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An organic geochemical study of outcrop oil shows in the Colville Hills, Mackenzie Corridor: oil-saturated Quaternary sand and Cretaceous sandstone and oil-stained Devonian dolostone

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2019

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Abstract

Outcrop samples collected from some visually oil-stained or oil-saturated exposures in the Colville Hills area were submitted for bulk and molecular organic geochemical analyses to investigate their crude oil quality, sources of the hydrocarbons, and/or their potential as petroleum source rocks. Results show that the apparently oil-stained Devonian Bear Rock Formation dolostone interval at Lac à Jacques cannot be considered as an effective source rock due to its low content of organic matter, nor can it be an efficient reservoir rock due to its low oil content. The Quaternary (?) oil sand deposit at Lac des Bois and the oil-saturated Cretaceous sandstone at Belot Ridge both contain hydrocarbons that have been subjected to very heavy to severe biodegradation, with a majority of their saturated and aromatic compounds having been removed due to microbial activities. Within their saturated and aromatic fractions only terpane biomarkers can be detected in these bituminous sands or sandstone. Although the characteristics of their main source rocks cannot be ascertained, their different distributions of tri-, tetra- and penta-cyclic terpanes appear to indicate that oil charges to the Quaternary sand at Lac des Bois and the Cretaceous sandstone at Belot Ridge are from source rock units developed within different depositional environments.

1. Introduction

At the onset of the Geo-mapping for Energy and Minerals (GEM) Program of the Geological Survey of Canada (GSC), the Colville Hills were identified as an area of interest for updated mapping and stratigraphic work based on oil and gas discoveries in Cambrian strata beneath the region (Hamblin, 1990; Janicki, 2004; Price and Enachescu, 2009). In 2015, a GSC team conducted fieldwork in and around the Colville Hills with the aim of improving the structural and stratigraphic framework for the petroleum system, and updating existing maps (Fallas et al., 2015). Outcrops known to be saturated with oil, or oil-stained were examined and sampled with the intention of learning more about the source of the oil. In particular, matching the oil found at surface to either Cambrian or Devonian source rocks could be useful in interpreting thermal maturity, migration pathways, and trapping mechanisms. With this aim, petroliferous samples were collected from three localities (Fig. 1a), and submitted to the Organic Geochemistry Labs at GSC-Calgary for bulk and molecular geochemical analyses to characterize the bulk organic matter and the hydrocarbon compositions, and to determine their possible sources.
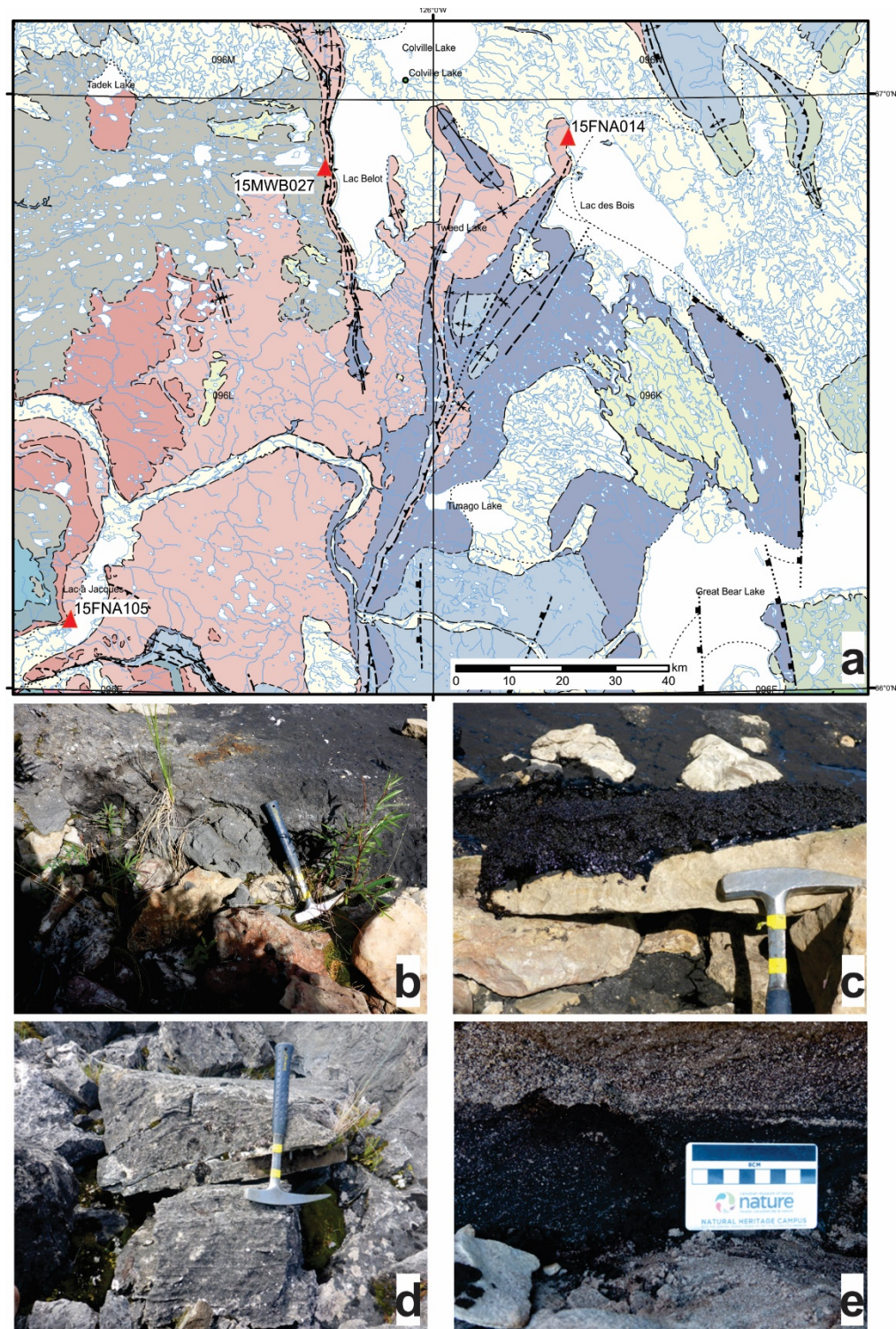
Figure 1. Outcrop samples used in this study. (a) map of sample locations (solid red triangles); (b) and (c) oil-saturated unconsolidated sand at locality 15FNA014; (d) oil-stained Devonian dolostone at locality 15FNA105; (e) oil-saturated Cretaceous sandstone at locality 15MWB027. See Table 1 for coordinates of sampling locations and sample ID

2. Samples and Methods

2.1. Samples

Table 1 lists the geological and geographic information for the four outcrop samples analyzed in this study. Samples C-596724 and C-596725 were collected from the western shore of Lac des Bois. About ten meters apart from each other in terms of their exact location, these two samples come from an oil-saturated, unconsolidated quartz sand deposit. The deposit is mixed with blocks of rubble scattered below outcrop of Devonian calcareous dolostone of the Bear Rock Formation, and is likely a Quaternary deposit and/or transported Cretaceous sandstone. The adjacent Devonian carbonate outcrop shows some oil staining, but there is no obvious seep location. Sample C-596724 is dark brown bituminous sand collected from underneath weathered surface (Fig. 1b). Sample C-596725 was collected from the part of the bituminous sand deposit where shiny black heavy oil was oozing out (Fig. 1c). In the lab these two samples look very much like the Cretaceous McMurray Formation oil sand from the Athabasca region of Northern Alberta.

Table 1: Outcrop samples collected at Colville Hills in Mackenzie Corridor

GSC Sample ID	Client ID	Sample Type	Latitude	Longitude	Proposed age	GSC Lab ID
C-596724	15FNA014B01	Oil saturated quartz sand deposit	66.936977	-125.424242	Cretaceous / Quaternary	X11777
C-596725	15FNA014B02	Oil saturated quartz sand deposit	66.936977	-125.424242		X11778
C-596743	15FNA105A01	Petroliferous, laminated dolostone	66.119302	-127.510463	Devonian	X11775
C-596769	15MWB027A03	Oil saturated quartz sandstone	66.885523	-126.465803	Cretaceous	X11776

Sample C-596743 (Fig. 1d) is a petroliferous, laminated, dolostone of the Devonian Bear Rock Formation collected on the west shore of Lac à Jacques. While the weathered surface is medium grey, it is dark brown on the fresh surface. Sample C-596769 is an oil saturated quartz sandstone of the Cretaceous Martin House Formation (Fig. 1e) from the west flank of Belot Ridge. The fine to medium grained, well-sorted sandstone is friable and cross-bedded, and has light grey weathered surface and medium brown fresh surface. The outcrop lies in the footwall of an east-side-up reverse or thrust fault on the west side of Belot Ridge. The Devonian Bear Rock Formation is in fault contact with the Martin House Formation at this location.

All four samples have been analyzed on Rock-Eval for the bulk organic properties and solvent-extracted and fractionated using open column fractionation followed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analyses of their saturated and aromatic fractions for their biomarker compositions. Rock-Eval analysis has also been performed on three solvent extracted samples as comparison.

2.2. Rock-Eval analysis

Rock-Eval/TOC analysis was performed on a Rock-Eval 6 Turbo device with pyrolysis and combustion dual functions. Aliquots of 20 to 70 mg (depending on organic richness) of crushed samples were used in each Rock-Eval analysis. During the pyrolysis stage, samples were initially heated at 300 °C for 3 minutes under nitrogen flow to volatilize free hydrocarbons for S1 peaks. Samples were then heated linearly from 300 to 650 °C at a rate of 25 °C/min, yielding an S2 peak representing products thermally decomposed from the kerogen, solid organic matter (OM) or heavy bitumen. The temperature at the maximum of S2 peak is converted to Tmax (°C), the widely accepted thermal maturity parameter. The S3 curve corresponds to the amount of CO_2 generated from OM during the 300–400 °C pyrolysis. CO_2 liberated between 400 °C and 650 °C during pyrolysis is from the thermal decomposition of carbonate minerals. The amount of productive organic carbon (PC) is determined by combining the S1, S2, S3 contributions according to a pre-defined formula (Behar et al., 2001). Pyrolysis mineral carbon is determined from the >400 °C portions of the CO and CO_2 curves.

Following pyrolysis, samples were transferred to the combustion furnace where they were linearly heated from 300 °C to 850 °C under air flow to determine the amount of residual organic carbon (RC: below 650 °C) and oxidation mineral carbon from CO and CO_2 generated during oxidation between 650 and 850 °C. The total organic carbon (TOC) content is the sum of the productive and residual organic carbon (PC+RC). Similarly, mineral carbon (MinC) is the sum of the pyrolysis and oxidation mineral carbon.

2.3. Solvent Extraction

About 0.5 to 20 grams of each powdered rock sample was subjected to Soxhlet extraction for 72 hours using dichloromethane as solvent. Activated copper grains were added to the extract

content at the end of extraction or during solvent removal stage to remove any elemental sulfur. After removing most of the solvent using a rotary evaporator, the extracted contents were filtered to remove copper, copper sulfide and any other solids. The residue was retained and weighed as total extract after removal of the remaining solvent using a gentle stream of nitrogen.

2.4. *Column chromatography fractionation*

Rock extracts were de-asphaltened with *n*-pentane and then separated into aliphatic, aromatic and polar fractions by open column chromatography using a mixture of silica gel and alumina (1:3 by weight) as support. *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.

2.5. *GC and GC-MS analysis of C_{12}^+ hydrocarbon fractions*

GC analysis of saturated fractions was completed on a Varian 3700 GC equipped with a flame ionization detector (FID). A 30m $\times$ 0.25mm $\times$ 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) →300°C (30min). The FID temperature was maintained at 320 °C.

GC-MS analysis of aliphatic fractions was carried out on an Agilent Triple Quad MS system in selected ion monitoring (SIM) mode. Split injection (1:10) was employed into a HP-5MS 30m $\times$ 0.25mm $\times$ 0.25µm capillary column with helium as carrier gas at a flow rate of 1.2 mL/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) operated in a SIM mode. Split injection was employed into a J&W DB-5 30m $\times$ 0.32mm $\times$ 0.25µm capillary column at 300 °C temperature. Helium was used as carrier gas at a flow rate of 1.2 mL/min. The GC oven temperature was programmed as follows: 40°C (@4°C/min)→325°C (15min hold).

Compound identification was based on comparison of GC retention times and mass spectra with those reported in literature and historical data in the GSC-Calgary organic geochemistry laboratories.

3. Results and Discussion

3.1. Bulk organic property by Rock-Eval analysis

Rock-Eval results including S1 and S2 peaks (mg HC/g Rock), TOC content (wt %), Tmax (°C), hydrogen index (HI: mg HC/g TOC) and oxygen index (OI: mg CO_2/g TOC) have been extensively used for evaluating hydrocarbon potential of conventional shale and carbonate source rocks (Peters, 1986; Behar et al., 2001) as well as for unconventional shale and tight hydrocarbon resources assessment and reservoir characterization (Jarvie, et al., 2007; Jarvie, 2012; Chen and Jiang, 2016). These parameters have been especially useful for evaluating the quantity and type of organic matter (OM), free oil content and the thermal maturity of source rocks. Table 2 presents the Rock-Eval results for the four outcrop samples used in this study before and after solvent extraction. Also included in Table 2 are the Rock-Eval results for an Athabasca oil sand sample (C-603524) for comparison.

Table 2. Rock-Eval results for the outcrop samples before and after solvent extraction

| Sample ID | C-596724 | | C-596725 | C-596743 | | C-596769 | | C-603254* | |
Sample status	original	extracted	original	original	extracted	original	extracted	original	extracted
S1 (mg HC/g Rock)	45.69	0.01	58.70	0.16	0.04	6.92	0.10	37.85	0.02
S2 (mg HC/g Rock)	72.05	0.14	65.68	1.18	0.96	14.30	1.80	84.32	0.24
S3 (mg CO_2/g Rock)	1.48	0.16	0.12	0.47	0.39	0.97	0.61	0.12	0.06
Tmax (°C)	412	420	415	424	430	418	424	426	422
TOC (%)	12.69	0.06	11.37	0.43	0.26	2.98	0.61	11.51	0.07
MinC% (%)	0.12	0.02	0.11	12.38	12.49	0.08	0.05	0.03	0.00
PI=S1/(S1+S2)	0.39	0.06	0.47	0.12	0.04	0.33	0.05	0.31	0.08
HI (mg HC/g TOC)	568	233	578	274	369	480	295	733	350
OI (mg CO_2/g TOC)	12	267	1	109	150	33	100	1	83
PC(%)	9.88	0.02	10.37	0.14	0.10	1.83	0.19	10.15	0.03
RC%	2.81	0.04	1.00	0.29	0.16	1.15	0.42	1.36	0.04

*C-603254 is an oil sand sample collected from the McMurray Formation of a borehole drilled in the Athabasca region of Northern Alberta at the depth of 80 m and is for comparison purpose in this work.

The oil-saturated Quaternary sand samples C-596724 and C-596725 from the Western shore of Lac des Bois display Rock-Eval results similar to those of the Athabasca oil sand. Their S1 peaks

are in the 40s to 50s of mg HC/g Rock; S2 peaks in 60s–70s mg HC/g Rock; total organic carbon (TOC) between 11 and 13%; hydrogen index (HI) from 500s to 700s mg HC/g TOC and Tmax between 410s and 420s °C. It would appear both samples have excellent oil potential as measured by their very high S1, S2 and TOC values; however, these quantitative parameters indicative of hydrocarbon potentials are almost reduced to zero once the samples were solvent extracted to remove the soluble oil and bitumen (Table 2). Figure 2 shows the hydrocarbon pyrograms from Rock-Eval analyses of pre- and post-solvent extraction of one oil sand sample. Both its S1 and S2 peaks collapsed to near zero after solvent extraction, indicating that almost all of the OM are solvent-soluble bitumen. In fact, the amount of oil/bitumen extracted from the two oil sand samples C-596724 and C-596725 account for 12.88% and 9.87% of the original sample weights (Table 3), respectively, which is in similar range to their TOC contents measured by Rock-Eval analysis. Therefore, the criteria of using these Rock-Eval parameters for source rock evaluation are not applicable to these oil sand samples, especially for OM type classification using HI and thermal maturity evaluation by Tmax values. Unlike shale and carbonate source rocks for which S2 represent the hydrocarbons that can be generated from kerogen upon further thermal cracking, the oil sand samples contain little kerogen that is insoluble in any organic solvents, and the components evolved under their S2 peaks are simply heavy hydrocarbons and bitumen already present in the samples that are not thermally liberated into S1 peaks at 300 °C during Rock-Eval analysis. However, these oil sands could become an excellent source for gas and lighter oil if they were to be buried deep enough to allow for further thermal conversion of the heavy hydrocarbons and bitumen into light and gaseous hydrocarbons.

Sample C-596769, an oil-saturated Cretaceous sandstone, shows similar Rock-Eval characteristics to the oil sand samples C-596724 and C596725, except that it contains a slightly higher amount of insoluble OM (Table 2). After solvent extraction, this sandstone sample also displays much reduced Rock-Eval S1and S2 peaks as well as TOC and PC values that are directly related to the two hydrocarbon peaks. The very low S1 and S2 peaks, 0.18 and 1.80 mg HC/g rock respectively, as well as a low TOC of 0.61% and PC of 0.19% after solvent extraction all indicate that the Cretaceous sandstone itself cannot be an effective source rock and is only impregnated by the migrated bitumen/oil. Therefore, similar to the oil sand samples, the Rock-

Eval parameters HI, OI and Tmax of the Cretaceous sandstone sample C-596769 should not be used for evaluating the type of OM and its thermal maturation level either.
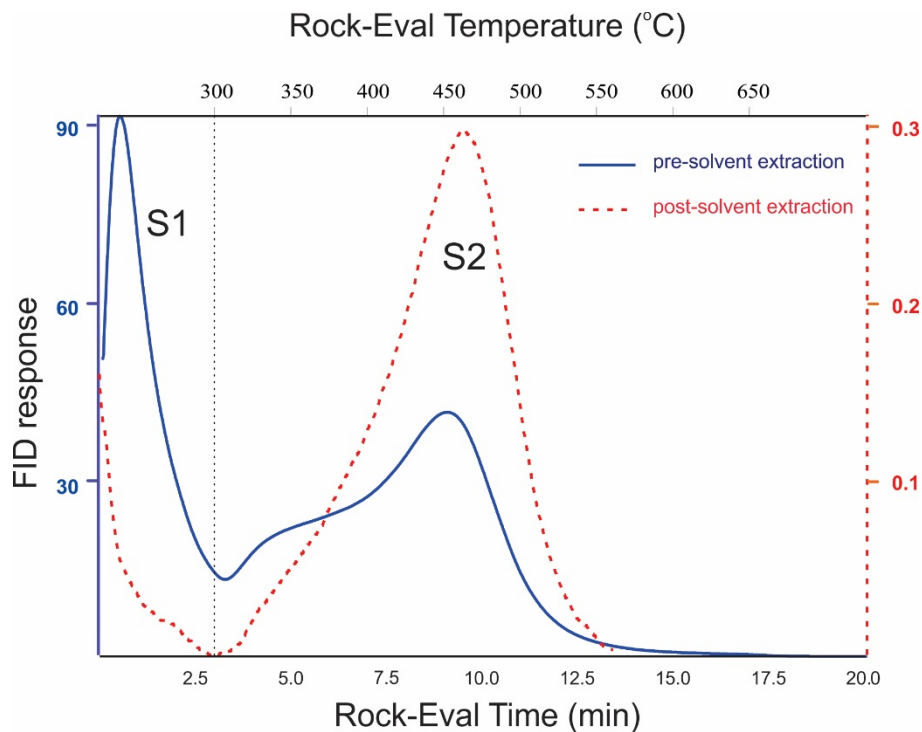

Figure 2. Rock-Eval hydrocarbon pyrograms showing the S1 and S2 peaks for oil sand sample C-596724 before (solid blue) and after (red dotted) solvent extraction. Solvent soluble bitumen account for more than 99% of the organic matter in the oil sand.

Rock-Eval analysis of the oil sand and oil-saturated sandstone samples all produce very low MinC values both before and after solvent extraction, which is in agreement with their carbonate-poor lithology. In contrast, the dolostone sample C-596743 has a MinC value >12% (Table 2), indicating that the sample is almost pure carbonate and is indeed a dolomite (Jiang et al., 2017). This is also partially responsible for the high OI value for the sample, as some carbonate minerals may have decomposed at <400 °C temperatures releasing CO_2 into the S3 peak used for OI calculation. Like most carbonates, this Devonian Bear Rock Formation carbonate sample has very low content of OM as represented by a 0.43% TOC, and 0.16 and 1.18 mg HC/g rock of S1 and S2 peaks, respectively, suggesting a poor petroleum source rock potential (Table 2). Although the dolostone sample appeared oil-stained in the outcrop during

sample collection, it has only a low content of free hydrocarbons. The Bear Rock Formation in the area is likely at early mature stage with respect to hydrocarbon generation of the OM in the carbonates containing Type II kerogen.

3.2. Molecular compositions from GC and GC-MS analysis: Hydrocarbons severely biodegraded in the oil-saturated sand and sandstone but pristine in the dolostone

Figure 3 shows the compositional fingerprints of saturated hydrocarbons from GC analysis of the saturated fractions of the solvent extracts for the four samples analyzed in this study. The saturated fraction GC traces for the two Quaternary oil sand and the oil-saturated Cretaceous sandstone samples are all dominated by a large unresolved complex mixture (UCM) hump atop which seat a few isolated small peaks that are likely tricyclic and pentacyclic terpanes (i.e., hopanes), while normal (*n*-) alkanes and acyclic isoprenoids such as pristane (Pr) and phytane (Ph) are absent. This is apparently an indication that hydrocarbons in the oil-saturated sands and sandstone have experienced very heavy to severe biodegradation, resulting in the total destruction of those acyclic alkanes (Peters et al., 2005).

In contrast to oil sand (C-596724 and C-596725) and sandstone (C-596769) samples, the saturated fraction of the dolostone sample C-596743 displays a much smaller UCM hump, and contains high concentrations of *n*-alkanes (Figure 3). It also contains much higher concentrations of terpanes relative to the UCM hump compared with the Quaternary oil sand and the Cretaceous oil-saturated sandstone. There is no apparent odd–even carbon number preference as to the *n*-alkane distribution for the dolostone sample, suggesting that the hydrocarbons were formed at maturity corresponding to mid- or late "oil window"; however the relatively high concentrations of pentacyclic terpanes indicate that these hydrocarbons were probably generated during early thermal maturation. This sample has a Pr/Ph ratio of 0.79, and a dibenzothiophene over phenanthrene (DBT/Phen) ratio of 1.41 from GC-MS analysis of its aromatic fraction (Table 3); such values are consistent with carbonate lithology (Hughes et al., 1994; Peters et al., 2005).

Figure 4 shows the distributions of tricyclic, tetracyclic and pentacyclic terpanes (m/z 191), the de-methylated terpanes or 25-norhopanes (m/z 177), and steranes (m/z 217) for the four outcrop samples. The distribution pattern, and the presence and absence of these aliphatic biomarkers are considered indicative of the depositional environment, organic input, thermal maturation level and microbial alteration of the crude oils and/or their source rocks (Peters et al., 2005; Bennett et al., 2006). As anticipated, the two Quaternary oil sand samples C-596724 and C-596725,

collected from the same location, have almost identical patterns of m/z 191, 177 and 217 mass chromatograms (Fig. 4a). Both regular steranes and rearranged steranes (or diasteranes) are nearly absent from these oil sands, indicating very heavy to severe degree of biodegradation. However, their terpane distributions do not seem to have been affected by the microbial activity as the related biodegradation products 25-norhopanes are very weak or absent from the m/z 177 mass chromatograms (Fig. 4a).
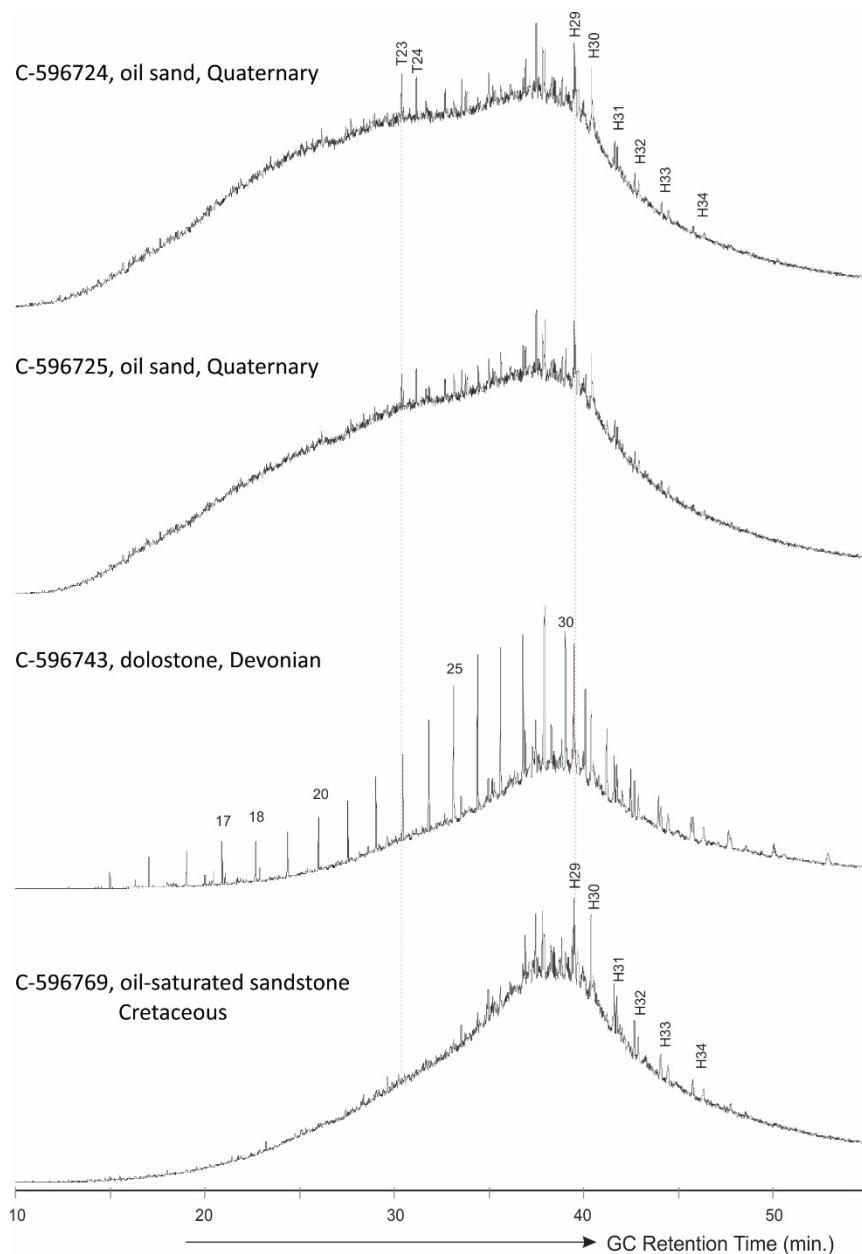

Figure 3. GC traces of saturated hydrocarbons fractions of solvent extracts for the studied samples. Number represent carbon numbers of the corresponding *n*-alkanes; T23 and T24 for corresponding C_{23} and C_{24} tricyclic terpanes; and H29 to H34 for C_{29} to C_{34} hopanes.
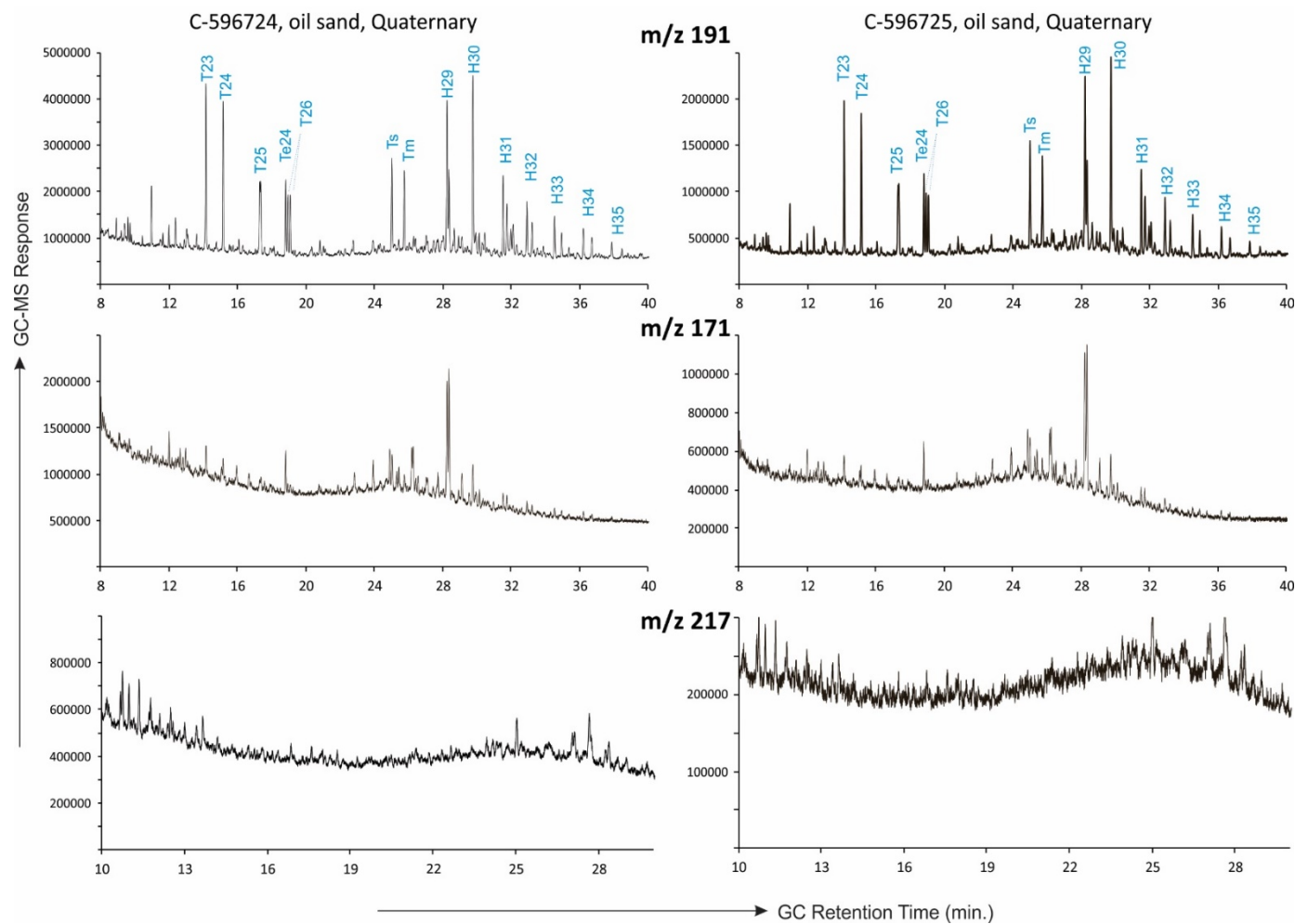
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Figure 4a. Mass chromatograms m/z 191, 177 and 217 showing the distributions of terpanes, 25-norhopanes and steranes in the solvent extracts for the outcrop samples in this study. Steranes and 25-norhopanes are absent from the Quaternary oil sand and oil-saturated Cretaceous sandstone. T23, T24…: C_{23}, C_{24}…. tricyclic terpanes; Te24: C_{24} tetracyclic terpane; H29, H30…: C_{29}, C_{30}…hopanes; St29: C_{29} steranes; D29: C_{29} diasteranes
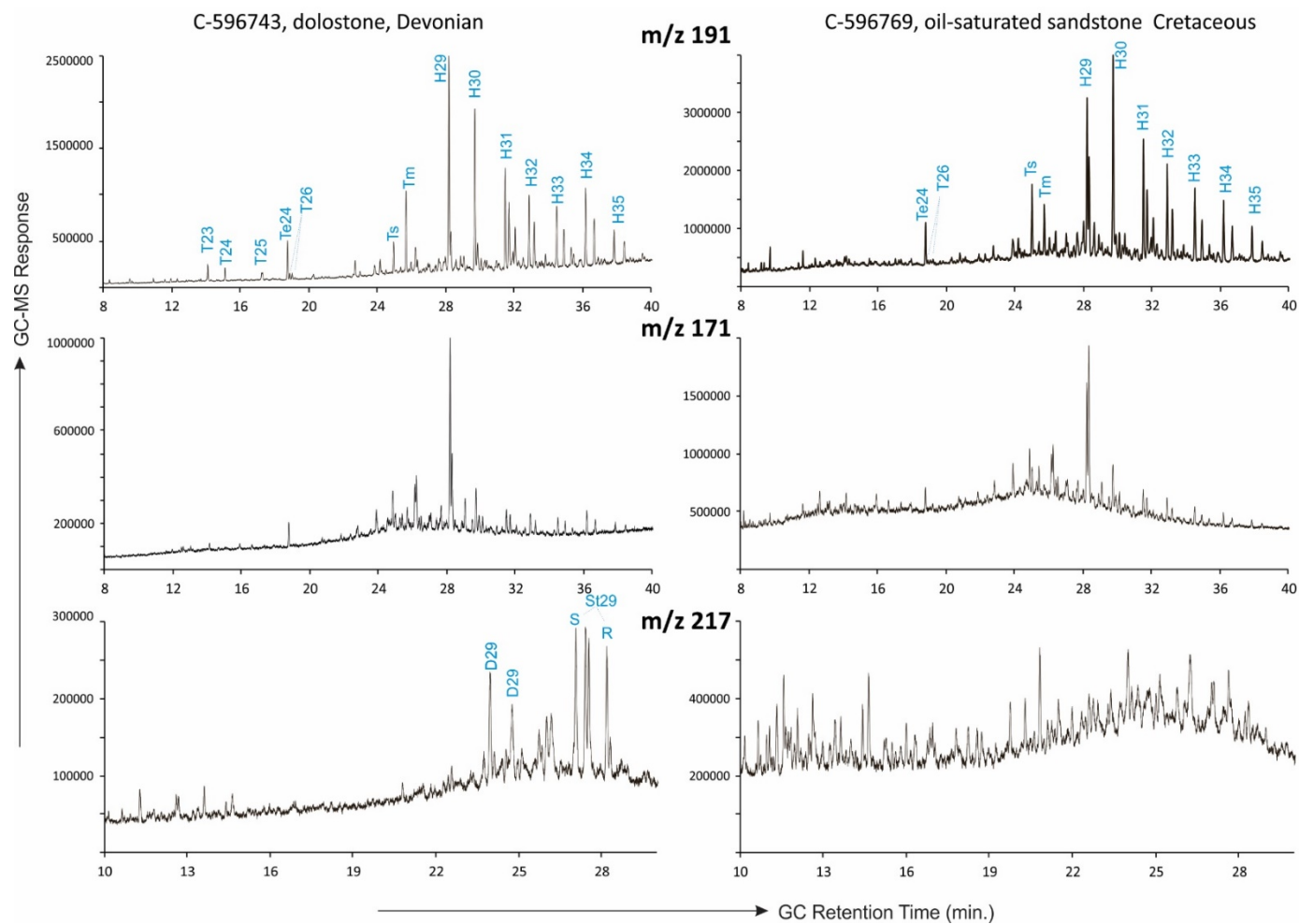
Figure 4b. Mass chromatograms m/z 191, 177 and 217 showing the distributions of terpanes, 25-norhopanes and steranes in the solvent extracts for the outcrop samples in this study. Steranes and 25-norhopanes are absent from the Quaternary oil sand and oil-saturated Cretaceous sandstone. St29: C_{29} steranes; D29: C_{29} diasteranes; S and R for 20S and 20R chiral isomers of the C_{29} $\alpha\alpha\alpha$ steranes.

Table 3. Molecular parameters based on saturate and aromatic fractions

Lab ID		X11777	X11778	X11775	X11776
Sample ID		C-596724	C-596725	C-596743	C-596769
Extract Yield (% of Rock)		12.88	9.87	0.09	2.87
Sat/Aro Ratio		2.46	1.10	1.35	5.17
% in Extracts	Hydrocarbons	29.30	71.52	37.14	16.68
	Polars	70.70	28.48	62.86	83.32
Saturated fraction GC analysis	Pr/Ph	n.a.	n.a.	0.79	n.a.
	Pr/nC17	n.a.	n.a.	0.35	n.a.
	Ph/nC18	n.a.	n.a.	0.44	n.a.
Hopanes C_{29}/C_{30}		0.86	0.86	1.38	0.76
Terpanes: C_{24}Tetracyclic/C_{26}Tricyclic		0.60	0.63	2.63	2.98
Gammacerane/C_{30}Hopane		0.21	0.18	0.32	0.22
C_{23}Tricyc terpane/C_{30} Hopane		0.79	0.64	0.10	0.06
Hopanes C_{31}-C_{35}/C_{30}		2.46	2.21	4.20	3.22
Ts/Tm		1.13	1.16	0.42	1.33
C_{29} ααα Steranes S/(S+R)		n.a.	n.a.	0.57	n.a.
C_{31} Hopanes: S/(S+R)		0.56	0.57	0.57	0.60
C_{32} Hopanes: S/(S+R)		0.63	0.63	0.62	0.63
Sterane distribution (%)	C_{27}	n.a.	n.a.	18.0	n.a.
	C_{28}	n.a.	n.a.	18.0	n.a.
	C_{29}	n.a.	n.a.	64.0	n.a.
Triaromatic Steranes (TAS; %)	C_{26}	n.a.	n.a.	4.8	n.a.
	C_{27}	n.a.	n.a.	18.2	n.a.
	C_{28}	n.a.	n.a.	77.0	n.a.
Dibenzothiophene/Phenanthrene		n.a.	n.a.	1.41	n.a.

Steranes and 25-norhopanes are also nearly absent from the Cretaceous oil-saturated sandstone sample C-596769 (Fig 4b), suggesting a severe biodegradation experienced by the hydrocarbons in the outcrop. However, the Cretaceous sandstone has a very different m/z 191 mass chromatogram compared with that of the Quaternary oil sand. The Quaternary oil sand has a much higher abundance of the tricyclic and tetracyclic terpanes relative to the hopanes (pentacyclic terpanes) (Table 3; Figs. 4a and b). On the other hand, the extended (C_{31}-C_{35}) hopanes are at higher abundances (relative to C_{29} and C_{30}) in the Cretaceous sandstone than in the Quaternary oil sand (Table 3). In addition, the Cretaceous oil-saturated sandstone has a much higher ratio of C_{24} tetracyclic over C_{26} tricyclic terpanes (Table 3). This indicates that the oils that migrated to and accumulated in the Quaternary oil sand and the Cretaceous oil-saturated sandstone are likely derived from separate source rock units deposited within different

depositional environments. However, the two source rock units may have reached similar thermal maturation levels as their hopane-based thermal maturity parameters Ts/Tm and C_{31} and C_{32} hopanes 22S/(22S+22R) ratios are in the same range (Table 3).

The Devonian Bear Rock Formation dolostone sample C-596743 has an interesting distribution of steranes and terpanes (Fig. 4b). In addition to the carbonate-typical signature of an enhanced Tm relative to Ts, a dominance of C_{24} tetracyclic over C_{26} tricyclic terpanes and a prominent C_{29} compared with C_{30} hopanes, this carbonate also displays a predominance of C_{34} hopane over the adjacent C_{33} and C_{35} hopanes. As with other Devonian sediments, C_{28} steranes are at much lower abundance relative to the C_{29} steranes in the dolostone as well (Peters et al., 2005). C_{27} steranes (either regular or rearranged) that are mostly at similar concentrations to the C_{29} steranes in Devonian shales and carbonates (e.g., the Devonian Canol shale in this area; Peters et al., 2005), however, are also at much lower level in this carbonate sample (Fig. 4b; Table 3). This C_{27}–C_{28}–C_{29} sterane characteristic is also reflected in the distribution of corresponding C_{26}–C_{27}–C_{28} triaromatic steroids (TAS), with C_{26} and C_{27} being much lower than C_{28} TAS (Fig. 5). While this C_{27}–C_{28}–C_{29} steroid distribution pattern has been mostly reported for source rocks and crude oils of either Cambrian and older age with special microbial input, or from younger source rocks and oils with predominantly terrestrial higher plant input such terrestrial coals (Peters et al., 2005), the absolute dominance of C_{28} TAS over C_{26} and C_{27} TAS has also been found in the organic-rich carbonate source rocks and crude oils from the Devonian Winnipegosis Formation in Williston Basin (Fig. 6). Therefore, the steroid distribution in the Bear Rock Formation carbonate may be indicative of the occurrence of special types of phytoplankton at the time of deposition of this carbonate interval.

In addition to the above mentioned ratio of DBT/Phen >1, the C-596743 dolostone sample also contains abundant benzohopanes (Fig. 5), which is consistent with its carbonate lithology. The green sulfur bacteria Chlorobiaceae derived biomarker aryl isoprenoids are also detected at high concentrations in the aromatic fractions of this sample (Fig. 5), suggesting euxinic (sulfidic) conditions in the photic zone of the water column during the deposition of the carbonate (Summons and Powell, 1986, 1987; Koopmans et al., 1996; Jiang et al., 2000, 2001; Zhang et al., 2011; Lu et al., 2015).
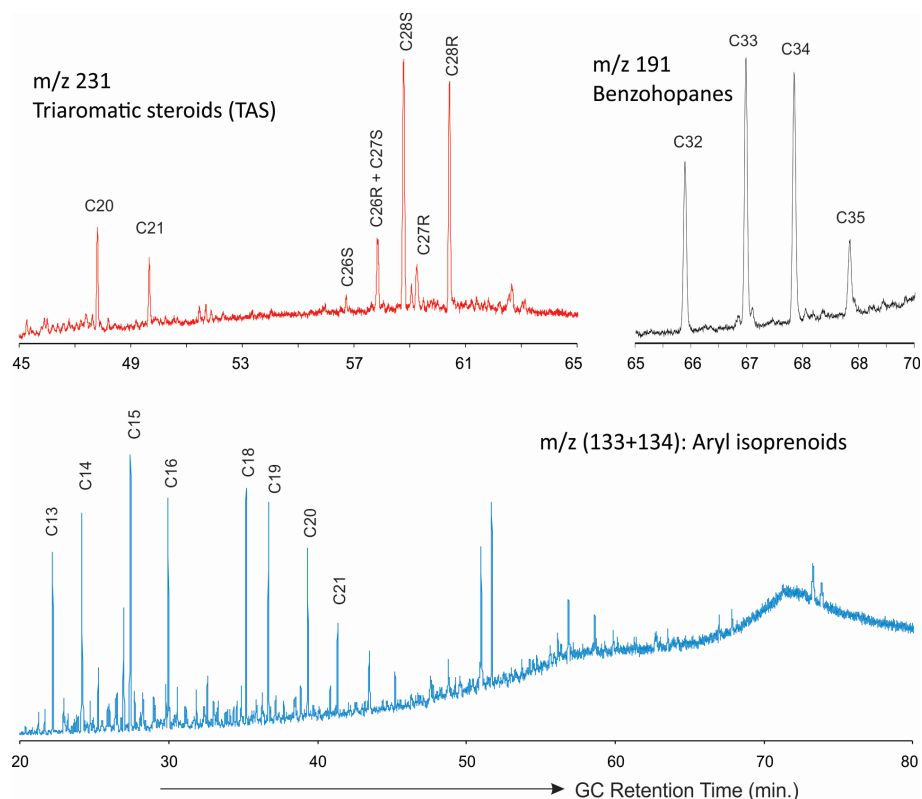
Figure 5. Mass chromatograms m/z 231, 191 and (133+134) showing the distributions of triaromatic steroids (TAS), benzohopanes and aryl isoprenoids in the aromatic fraction of the Devonian Bear Rock Formation dolostone sample C-596743. Peak top labels for the corresponding carbon numbers; S and R for the corresponding isomers.

Figure 7 shows the total ion chromatograms (TICs) from GC-MS analysis of the aromatic fractions for the four outcrop samples. In contrast to the oil-stained dolostone sample C-596743 in which polycyclic aromatic hydrocarbons (PAHs) such as naphthalenes and phenanthrenes are dominant components in the aromatic fraction, these 2–3 ring PAHs that are typically present in non-altered crude oils and source rock extracts are either near absent or below detection limit in the aromatic fractions of both the Quaternary oil sand and the Cretaceous oil-saturated sandstone samples (Fig. 7), most likely as a result of the severe biodegradation they have been exposed to. Furthermore, TASs, a group of PAHs that are very resistant to biodegradation (Peters et al., 2005), are hardly detectable on the m/z 231 mass chromatograms of the bitumen-rich outcrop sand and sandstone samples.

It is apparent that there are hardly any individual peaks, except those of the internal standards (IS) sitting atop the large UCM humps on the aromatic fraction TICs of the two Quaternary oil

sand samples (Fig. 7). Although its TIC is also dominated by the large UCM hump, the Cretaceous sandstone sample C-596769 shows a strong presence of 4-5 ring PAHs such as benzo(a)anthracene, benzofluoranthenes and benzopyrenes. These high member PAHs are typically derived from incomplete combustion of organic matter during forest fires or pyrolysis of OM associated with abnormal burial and thermal history (Jiang et al., 1998; Peters et al., 2005). As benzopyrenes are very resistant to biodegradation, their abundant presence in the Cretaceous sandstone bitumen seems to suggest a source different than that of hydrocarbons occurring in the Quaternary oil sand, which is consistent with the conclusion based on their terpane distributions.
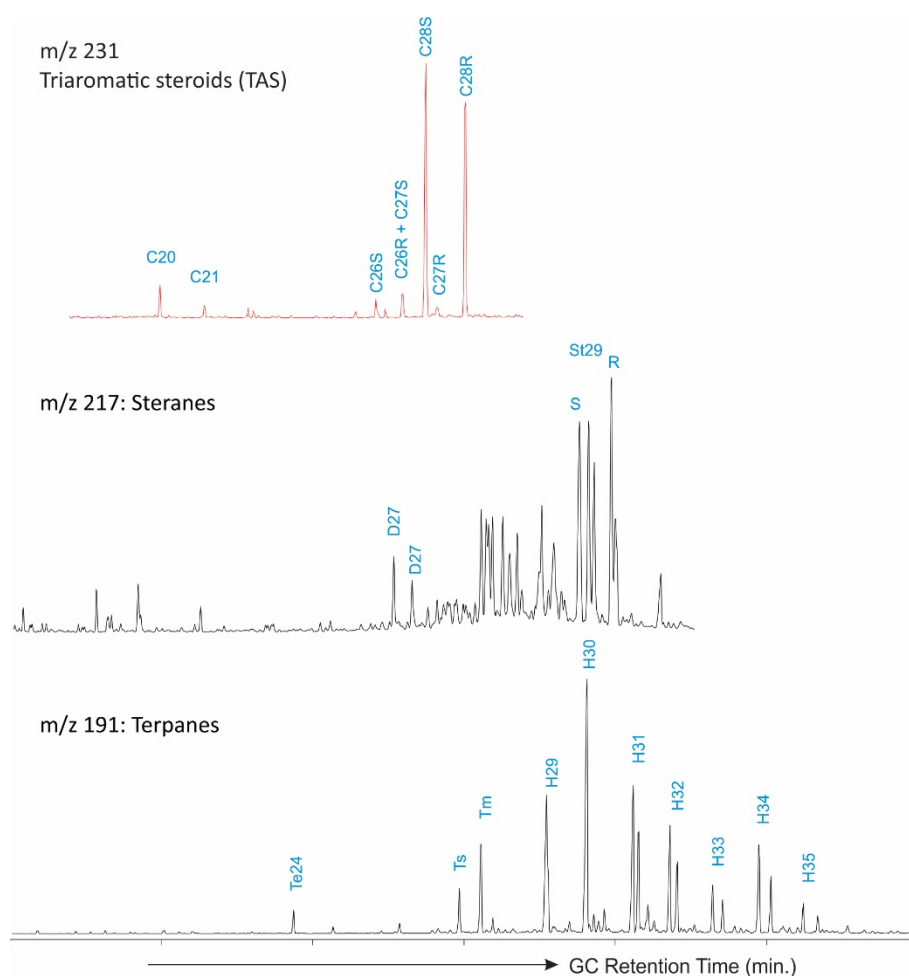

Figure 6. Mass chromatograms showing the distributions of triaromatic steroids (m/z 231), steranes (m/z 217) and terpanes (m/z 191) in Devonian Winnipegosis Formation carbonate petroleum source rock (GSC sample C-321861) from the Williston Basin. See Figures 4 and 5 for peak identification.
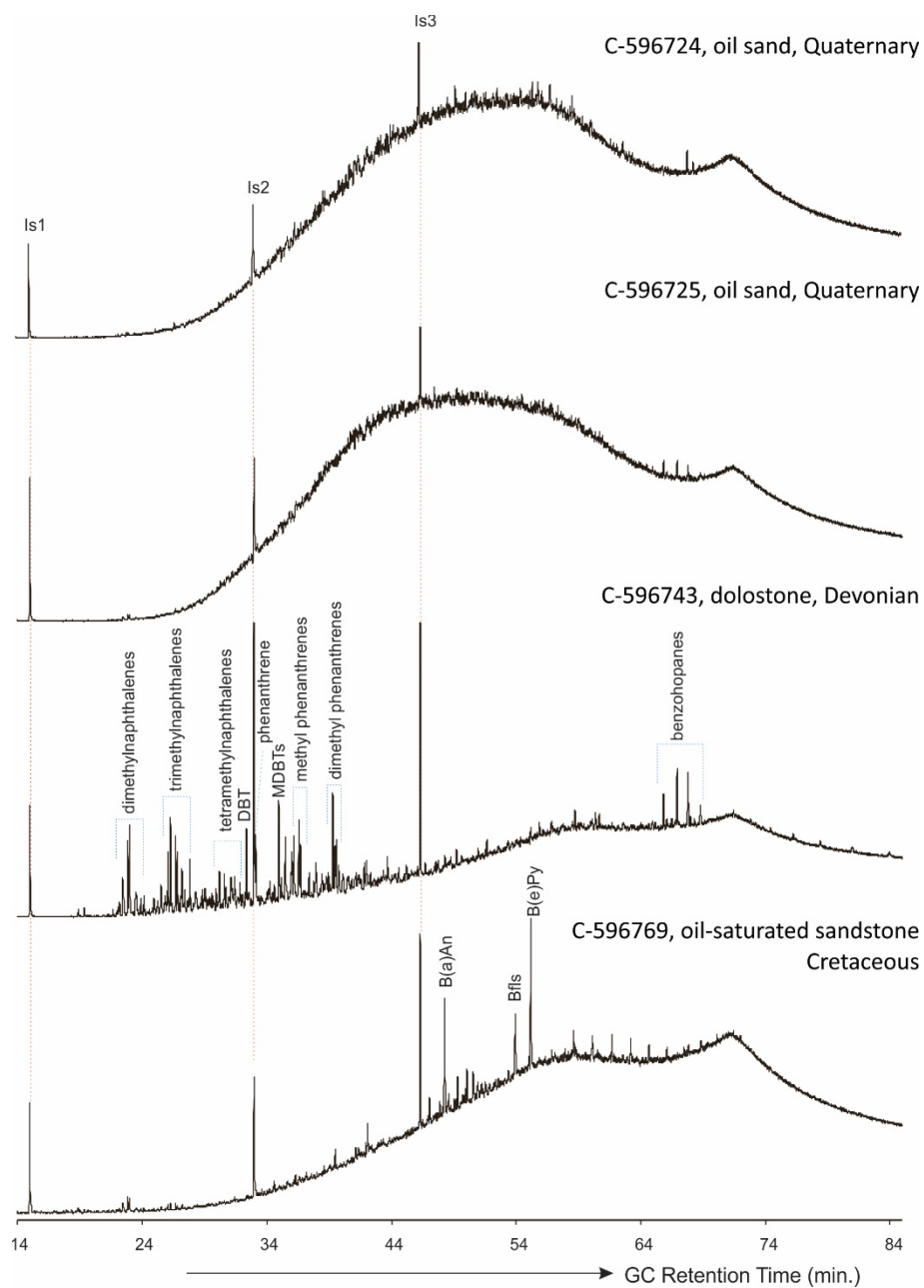
Figure 7. Total ion chromatograms from GC-MS analysis of aromatic fractions for the four outcrop samples in this study. IS internal standards; DBT for dibenzothiophene; MDBT for methyl dibenzothiophenes; B(a)An for benzo(a)anthracene; Bfls for benzofluoranthenes; B(e)Py for benzo(e)pyrene.

3.3. Sources of the hydrocarbons in the petroliferous outcrop samples

Hydrocarbons in the studied outcrop samples appear to have originated from separate source rock units formed within different depositional environments. As revealed by results in Tables 2 and 3, the dolostone sample contains a very low content of free oil (i.e., a value of 0.16 for Rock-Eval S1 peak and a 0.09% extract yield from solvent extraction) and TOC (0.43% by Rock-Eval), suggesting that the Devonian Bear Rock Formation carbonate cannot be considered as either an effective reservoir rock due to low oil content or an efficient potential source rock due to the low TOC content. Hydrocarbons hosted in the dolostone are most likely derived from the carbonate itself, and this is evident from several biomarker signatures including (1) the terpane distribution pattern showing a dominance of C_{29} over C_{30} hopanes, a prominence of C_{24} tetracyclic over C_{26} tricyclic terpanes and a predominance of C_{34} over C_{33} and C_{35} hopanes (Figure 4 and Table 3); (2) the presence of benzohopanes; and (3) the ratios of Pr/Ph<1 and DBT/Phen>1. The carbonate sample has a C_{29} $\alpha\alpha\alpha$ steranes 20S/(20S+20R) ratio of 0.57, and C_{31} and C_{32} hopanes 22S/(22S+22R) ratios of 0.57 and 0.62 respectively, indicating that these hydrocarbons were likely generated at a maturity level close to peak oil generation window. The low abundances of isoprenoids relative to *n*-alkanes (e.g., Pr/nC$_{17}$ and Ph/nC$_{18}$ in Fig. 4 and Table 3) also indicates that hydrocarbons in the dolomite is thermally mature. The biomarker-based thermal maturation level for the hydrocarbon fluid in the dolostone sample, however, seems to be higher than the maturity of the carbonate itself as indicated by its Rock-Eval Tmax value of 427-430 °C (Table 2). This suggests that part of the hydrocarbons in the dolostone may have been generated in and migrated from a source rock unit that was buried deeper and thus was thermally more mature than at the sampling location.

The hydrocarbons in oil-saturated Quaternary sand at the Lac des Bois and Cretaceous Martin House Formation sandstone at Belot Ridge have both experienced very heavy to severe degrees of biodegradation. This is not surprising to most petroleum geologists considering that the outcrop sections, being either sand deposits or porous sandstone, actually present the ideal conditions (e.g., temperatures between 4 and 80 °C, occurrence of water with nutrients and abundance of hydrocarbons as food) required for the occurrence of oil biodegradation. Except for terpanes, all other saturated biomarkers including *n*-alkanes, acyclic isoprenoids and steranes that are typical components of normal crude oils have been consumed or altered by the microbial

activities and thus are not detectable in the solvent extracts. One- to three-ring aromatic compounds typically present in source rocks and normal crude oils are also absent from the oil-saturated and yet biodegraded outcrop sections. The scarcity of biomarkers makes it very difficult to ascertain the source rock characteristics of the hydrocarbons at these two locations. However, the Cretaceous Martin House Formation sandstone at Belot Ridge shows a different distribution of tri-, tetra- and penta-cyclic terpanes compared with the Quaternary oil sand at Lac des Bois (Fig. 4 and Table 3). In addition, the Cretaceous sandstone also contains high concentrations of PAHs of pyrolytic origin (e.g., benzopyrenes) that are absent from the Quaternary oil sand. Therefore, hydrocarbon charges to these two intervals/locations are likely derived from different source rocks that had different organic input during their deposition and/or different diagenetic and catagenetic histories.

The terpane distribution of the Cretaceous Martin House sandstone is closer to that of the Devonian Bear Rock dolostone in terms of the abundances of tricyclic relative to pentacyclic and tetracyclic relative to tricyclic terpanes, indicating a possibility of source contribution from the Bear Rock Formation carbonate interval or other potential carbonate source rocks. The fault contact between the Cretaceous Martin House sandstone and the Devonian Bear Rock carbonates at the Belot Ridge sampling location provides favourable conditions for fluid migration between the two intervals to occur. This sandstone also overlies an angular unconformity, putting it in contact with the Bear Rock directly underneath this outcrop. Moreover, further to the west of the outcrop, the Martin House sandstone overlies the Hume, Hare Indian, and Ramparts formations. Therefore, it is possible that oil hosted in the sandstone could have migrated from any of the Devonian units and simply been trapped up dip in the footwall of the fault.

Likewise, the source characteristics for the oil accumulation in the Quaternary sand deposit at Lac des Bois cannot be ascertained due to a lack of biomarkers indicative of depositional environment and organic input; however, their terpane distributions do seem to indicate a less calcareous character for its main source rock than that of the hydrocarbons hosted in the Cretaceous Martin House sandstone. Although the two oil sand samples have almost identical biomarker signatures, they display very different SARA compositions (Table 3). Bitumen in sample C-596725 is more enriched in hydrocarbons, and sample C-596724 has a larger proportion of polar components including resin and asphaltene. The different SARA

compositions between the two oil sand samples seem to be reasonable based on sample appearance in the outcrop. Sample C-596725 with high hydrocarbon content was indeed softer and more flowable (or less viscous) than sample C-506724 (Fig 1c vs Fig 1b). This appears to suggest active oil movement within the oil sand deposit at Lac des Bois, and thus further indicates the presence of active oil charging and migration in the subsurface at this locality.

4. Conclusions

Rock-Eval analytical results indicate that the Devonian Bear Rock Formation dolostone interval at the Lac à Jacques has low contents of organic matter and free oil, and thus cannot be considered as an effective reservoir rock and potential petroleum source rock. Nevertheless, hydrocarbons hosted in the dolostone have been mostly derived from a carbonate source, either the Bear Rock or other formations of the Devonian Formation but at deeper locations.

The Quaternary oil sand and the oil-saturated Cretaceous Martin House Formation sandstone outcrop samples both have high content of free oil, and show similar Rock-Eval bulk geochemical properties to the Athabasca oil sand. Oils occurring in the outcrop sections of both sand deposit and sandstone have been severely biodegraded, resulting in the removal of all biomarkers but the terpanes. The Quaternary oil sand and the Cretaceous sandstone do display different distributions of terpanes, suggesting that they were generated from different source rocks. The main source rock for the Cretaceous sandstone is likely more calcareous than that for the Quaternary oil sand. In addition, different physical properties and SARA compositions displayed by the two Quaternary oil sand samples, though collected only ten meters apart, seem to suggest the presence of an active petroleum system in the study area with oil charging and migration processes still taking place.

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