂₈	C ₂₉	
X11801	0.47	0.42	0.60	0.61	0.30	5.6	38.9	55.5	
X11802	0.67	0.40	0.60	0.62	0.29	8.1	36.2	55.6	
X11803	0.78	0.40	0.60	0.63	0.33	7.4	36.2	56.4	
X11804	0.67	0.41	0.61	0.62	0.32	7.3	36.8	55.8	

Table 3. Selected biomarker maturity and organic input parameters for Mabou Group samples from the PO-06 well

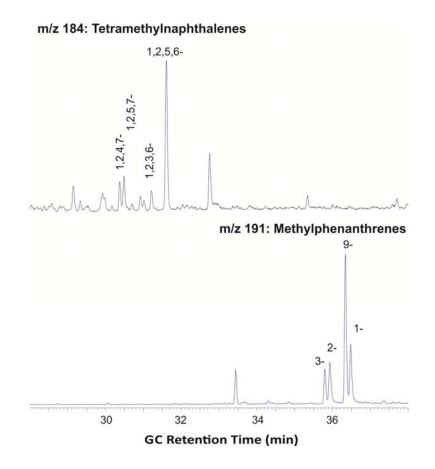


Figure 9. Mass chromatograms m/z 184 and 192 showing the distribution of tetramethyl naphthalenes and methyl phenanthrenes for sample X11803. They are dominated by their 1,2,5,6-tetrtamethyl and 9-methyl isomers respectively.

Source Characterization of the Hydrocarbons

The biomarker composition of the saturated and aromatic hydrocarbons extracted from the Mabou Group sediments provides information regarding the depositional environment and organic input of their source rocks. Carotenoid structures have been reported from a variety of ancient lacustrine sediments, and they are mostly formed under reducing condition in saline and hypersaline depositional environments (Jiang and Fowler, 1986; Fowler et al., 1993; Yawanarajah et al., 1993). These compounds have their precursors (a family of yellow to orange-red terpenoid pigments) found in a variety of photosynthetic organisms such as higher plants, algae, fungi and some bacteria (Barbosa-Filho et al., 2008; Kirti et al., 2014). Thus the abundant occurrence of β -carotane in the studied samples may not point to a specific type of organism but certainly suggests that the hydrocarbons are derived from source rocks likely deposited in saline reducing lacustrine environments in the photic zone (Figs. 5 and 6).

As hopanes are originated from bacteriohopanepolyols in the bacterial cell membranes (Farrimond et al., 2004; Peters et al., 2005), their dominance in the saturated fractions (Fig. 5) indicates a strong contribution of bacteria to the organic matter preserved in the Mabou Group mudstone or in the unknown source rocks of the migrated hydrocarbons hosted in the coarser-grained Mabou Group sediments. More interestingly, 2-methyl hopanes are also indicated by GC-MS analysis to be present in the saturated fractions of the solvent extracts from these samples, though at much less abundance than hopanes, together with 3-methyl hopanes (Fig. 10). Geological and microbiological studies suggested that 2-methyl hopanes is derived from cyanobacteria and 3-methyl hopanes originate from methanotrophic bacteria (Farrimond et al., 2004; Peters et al., 2005; Eigenbrode et al., 2008). Therefore, the abundant occurrence of these special hopanoids in the extracts from Mabou Group sediments at the PO-06 well further indicates that cyanobacteria may have been a major type of bacteria in the microbial community during the deposition and early diagenesis of the source organic matter, together with some methanotrophic bacteria.

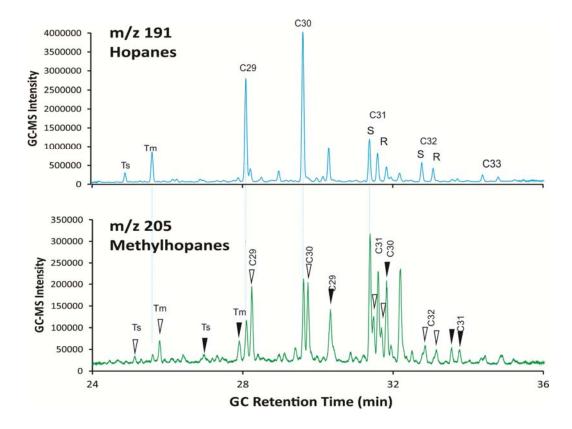


Figure 10. Mass chromatograms m/z 191 and 205 showing the distribution of hopanes and methylhopanes in sample X11801. The carbon numbers of hopanes are marked. Ts and Tm are $18\alpha(H)$ – and $17\alpha(H)$ -trisnorhopanes; 2α -methylhopanes (open triangles) and 3 β -methylhopanes (filled triangles) are similarly marked but with the carbon number excluding the additional methyl group. Methylhopane identification was based on comparison with Farrimond et al (2004).

The Mabou Group cuttings in this study also have similar C_{27} - C_{28} - C_{29} sterane distributions as represented in Figure 7 and Table 3. A striking feature for these samples is the extremely low concentrations of C_{27} steranes (5.6–8.1%) compared with C_{28} (36.2–38.9%) and C_{29} (55.5–56.4%) steranes. This is also reflected in the distribution pattern of C_{26} - C_{27} - C_{28} triaromatic steranes (the aromatized derivatives of steranes), with C_{26} accounting for less than 10% and C_{28} for about 55% (Fig. 11). Although C_{29} sterols are common in higher plants, it is also known that certain variety of algae and cyanobacteria are important sources of C_{29} sterols (Tissot and Welte, 1984; Volkman, 1986; Volkman et al., 1999). While source rocks with terrestrial higher plants as dominant organic input usually show a dominance of C_{29} steranes, there are examples of crude oils and sediments that display dominant C_{29} steranes but are not sourced from terrestrial organic matter (McKirdy et al., 1983 and 1985; Grantham, 1986). Therefore, the sterane distribution pattern may also indicate that cyanobacteria and also some algae have made significant contribution to the organic matter of the source rocks of the hydrocarbons in the PO-06 Mabou Group sediments. Nonetheless, given the age (Carboniferous) and general depositional interpretation of the Mabou Group (continental to marginally marine; St. Peter and Johnson, 2009), minor input of terrestrial organic matter is still possible, although given the high HI and low OI values, such input would be minimal.

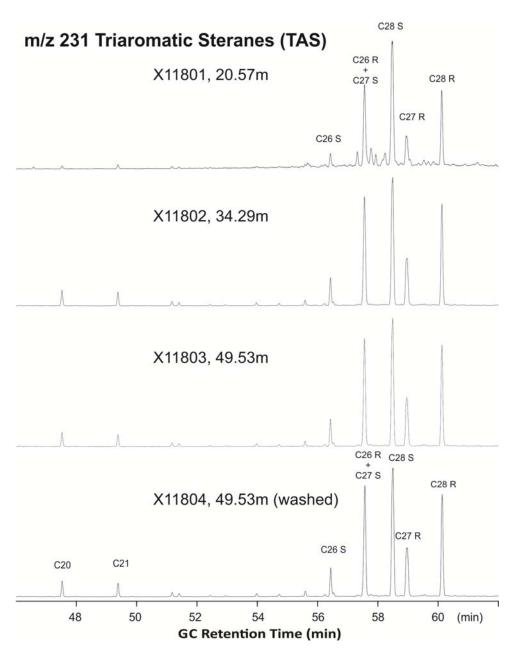


Figure 11. Mass chromatograms m/z 231 showing the distribution of triaromatic steranes for the Mabou Group cuttings from PO-06 well at the McCully gas field.

Another notable feature about the distribution of steranes in the Mabou Group samples is the low concentrations of diasteranes (or rearranged steranes) compared with regular steranes (Fig. 7). This may be due to the low thermal maturity of their source rocks and/or because their source rocks are calcareous, as both conditions can lead to reduced diasteranes (Peters et al., 2005).

Possible Sources for Mabou Group Hydrocarbons at PO-06 well

The unusual sterane distribution pattern of $C_{29}>C_{28}>C_{27}$ as discussed above has been reported to be a common feature for the organic-rich Carboniferous lacustrine source rocks and the associated oils in Atlantic Canada (Chowdhury et al., 1991; Fowler et al, 1993). A study by Chowdhury et al (1991) showed that some crude oils produced from the Albert Formation of the Horton Group (Lower Carboniferous or Tournaisian) from the Stoney Creek oil and gas field in New Brunswick have low C_{27} compared with the C_{28} and C_{29} steranes. Methylhopanes also seem to be present in those Stoney Creek oils (GSC internal data). However, compared with hydrocarbons extracted from the PO-06 Mabou Group samples, the Stoney Creek oils are more mature and therefore their saturated fraction GC traces are dominated by n-alkanes with carotenoids being a minor component. Furthermore, the C_{27} steranes seem to be at a higher percentage among the C_{27} - C_{28} - C_{29} distribution in the Stoney Creek oils that were interpreted to be sourced from the mature Albert Formation lacustrine shales (Chowdhury et al., 1991).

In addition to the Stoney Creek oils from New Brunswick, oil seep samples extracted from the oil-stained Horton and Windsor groups outcrop sandstones and limestones from the Lake Ainslie area in Nova Scotia also display a $C_{29}>C_{28}>C_{27}$ sterane distribution pattern and low concentrations or near absence of diasteranes (Fowler et al., 1993). While most of these oil seeps have experienced biodegradation with their n-alkanes removed but their carotenoids being prominent, one oil seep appears to be a normal crude oil with composition dominated by n-alkanes. Being more mature than the hydrocarbons in the Mabou Group rocks from PO-06 in this study, the Lake Ainslie seep samples also display different terpane distributions, especially being more enriched in the extended tricyclic terpanes (Fowler et al., 1993). Based on the general similarity of biomarker signatures to those of the Albert Formation shale extracts and the Stoney Creek oils, a carbonate source rock of Albert Formation age and lacustrine depositional setting was proposed by Fowler et al (1993) for the oil seeps in Nova Scotia as well.

Considering the above discussed biomarker characteristics, that is, (1) $C_{29}>C_{27}$ steranes; (2) low concentrations of diasteranes; (3) prominence of carotenoid; (4) the elevated occurrence of methylhopanes, it can be reasonably speculated that hydrocarbons hosted in the Mabou Group interval from the shallow PO-06 well are likely sourced from calcareous source rocks deposited in lacustrine settings similar to that of the shales form the Albert Formation. Shales from the Frederick Brook Member of the Albert Formation are considered to be the source of natural gas found in the McCully gas field. The hydrocarbons extracted from the PO-06 Mabou drill cuttings could be a mixture of low maturity oil sourced locally and a more mature but biodegraded oil sourced from deeper source rocks units such as the Albert Formation shale in the Horton Group and/or the organic-rich Macumber Formation limestone in the Windsor Group. As there is no obvious predominance of C_{35} over C_{34} hopanes, contribution from a carbonate source seems to be insignificant. The low pristane-over-phytane ratios (Pr/Ph in Table 3) together with the seemingly low concentrations of sulfur-containing compounds such as dibenzothiophene appear to relate the oil to shales deposited in sulfate-poor lacustrine environments. However, this has to be confirmed via further studies on a more extensive sample sets.

CONCLUSIONS

Cuttings samples from water wells PO-01 to 05 drilled into the Carboniferous Mabou Group at the McCully gas field in southern New Brunswick are red colored and contain little organic matter as revealed by Rock-Eval analysis, thus having no hydrocarbon potential at all. In contrast, the Mabou cuttings samples collected from the PO-06 well are grey to dark-grey colored, and contain small amounts of soluble (e.g. S1<0.1%) and non-soluble organic matter (e.g. TOC<0.40%). The content of organic matter could have been higher in the darker mudstone layers if they had been analyzed separately. Rock-Eval analyses further indicate that the thermal maturity of Mabou section at the PO-06 well is around the onset of oil generation. However, the whole section in general is not qualified as an effective or potential source rock interval due to its organic leanness.

The free hydrocarbons in the Mabou group drill cuttings from the PO-06 well are characterized by a dominance of steranes, hopanes and β -carotane, and a low abundance of n-alkanes seated

atop minor UCM humps, which are typical characteristics of low maturity oil and oil subjected to minor biodegradation. Their $C_{29}>C_{28}>C_{27}$ sterane distribution patterns are typical of Carboniferous lacustrine shales and related oils reported for the east Atlantic Canada. Their hopane distributions seem to indicate significant bacterial and algal contributions to the organic input of their source rocks. The hydrocarbons hosted in the Mabou Group sediments are likely a mixed oil, part of which could have been generated from the local dark-colored Mabou mudstones and part of which could have migrated from deeper lacustrine shale and been biodegraded since accumulation in the Mabou sandstones. The Albert Formation oil shale in the Horton Group is likely one of the non-local source rocks, with the organic-rich Macumber Formation limestone in the Windsor Group being another potential one.

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