Article
Vol. 22, No. 5, p. 751–763, October 2018
https://doi.org/10.1007/s12303-018-0021-4
pISSN 1226-4806 eISSN 1598-7477
Geosciences Journal GJ

Biodegradation characteristics of bitumen from the Upper Devonian carbonates (Grosmont and Nisku Formations) in Alberta, Canada

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ABSTRACT: In this study, we investigated the biodegradation processes of bitumen from the Upper Devonian carbonates (Grosmont and Nisku Formations) in Alberta using GC and GC-MS analyses of four drilling cores. The analyzed samples contain notable rich extracted bitumen, which is predominantly composed of NSO and asphaltene compounds and has lesser amounts of saturated and aromatic hydrocarbons (HCs). The GC and GC-MS results for both saturated and aromatic HCs indicate that there are considerable variations among the samples, which are primarily attributed to the differences in the degree of biodegradation involving microbial activity. The sulfur content and its isotope values for the samples also support biodegradation. Three groups can be classified based on the biomarker distributions as follows: (1) in Group 1, C_{19}-C_{25} tricyclic terpanes are most abundant, particularly the C_{23} compounds; (2) Group 2 has no C_{30}-C_{35} αβ hopanes and more abundant 25-norhopanes than the other two groups; and (3) Group 3 is similar to Group 1, but generally has less abundant C_{19}-C_{25} tricyclic terpanes than Group 1. The reservoir alteration processes have notably influenced the biomarker properties of the samples. The most pronounced effects are the reduction of the amounts of C_{30}+ hopanes and increasing demethylated hopanes, particularly in Groups 1 and 2, but not in Group 3. For Group 3, unlike Group 1, the degradation of hopanes apparently does not result in demethylated hopanes, indicating that there is another pathway to produce hopanes and/or destroy demethylated hopanes. These findings indicate that the biodegradation processes that occurred in the Grosmont and Nisku Formations have been spatially and vertically varied due to the different environmental conditions and microbial processes.

Key words: biodegradation, GC and GC-MS analyses, biomarker, Upper Devonian carbonates, Alberta

Manuscript received August 7, 2017; Manuscript accepted April 23, 2018

1. INTRODUCTION

Biomarkers (also known as biological markers, chemical fossils, or molecular markers) are specific organic compounds found in crude oil, bitumen or petroleum source rock (Peters et al., 2005). Essentially, biomarkers in geological samples have been derived from formerly living organisms that have undergone primarily reductive and oxidative alteration processes (Simoneit, 2004; Wang et al., 2006). Various biomarkers have been broadly applied to correlate source rock and oil, to evaluate oil maturity, and to identify the organic facies. In addition, the investigation of biomarker structures and their compositional properties can be used for the assessment of major source species of organisms but also the level of petroleum biodegradation because certain species of biomarkers (e.g., steranes and triterpanes) are more degradation-resistant relative to other hydrocarbon (HC) groups such as alkanes and aromatic HC compounds (Volkman et al., 1983; Moldowan et al., 1992; Wang et al., 1998; Peters et al., 2005; Zhao and Machel, 2011).

The study of biomarkers can be a powerful tool for the documentation of the bitumen or oil properties (e.g., API gravity, viscosity, thermal maturity, degree of biodegradation) from the Upper Devonian carbonates, which contain approximately 400 billion barrels of original oil in place (ERCB, 2010). The Grosmont platform is the largest heavy oil and bitumen

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reservoir in the world and is currently under consideration for commercial development by several companies and consortia using solvent-cyclic steam-assisted gravity drainage (SC-SAGD) (ERCB, 2010; Laricina, 2011; Solanki et al., 2011). However, this reservoir exhibits extreme levels of biodegradation that are easily observed in the analyzed biomarker chromatographs, such as loss of regular steranes, detection of strongly biodegraded hopanes and distribution of tricyclics and diasteranes (e.g., Wenger et al., 2001; Zhao and Machel, 2011; Machel et al., 2012). Additionally, our previous studies, including the GC-MS analyses (Choi et al., 2011; Park et al., 2013), do not show a marked variation among samples and wells caused by severe biodegradation. The physical and chemical properties of biodegraded oil affect the oil production and refining processes; thus, they are critical factors for commercial exploitation (Barker, 1979; Zhao and Machel, 2011).

In this study, we analyzed a series of biomarkers consisting of a total of 12 bitumen samples from the Upper Devonian carbonates (Grosmont and Nisku Formations) in Alberta that contained sufficient bitumen for the biomarker evaluation. The main aim of this study was to document and understand the detailed biodegradation characteristics of bitumen.

2. GEOLOGICAL SETTING

Carbonate production proceeded on a shallow shelf in the Upper Devonian age, resulting in the deposition of the Grosmont platform in the Alberta Basin, which is in the western part of the Western Canada Sedimentary Basin (WCSB) (ERCB, 2011; Machel et al., 2012). This platform formed in a northwest-southeast trending Upper Devonian broad and shallow marine carbonate environments approximately 150 km wide and at least 600 km long, covering an area of approximately 100,000 km^2 (Fig. 1; Harrison, 1982, 1984; Switzer et al., 1994). The southern and western limits of the platform are transitional from shallow platform facies to deep-water basinal facies, whereas the northern extent remains poorly described due to the lack of geological surveys. The up-dip eastern margin is truncated by a sub-Cretaceous unconformity.

The Grosmont platform consists of the Grosmont Formation at the base interbedded with evaporates and is overlain by the Upper Ireton and Nisku Formations (Machel et al., 2012). The thickness of the Grosmont Formation is variable on a regional scale, but averages approximately 150 m over much of the Grosmont complex. This formation can be largely subdivided

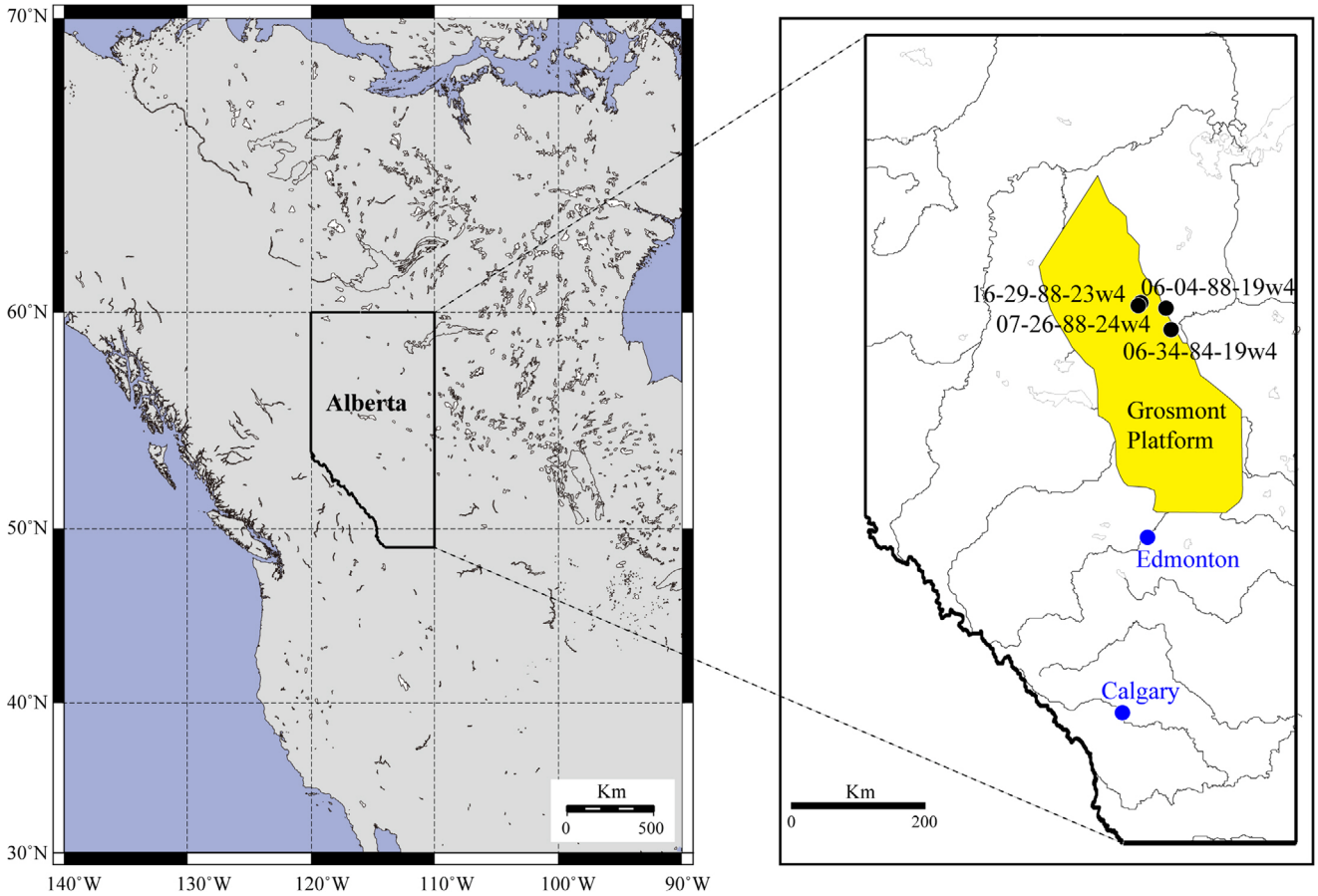

Fig. 1. Location of the four cores used in this study.

into four stratigraphic units on the basis of three thin marly intervals (known as shale breaks); Lower Grosmont (LGM), Upper Grosmont 1 (UGM1), Upper Grosmont 2 (UGM2), and Upper Grosmont 3 (UGM3) in ascending order (Harrison and McIntyre, 1981; Harrison, 1982). The entire interval of the Grosmont Formation is roughly equivalent to the uppermost part of the Cairn Formation in Alberta, which has also been similarly affected by multi-stage diagenesis. Among these units, bitumen is mostly contained in the UGM2 and UGM3 units (Geldsetzer, 1988). However, the Upper Ireton Formation consists of argillaceous or silty dolostone in the northern part and changes southward into marlstone. The Nisku Formation is composed of crystalline dolomite, green mudstone, and anhydrite, which is similar to that of the UGM3 unit (Machel and Anderson, 1989; Machel et al., 2012).

The Grosmont platform has been subject to various stages of diagenesis, such as cementation, compaction, dolomitization, karstification, sulfate dissolution and fracturing. Early dolomitization has resulted in the formation of dolostones composed mainly of fine subhedral to euhedral dolomite with high porosity (20%) and permeability (50–70 mD) (Luo et al., 1993, 1994; Kil et al., 2012; Seol et al., 2015). In the next stage of diagenesis, karstification has considerably altered the fabric of the Grosmont carbonates and, in turn, enhanced the reservoir characteristics because the development of irregular dissolution vugs and fractures has increased the porosity locally to levels exceeding 40%, and permeability can be up to 30,000 mD (Machel and Hawlader, 1990; Luo et al., 1993). The carbonates have been charged with oil and bitumen that have undergone heavy biodegradation (Buschkuehle et al., 2007).

Previous organic geochemical studies have been performed on bitumens from the Lower Cretaceous oil sands and the Upper Devonian carbonates and explained their common organic geochemical properties (e.g., Mackenzie et al., 1983). However, the maturity and source of the Grosmont bitumen are similar to those in Cretaceous oil sands but were subject to a considerably higher degree of biodegradation (Hoffmann and Strausz, 1986). Bennett et al. (2010) also reported a severe degree of biodegradation in the Devonian carbonate reservoirs based on the biomarker and isotope results.

3. MATERIALS AND ANALYTICAL METHODS

A total of 12 bituminous samples from four drill cores containing enough bitumen for the biomarker analyses were selected from the CRC (Core Research Centre) at Calgary in Alberta (Fig. 1; Table 1). Ten samples were collected from the Upper Devonian Grosmont Units (LGM, UGM1, UGM2, and UGM3) and two samples (Sample Nos. 5 and 6) were collected from the Nisku Formation (Table 1).

A series of organic geochemical analyses were performed on these samples, including Rock-Eval analysis, solvent extraction, asphaltene precipitation, MPLC (Medium Pressure Liquid Chromatography), and SIM (Selective Ion Monitoring) GC-MS at the Korea Institute of Geoscience and Mineral Resources (KIGAM) and Fugro Lab in Norway. Total Organic Carbon (TOC) analysis was performed using the Rock-Eval Turbo 6 at the KIGAM, determining both the pyrolyzed carbon (PC) and residual carbon (RC) content (Arthur et al., 1998; Lafargue et al., 1998; Kim et al., 2007, 2014). IFP 160000 (Vinci-Technologies, France) was used as a standard for the Rock-Eval analysis. The samples were extracted using a Tecator Soxtec HT-System for the solvent extraction of organic matter (EOM). Carefully weighed samples in pre-extracted thimbles and some copper were added to the extraction cup and the samples were boiled for 1 hour and rinsed for 2 hours. A dichloromethane/methanol (93% volume/7% volume) solution was used as an extraction solvent. The extracted solution was transferred to a glass flask and the solvent was removed by rotary evaporation (200 mb, 30 °C). The amount of EOM was determined gravimetrically.

Table 1. Summary of the sample information used in this study

Sample No.	Site	Latitude (°N)	Longitude (°W)	Depth (m)	Formation/Unit	Group
1	16-29-88-23w4	56.666121	113.624201	414.7	UGM2	1
2	16-29-88-23w4	56.666121	113.624201	406.3	UGM2	1
3	07-26-88-24w4	56.658801	113.710605	465.2	UGM2	1
4	07-26-88-24w4	56.658801	113.710605	419.7	UGM3	1
5	07-26-88-24w4	56.658801	113.710605	370.4	Nisku	2
6	07-26-88-24w4	56.658801	113.710605	354.2	Nisku	2
7	06-04-88-19w4	56.600648	112.972866	284.0	UGM2	3
8	06-04-88-19w4	56.600648	112.972866	277.5	UGM2	3
9	06-04-88-19w4	56.600648	112.972866	272.0	UGM2	3
10	06-04-88-19w4	56.600648	112.972866	306.6	UGM1	3
11	06-34-84-19w4	56.324443	112.919417	363.0	UGM2	1
12	06-34-84-19w4	56.324443	112.919417	375.3	UGM2	1

https://doi.org/10.1007/s12303-018-0021-4

The EOM was dissolved using n-pentane using a glass flask to precipitate the asphaltenes by ultrasonic bath for 3 min, and the flask was stored in the dark for at least 8 hours at ambient temperature. The solution was later filtered (Baker 10-spe system) and the precipitated asphaltenes were returned to the original glass flask by dissolution in dichloromethane. The solvent was removed by rotary evaporation at 200 mb and 30 °C.

The asphaltenes removed by EOM were injected into the MPLC and separated using hexane as an eluent. The saturated and aromatic HC fractions were collected, and the solvent was removed using a rotary evaporator at 30 °C. Each fraction was transferred to small pre-weighed glass vials and evaporated to dryness overnight. The glass vials were subsequently reweighed to obtain the weights of both the saturated and the aromatic HC fractions. The weight of the nitrogen, sulfur and oxygen (NSO) fraction was obtained by the weight difference.

The GC-MS analyses were performed on an Autospec Ultima system interfaced to a Hewlett Packard 5890 gas chromatograph (GC). The GC was fitted with a fused silica SE54 capillary column directly into the ion source. Helium (12 psi) was used as the carrier gas and the injections were performed in splitless mode. The GC oven was programmed to increase in temperature from 45 °C to 150 °C at a rate of 35 °C/min, at which point the programmed rate was reduced to 2 °C/min for a continued increase in temperature up to 310 °C, where the column was held isothermally for 15 min. For the aromatic HCs, the GC oven was programmed to increase in temperature from 50 °C to 310 °C at 5 °C/min and held isothermally at 310 °C for 15 min. The mass spectrometer was operated in electron impact (EI) mode at 70 eV ionization energy, with a trap current of 500 uA and a source temperature of 220 °C. The instrument resolution used was 1,500 (10% value) and the data system used was a VG OPUS system. The samples were analyzed in multiple ion detection mode (MID) at a scan cycle time of approximately 1.1 sec. The calculation of peak ratios was performed using peak heights in the appropriate mass fragmentograms.

Aliquots of EOM were used to analyze the sulfur (S) content and sulfur isotope ($\delta^{34}S$) ratio at the Isotope Science Laboratory, Calgary University using a Fisons NA1500 elemental analyzer with a combustion column set at 1,020 °C interfaced to a Finnigan Mat Delta-plus XL IRMS. International reference materials IAEA S1 (–0.3‰), IAEA S2 (22.7 ± 0.2‰) and UAEA S3 (–32.6 ± 0.2‰) were used to calibrate the measurement. The precision and accuracy are ±0.3‰ (1σ, n = 10) based on repeated lab standards measurement.

4. RESULTS

4.1. EOM Extraction and Separation

All analyzed samples had high TOC and very rich yields of EOM ranging from 1.55 to 24.64 wt% and from 29,500 to 103,300 μg/g (Table 2), respectively. The fraction data for the EOM from asphaltene precipitation and MPLC separation of the remaining maltenes are presented in Table 2. The saturated and aromatic HCs are low in EOM, ranging from 11.0 to 15.9% and 17.5 to 22.6%, respectively, while non-HCs (62.1–69.7%) with 30.6–35.7% NSO and 27.6–37.0% asphaltenes are predominant. The calculated saturated/aromatic HCs ratio is less than 1 in all samples and ranges from 0.43 to 0.61 (Table 2).

4.2. Biomarkers

Apart from Sample Nos. 2, 6, 9, 11, and 12, the only resolved components of the saturated HC fractions are likely to be primarily cyclic alkanes (triterpanes and diasteranes) (Fig. 2a). In contrast, C_{15} to C_{25} n-alkanes, including pristane and phytane, are identified in Sample Nos. 2, 6, 9, 11, and 12 (Fig. 2). The triterpane

Table 2. Extraction results by MPLC, analyzed sulfur content, and sulfur isotope values of the samples

Sample No.	Weight (g)	TOC (wt%)	EOM (mg)	Saturated HC/EOM	Aromatic HC/EOM	Asphaltenes/ EOM	NSO/ EOM	HC/ EOM	Non-HC/ EOM	Saturated HC/ Aromatic HC	HC/ Non-HC	Sulfur (wt%)	Sulfur Isotope (‰)
1	0.6	5.55	58.50	13.56	19.53	35.97	30.93	33.10	66.90	0.69	0.49	–	–
2	0.6	5.45	48.40	13.27	21.94	34.18	30.62	35.21	64.79	0.60	0.54	–	–
3	0.7	1.55	38.20	13.20	19.55	34.98	32.26	32.75	67.25	0.68	0.49	5.0	5.2
4	0.6	5.21	58.90	12.41	21.58	33.09	32.91	33.99	66.01	0.57	0.51	3.8	5.8
5	0.5	24.64	35.60	12.09	20.15	37.03	30.73	32.24	67.76	0.60	0.48	3.3	5.7
6	0.7	4.27	37.20	12.84	17.46	36.82	32.87	30.30	69.70	0.74	0.43	3.7	5.9
7	0.6	3.73	25.40	13.24	22.30	32.41	32.05	35.54	64.46	0.59	0.55	4.2	5.6
8	0.6	4.12	51.80	11.00	21.09	34.91	33.00	32.09	67.91	0.52	0.47	4.3	5.8
9	0.6	1.94	17.90	14.10	22.56	27.61	35.73	36.67	63.33	0.63	0.58	–	–
10	0.6	1.64	17.70	15.88	22.06	27.65	34.41	37.94	62.06	0.72	0.61	4.3	5.7
11	0.6	11.86	62.00	13.14	20.19	35.90	30.77	33.33	66.67	0.65	0.50	–	–
12	0.7	4.90	70.60	11.97	20.17	34.46	33.40	32.14	67.86	0.59	0.47	–	–

–: no measurement.

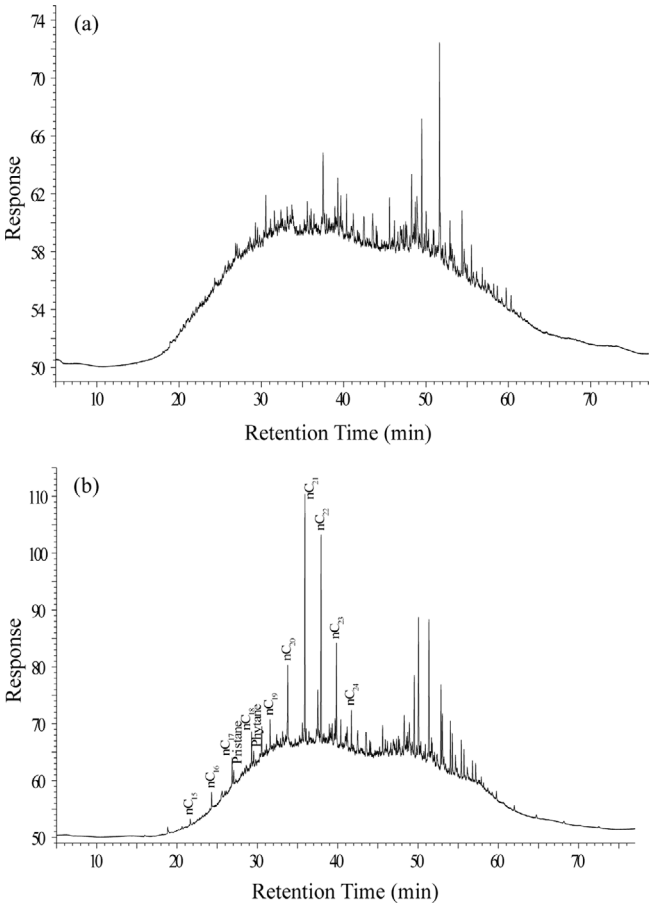

Fig. 2. Saturated hydrocarbon gas chromatograms of (a) Group 3 (Sample No. 7) and (b) Group 2 (Sample No. 6), showing no n-alkanes and a narrow envelope of n-alkanes, respectively.

distributions show marked variations among the samples (Fig. 3). Thus, based on the terpane fragmentograms (i.e., m/z 177, 191, and 205) (Fig. 3), the analyzed samples can be largely classified into three groups. The major differences are in the abundances of three main groups of compounds, i.e., the C_{19}-C_{25} tricyclic terpanes, the C_{30}-C_{35} αβ hopanes, and the 25-norhopanes (Fig. 3). The C_{19}-C_{25} tricyclic terpanes are most abundant in Group 1 (Sample Nos. 1, 2, 3, 4, 11, and 12 in Tables 1 and 2) from the UGM2 and UGM3 units of the Grosmont Formation, particularly the C_{23} compound. The C_{28} to C_{31} tricyclic terpanes are also prominent compounds. The C_{27} (e.g., 27Ts) to C_{35} hopanes (e.g., 35αβR) are present all in the Group 1 samples and the sum of the C_{30-35} αβ hopanes ranges from ~450 to 980 μg/g EOM. The C_{29} αβ hopane is predominant in all of the Group 1 samples but it is marginal in Sample Nos. 4 and 11, where the C_{30} compound (30αβ) is slightly more abundant. In addition, the Group 1 samples have abundant C_{28} to C_{34} demethylated 25-norhopanes and minor amounts of C_{28} bisnorhopane (αβ hopane and C_{29} βα moretane are also present) in the m/z 177 fragmentograms (Fig. 3).

Group 2 (Sample Nos. 5 and 6), collected from the Nisku Formation, has virtually none of the C_{30}-C_{35} αβ hopanes (abundance: ~20 μg/g EOM), with the C_{29} compound 25nor30αβ being identified as the predominant compound. The Group 2 samples have more abundant 25-norhopanes than the Group 1 and Group 3 samples (103 and 135 μg/g EOM for the 25nor30αβ hopane compound from two samples of Group 2, compared with 26–82 μg/g EOM in Group 1 and less than 10 μg/g EOM in Group 3 from Sample Nos. 7, 8, 9, and 10) (Fig. 3). The full series of demethylated hopanes can be seen in the m/z 177 fragmentograms, where the predominant compound is 25nor29αβ (Fig. 3).

Group 3 from the UGM1 and UGM2 units of the Grosmont Formation is similar to Group 1, e.g., the sum of C_{30-35} αβ hopanes is slightly lower in magnitude (~274–466 μg/g EOM) in overall distribution. However, the samples of Group 3 have variable and generally less abundant tricyclic terpanes than Group 1 and, they show virtually no sign of the demethylated hopanes found in Group 1 (Fig. 3). Particularly, the main feature of the Group 1 samples is that it has the most pronounced C_{19}-C_{25} tricyclic terpanes of the three groups, with dominance of C_{23} compound (Fig. 3).

The m/z 217 fragmentograms for all samples show a predominance of the C_{27} to C_{29} diasteranes, whereas the regular steranes (i.e., ααα and αββ steranes) are either present in low concentrations or absent (Fig. 4). Terpanes exhibit a considerable variation in the abundance of different compound groups. Most samples have predominant light (short side chain C_{21} and C_{22} compounds) steranes along with the diasteranes (Fig. 4). In the more biodegraded samples, some of the 25-norhopane series appear in the sterane fragmentogram simply because the steranes are present in much lower concentrations than the hopanes (e.g., the total sum of C_{27}-C_{29} αα and ββ steranes ranges from 13.25 to 32.5 μg/g EOM compared with > 200 μg/g EOM for C_{30}-C_{35} αβ hopanes). Based on the m/z 218 fragmentograms, ββ steranes are virtually absent, although there may be traces (e.g., the 29ββR compound) because most ββ steranes peak at this retention time as C_{28} bisnorhopane (28αβ) (Fig. 4).

In the aromatic hydrocarbon fractions, the lighter aromatics are generally superimposed on a marked rise in the baseline (Fig. 5). The combined fragmentograms of the lighter aromatics, the C_1-, C_2- and C_3-naphthalenes, show only low to moderate amounts of these in all samples with C_1-C_3 naphthalene concentrations, ranging from 1.68 to 13.35 μg/g EOM (Fig. 5). The phenanthrene and alkyl phenanthrene fragmentograms are relatively insignificant components with only trace to minor amounts (1.2–3.5 μg/g EOM) (Fig. 6). Similarly, the sulfur aromatics identified using the m/z 184 and 198 fragmentograms (not shown here) display only trace amounts of these compounds. In contrast to the lighter aromatics, the tri- and mono-aromatic sterane

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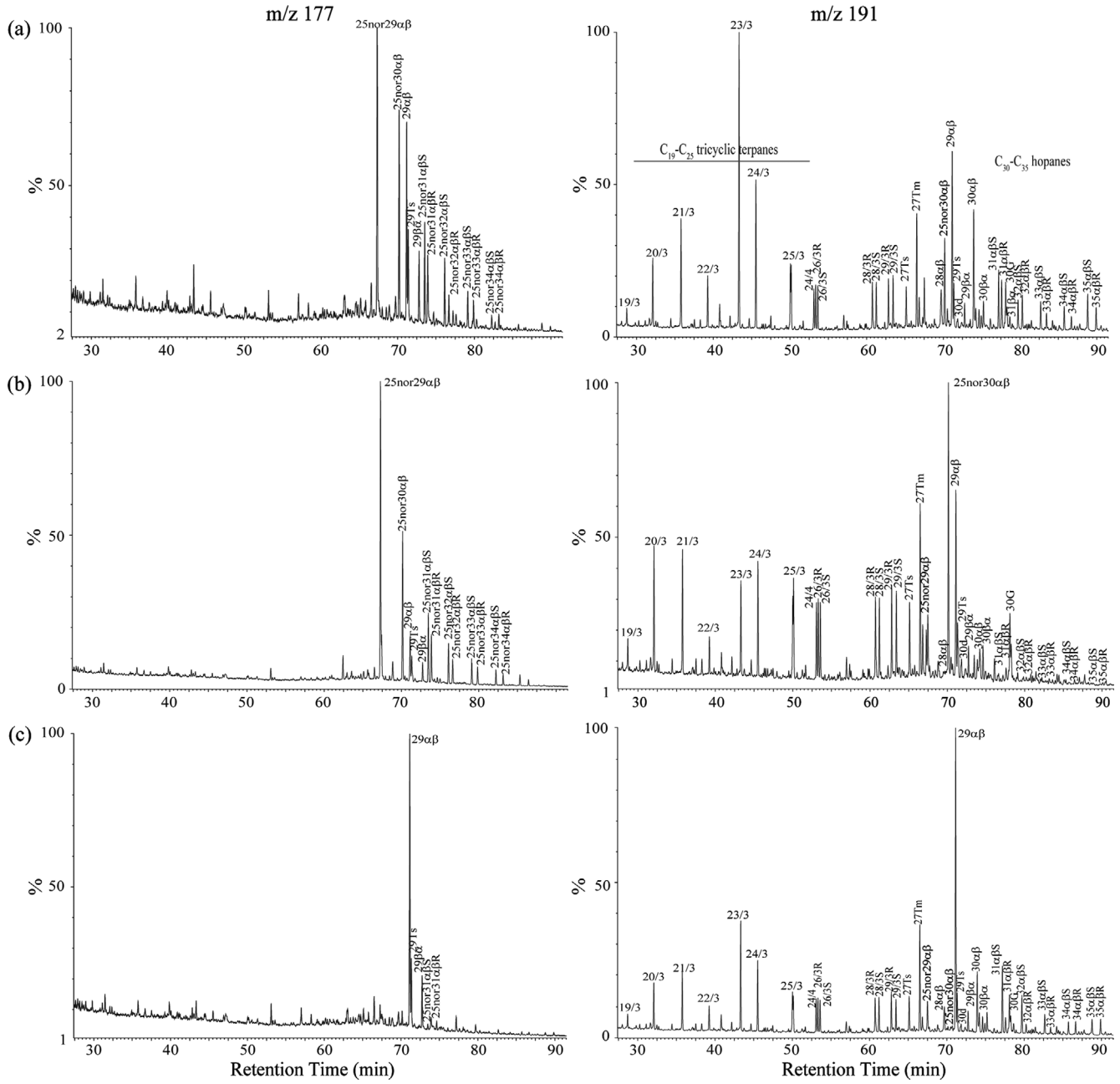

Fig. 3. Triterpanes distribution in fragmentograms (left: m/z 177, right: m/z 191) from (a) Group 1 (Sample No. 1), (b) Group 2 (Sample No. 5), and (c) Group 3 (Sample No. 7).

biomarkers are considerable more abundant in the m/z 231 and 253 fragmentograms, respectively (Fig. 6). There are low amounts of the short alkyl side chain (C_{20} and C_{21}) tri-aromatic steranes but similar and abundant amounts of the C_{26}-C_{28} peaks in all samples. The relative peak patterns are also similar, where the C_{28} compounds are more abundant than the C_{27} and C_{26} compounds (Fig. 6).

4.3. Sulfur Content and Isotope

The sulfur content of all analyzed samples showed a relatively constant value irrespective of groups, ranging from 5.2 to 5.9 wt% (average = 5.7 ± 0.2 wt%) (Table 2), while $\delta^{34}S$ displayed variations among the groups. Groups 2 and 3 have relatively constant values of $\delta^{34}S$, ranging from 3.3‰ to 3.7‰ and from 4.2‰ to 4.3‰, respectively, whereas the $\delta^{34}S$ values for the Group 1 samples vary from 3.8‰ to 5.0‰ (Table 2).

5. DISCUSSION

The EOM of all bitumen samples from the Grosmont and Nisku Formations is predominantly composed of non-HCs with

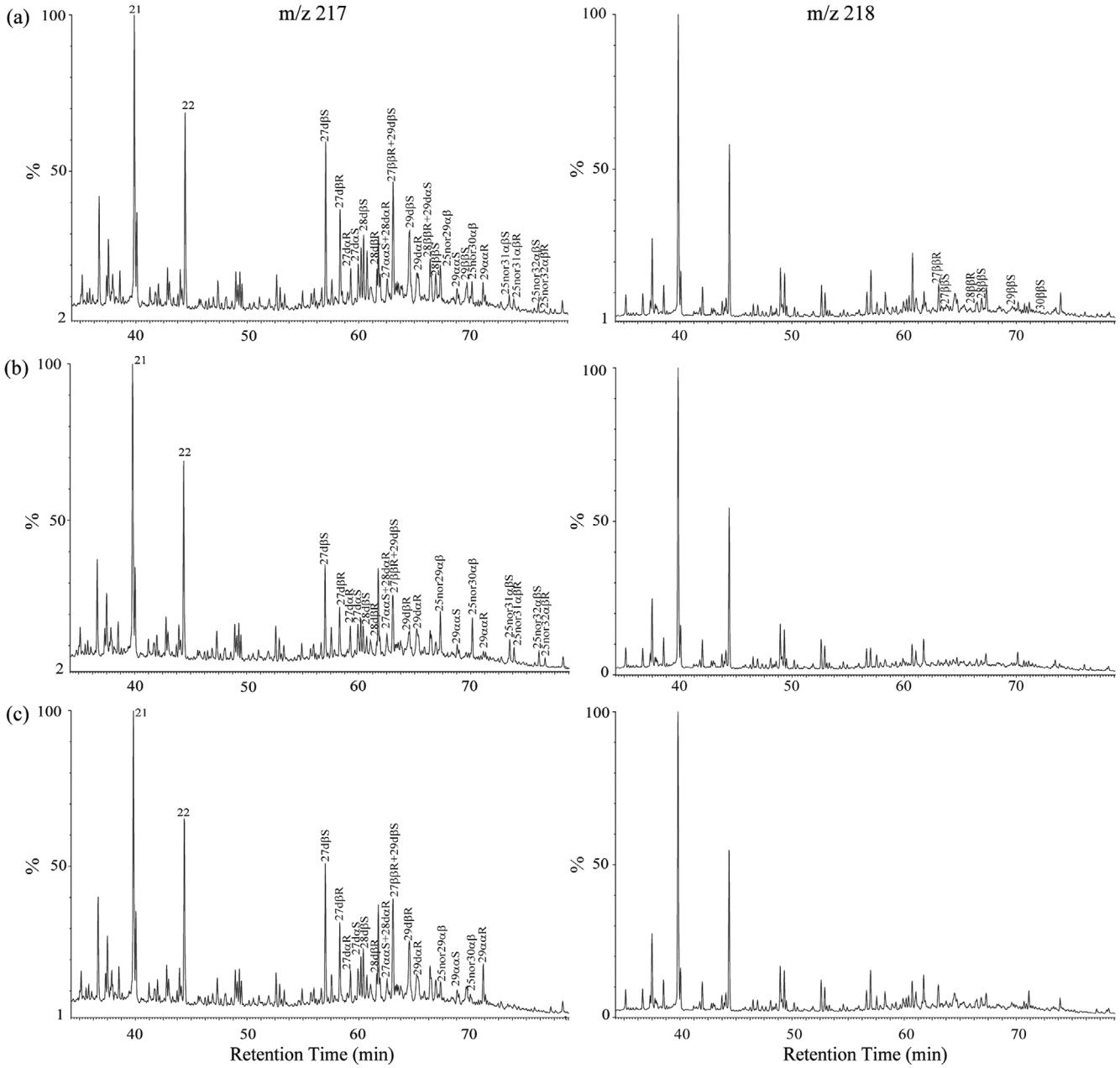

Fig. 4. Steranes distribution in the fragmentograms (left: m/z 217, right: m/z 218) from (a) Group 1 (Sample No. 1), (b) Group 2 (Sample No. 5), and (c) Group 3 (Sample No. 2).

NSO and asphaltenes and has lesser amounts of by the saturated/aromatic HCs. In addition, the saturate/aromatic HCs ratio is less than 1. When oil has undergone biodegradation associated with microorganisms, an unresolved complex mixture (UCM) of cyclic and highly branched alkanes usually remains and the n-alkanes are minimal or absent (Peters and Moldowan, 1993; Zhao and Machel, 2011). Brooks et al. (1988, 1989) also indicated that the biomarker compounds in the heavy oil, oil sands, and bitumen carbonate located in the WCBS are generally removed in the following order: n-alkanes > acyclic isoprenoid > regular steranes > hopanes > rearranged steranes > tricyclic terpanes. Hence, the fraction of EOM in our analyzed bitumen samples from the Grosmont and Nisku Formations demonstrates that bitumens from these two formations have been experienced severe biodegradation. The sulfur content and sulfur isotope ratio of the analyzed samples provide additional evidence for the influence of severe biodegradation because their values are consistent with those values of oil and core samples collected from the Mannville Formation in the WCBS influenced by severe biodegradation (Méhay et al., 2009).

If the oil source does not change substantially, the removal of saturated HCs during biodegradation might partly account for

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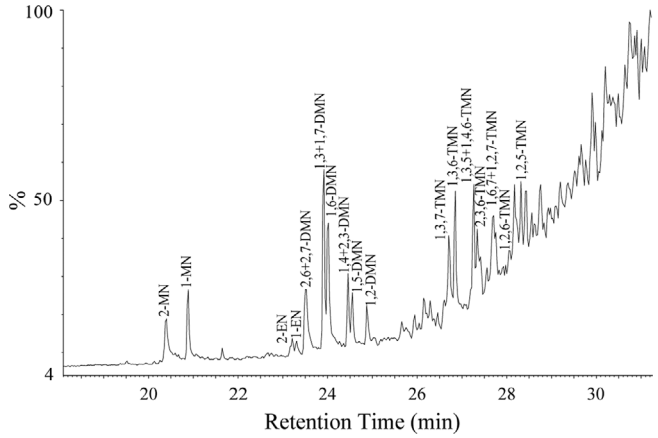

Fig. 5. Naphthalenes distribution in the fragmentograms (combined m/z 142, 156, and 170) from Group 1 (Sample No. 1).

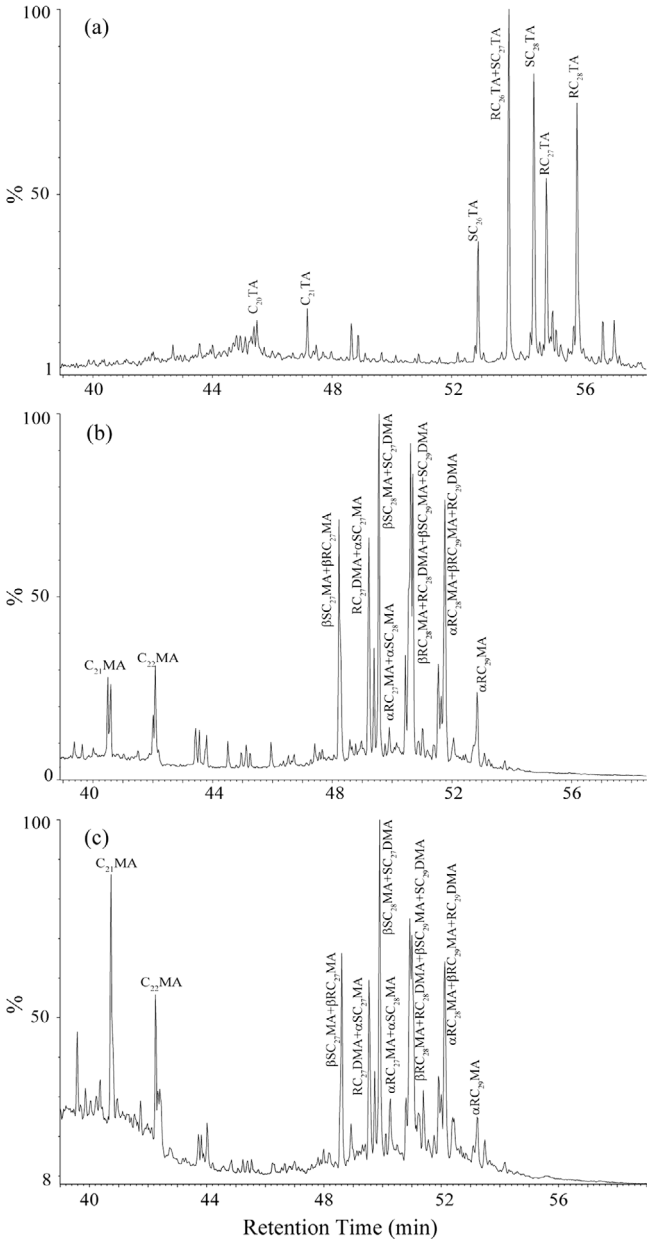

Fig. 6. (a) Tri-aromatic steranes distribution in the fragmentograms (m/z 231) from Group 1 (Sample No. 3). Mono-aromatic steranes distribution in the fragmentograms (m/z 253) from (b) Group 2 (most biodegraded; Sample No. 5), and (c) North Sea Oil Standard.

the higher sulfur content in the most biodegraded bitumen since sulfur in organic compounds and organic matter (resins, asphaltenes) is not easily released by microbial alteration, at least in the first stages of biodegradation (Orr, 1978). In addition, this reaction generally leads to enriched $\delta^{34}S$ values in the residual oil preferentially removed by isotopically light S (Bechtel et al., 1996; Cai et al., 2005, 2009; Zhang et al., 2005). However, the sulfur content and $\delta^{34}S$ variations can be attributed to the oils generated by various source rocks, particularly in the case of biodegraded oils, where the biomarkers are altered (Cai et al., 2009; Méhay et al., 2009); thus, caution should be utilized when sulfur content and $\delta^{34}S$ variations are used as proxies for biodegradation.

C_{19}-C_{25} and C_{28} to C_{31} tricyclic terpanes are abundant and C_{27} to C_{35} hopanes are present in Group 1 (Fig. 3), which are mainly caused by the biodegradation affecting the C_{30}+ compounds to a variable extent. Therefore, the variations of the triterpane distributions in the Group 1 samples are mainly attributed to the differences in the degree of biodegradation. This is particularly noticeable in the variation in the C_{30}-C_{35} αβ hopanes abundance relative to less easily biodegraded compounds, such as gammacerane (30G) (Reed, 1977; Seifert and Moldowan, 1979; Seifert et al., 1984) because the m/z 191 fragmentogram from Sample No. 12 has slightly more C_{30}-C_{35} αβ hopanes relative to gammacerane than that from Sample No. 1 (Fig. 3). Gammacerane relatively unaffected by biodegradation exhibits considerable abundance in all three groups, ranging from 30 to 60 μg/g EOM, which indicates that the overall degree of biodegradation is similar among the three groups. However, there are variations in the abundance of triterpane compounds degraded or generated during biodegradation with respect to groups, possibly due to differences in the degree of biodegradation involving microbial activity.

Group 2 has none of the C_{30}-C_{35} αβ hopanes and has a full series of demethylated hopanes because it has more extensive biodegradation than Group 1 (Fig. 3). The presence of 25-norhopances in biodegraded bitumen is usually an indication that an accumulation has been heavily biodegraded (at least Rank 6 or greater; Peters and Moldowan, 1993). The biodegradation is also slightly affected the C_{19}-C_{25} tricyclic distributions in this group with the content of the C_{21} and C_{23} compounds slightly reduced relative to the adjacent compounds.

Group 3 has been affected differently by biodegradation than either Group 1 or Group 2, since only minor amounts of the

demethylated hopanes are present in Group 3, and there is a full range of hopanes from C_{27} to C_{35}, although the C_{30}-C_{35} αβ compounds are depleted and the 22S compound is considerably larger than the 22R compound for the C_{31} to C_{33} αβ hopanes (except for Sample No. 9) (Fig. 3). When severe biodegradation has occurred in oil, the presence of 25- norhopanes is commonly recognized as a geochemical proxy for it because the 25-norhopanes are formed by the microbial removal of the methyl group at C-10 in the hopane nucleus (Seifert and Moldowan, 1979; Volkman et al., 1983; Peters et al., 1996; Tocco and Alberdi, 2002; Bennett et al., 2006). However, many seep oils and tar sand from Athabasca, South Texas, Greece, Central Adriatic Basin, and offshore West Africa have reported no identification or are devoid of 25-norhopanes even though hopanes were degraded (Williams et al., 1986; Moldowan et al., 1992; Bigge and Farrimoine, 1998; Wenger and Isaksen, 2002; Bennett et al., 2006), which are consistent with our analyzed results of the Group 3. Hence, the variation between hopane and 25-norhopane in our three groups from the Grosmont and Nisku Formations also indicated that these compounds are not consumed and produced by the specific biodegradation pathways but are results of complex reactions in association with the many different combination of environmental conditions and microbial processes (Peters et al., 2003; Bennett et al., 2006). There are required conditions for the occurrence of the biodegradation of bitumen such as water, electron acceptors, temperature, which support microbial life. Hoffmann and Strausz (1986) revealed that the regional groundwater flow and amount, and weathering of carbonate formation in the subsurface are critical factor for the numbers of microbial populations that undertook bitumen biodegradation in the Grosmont Formation. Therefore, the water chemistry of each sampling site in our study area may have significantly influenced the microbial environment. In addition, the stratigraphy may have partly influenced the biodegradation because the degree of biodegradation shows the significantly difference between the Grosmont and Nisku Formations at Site 07-26-88-24w4.

The degree of biodegradation is generally more severe in the Nisku Formation than in the Grosmont Formation since the Group 1 and Group 3 samples are from the Grosmont Formation, while the Group 2 samples are from the Nisku Formation. However, Brooks et al. (1989) demonstrated that the Grosmont bitumen has been more severely biodegraded than the Nisku bitumen. On the other hand, Zhao and Machel (2011) revealed that the biodegradation degree of Grosmont and Nisku bitumens has been partly different with sampling location. Even though our data are consistent with Zhao and Machel (2011), this discrepancy of the biodegradation degree between the Grosmont and Nisku Formation has remained a subject of debate due to the limited number of biomarker results. Hence, more biomarker results of bitumens from the Grosmont and Nisku Formations are needed to characterize the biodegradation degree and processes between them.

The calculated peak ratio data from the m/z 191 triterpane fragmentograms show the variation in ratio 1 [27Tm/(27Tm + 30αβ + 30βα)] and in ratio 2 [C_{24} tricyclic (24/3) terpane/30αβ hopane] (Table 3), which are also mainly related to the changes in abundance of the C_{30} compounds and 30αβ hopane caused by the difference in the degree of biodegradation. The higher values of ratio 3 for Group 1 and Group 2 samples (i.e., values from 0.18–0.34) are also considered to be due to stronger biodegradation of the 30αβ hopane and the relatively lower level of biodegradation

Table 3. Triterpanes and steranes peak height ratios in EOM of the samples

Sample No.	Triterpanes				Steranes			
	Ratio 1	Ratio 2	Ratio 3	Ratio 4	Ratio 5	Ratio 6	Ratio 7	Ratio 8
1	0.73	1.24	0.18	45.57	1.34	40.16	0.89	0.84
2	0.75	0.86	0.13	45.51	1.40	32.38	0.87	0.83
3	0.74	1.09	0.18	56.22	1.37	41.87	0.86	0.82
4	0.74	0.48	0.09	59.75	1.34	29.50	0.88	0.84
5	0.70	5.69	0.19	–	1.59	50.27	0.93	0.88
6	0.73	7.96	0.34	–	1.54	61.76	0.93	0.87
7	0.75	1.18	0.11	80.83	1.35	24.16	0.87	0.84
8	0.75	0.35	0.11	74.43	1.33	22.52	0.89	0.85
9	0.75	0.78	0.10	53.70	1.31	24.18	0.88	0.85
10	0.76	1.42	0.11	77.90	1.37	21.89	0.86	0.82
11	0.75	0.54	0.11	61.44	1.30	29.45	0.86	0.82
12	0.74	0.89	0.13	64.76	1.37	37.46	0.88	0.84

Ratio 1: 27Tm/(27Tm + 27Ts), Ratio 2: 24/3/30αβ, Ratio 3: (29βα + 30βα)/(29αβ + 30αβ), Ratio 4: 32αβS/(32αβS + 32αβR)%, Ratio 5: (27dβS + 27dβR + 27dαR + 27dαS)/(29dβS + 29dβR + 29dαR + 29dαS), Ratio 6: 29ααS/(29ααS + 29ααR)%, Ratio 7: 21α + 22α/(21α + 22α + 29ααS + 29ββR + 29ββS + 29ααR), Ratio 8: 21α + 22α/(21α + 22α + 28dαS + 28ααS + 29dαR + 29ααS + 29ββR + 29ββS + 29ααR).
–: no measurement.

https://doi.org/10.1007/s12303-018-0021-4

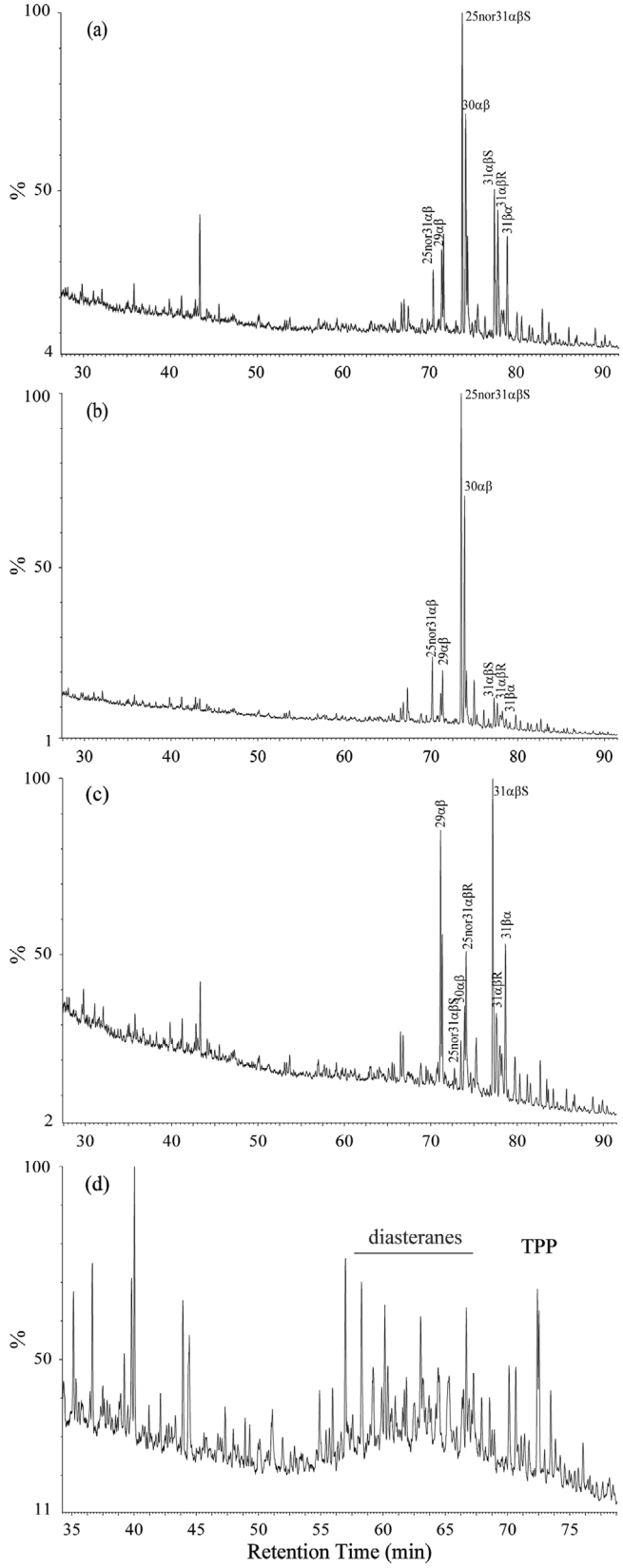

Fig. 7. Terpanes distribution in the fragmentograms (m/z 205) from (a) Group 1 (Sample No. 1), (b) Group 2 (Sample No. 5), and (c) Group 3 (Sample No. 7). (d) Steranes distribution in the fragmentograms (m/z 259) from Group 2 (most biodegraded; Sample No. 5) where the TPP doublet (twin peak) is relatively more abundant than other groups.

of the βα compounds (Table 3). In addition, the wide variation in ratio 4 is due to differences in biodegradation. The variation marks a particular stage in biodegradation where three of the four Group 3 samples have much higher values of ratio 4 than can be explained by maturity (Table 3).

The predominant compounds observed in the m/z 205 fragmentograms of the samples are either the C_{31} αβ 22S and 22R hopanes and the C_{31} βα moretane or the two C_{30} demethylated hopanes 25nor31αβ 22R and 22S. These two C_{30} demethylated hopane compounds are predominant in those samples where the two C_{31} αβ 22R and 22S hopanes are the most biodegraded (Fig. 7).

Sterane ratios are not calculated in all ratios since the peaks of the sterane are lacking due to biodegradation. However, the C_{27}/C_{29} diasterane ratio (ratio 5 in Table 3) is relatively constant, ~1.3–1.4, which is fairly typical for marine source rocks (Moldowan et al., 1985; Peters and Moldowan, 1993; Al-Areeq and Maky, 2015). The higher C_{27}/C_{29} diasterane ratio values for the more biodegraded Group 2 samples (1.54 and 1.59) are probably influenced by biodegradation (i.e., more advanced biodegradation of the C_{29} components) (Table 3). The ratio 6 for the samples reflected the degree of conversion for the 20R→20S compounds with increasing maturity generally (Table 3) and indicates values close to equilibrium (or maximum values), i.e., ~50%, for samples from Groups 1 and 2 and values for the Group 3 samples indicating slightly lower maturities (32–44%). However, this difference is probably mainly due to a higher degree of biodegradation for Groups 1 and 2 than Group 3. Ratios 6 and 7 in Table 3 are high due to the high proportion of the $C_{21\text{-}22}$ steranes. The amounts of the C_{26}-C_{28} peaks in the heavier aromatics (e.g., tri- and monoaromatic steranes) are more abundant in all samples and the C_{28} compounds, which are more resistant to biodegradation, particularly the 20S compound, are considerably more abundant than the C_{27} and C_{26} compounds (Fig. 4) (Peters et al., 2005).

Phenanthrene and alkyl phenanthrene, as well as sulfur aromatic HCs, indicate only minor or trace levels in the light aromatic HCs. The low content of these compounds is mainly due to losses of most of the lighter compounds through biodegradation.

6. CONCLUSIONS

1. The studied samples yield rich extracted bitumen, where the fraction of NSO and asphaltene compounds is higher than the saturated and aromatic HCs. The results of this study indicate that all samples have undergone severe biodegradation. The sulfur content and sulfur isotope values for the analyzed samples are also consistent with those values for oil and core samples from the Mannville Formation in the WCSB, which are

also influenced by biodegradation.

2. The GC and GC-MS data for both the saturated and aromatic HCs show remarkable variations among the samples. Most of these variations are probably due to variations in the degree of biodegradation. Based on the distribution of biomarkers, the analyzed samples can be classified into three groups. Groups l (Sample Nos. 1, 2, 3, 4, 11, and 12) and 3 (Sample Nos. 7, 8, 9, and 10) were collected from the Grosmont Formation and Group 2 (Sample Nos. 5 and 6) was collected from the Nisku Formation. Biomarker data also show that the degree of the biodegradation is more severe in the Nisku Formation than in the Grosmont Formation, which indicates a discrepancy with previous findings (Brooks et al., 1989). The primary cause of the discrepancy is likely the local characteristics or the limited number of samples for this study.

3. Reservoir alteration processes have altered the samples considerably. The most pronounced effects appear to be reduced amounts of the $C_{30}+$ hopanes and abundant demethylated hopanes, particularly in the Group 2 samples and the Group 1 samples but not in the Group 3 samples. For the Group 3 samples, unlike Group 1 samples, degradation of the hopanes apparently does not result in demethylated hopanes, suggesting another pathway to the destruction of the αβ hopanes for the Group 3 samples.

ACKNOWLEDGMENTS

We thank Dr. I.L. Ferriday and Mr. P.B. Hall of FUGRO GEOLAB NOR AS for their kind helps with geochemical analyses and Prof. S.J. Choh (Korea University) for providing the carbonate rock samples. This study was funded by Korea Institute of Energy Technology Evaluation and Planning under the support of Korean Ministry of Trade, Industry and Energy (Project No. 20162010201980). Additional supports were from Gas Hydrate Exploration and Production Study (18-1143) under the management of the Gas Hydrate Research and Development Organization (GHDO) funded by the Korean Ministry of Trade, Industry and Energy and from Research and from Development on Geochemical Proxies of Isotope and Trace Element for Understanding of Earth and Universe Evolution Processes (GP2017-018) funded by the Korea Ministry of Science and ICT.

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