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Effects of Sub-Aerial Weathering on Hydrocarbon Distributions in Oil Sands (Athabasca Oil Sand, Canada and Parana Basin, Brazil)

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Abstract: ***Sub-aerial weathering plays a significant role in the reduction of low molecular weight hydrocarbons in surface exposed oils. In order to investigate the detailed effects of sub-aerial weathering as opposed to sub-surface biodegradation, a suite of ten (10) oil sand samples were solvent extracted and analyzed in the laboratory using liquid column chromatography separation, gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The gas chromatograms showed total loss of n-alkanes and isoprenoids while the ion mass chromatograms showed alternation in steranes, little loss of hopanes and no pronounced loss of higher molecular weight of triaromatic steroids; thus, they were at between levels 5-8 on the Peters and Moldowan (PM) scale of biodegradation. GC-MS analysis was performed to analyze biological markers. Among the biological markers, the most important and noticeable effects were a decrease in the 20S/20R diastereomer ratio of the C_{29} steranes. There were also evident effects on the overall distributions and abundance of pentacyclic terpanes thus, leading to alteration of biomarker parameters which could result in erroneous interpretation of source depositional environments, source correlation and maturity.***

Keywords: Sub-aerial weathering, biodegradation, oil sand, hydrocarbon distributions, biological markers

1. Introduction

There have been numerous reviews concerned with the alterations in the distributions of hydrocarbons of crude oil biodegraded in the reservoir and also during the weathering of surface seeps or spills (Palmer, 1993; Douglas *et al.*, 1996; Swannell *et al.*, 1996). Weathering is an oxidation process where sediments or oil sands are exposed to the external environment for an extended period of time or are not deeply buried under the overburden (Lo and Cardott, 1995). These weathering processes include biodegradation, evaporation, dissolution and photo-oxidation (Albaiges and Albrecht, 1979). Hydrocarbon oxidation in the subsurface occurs mainly as biodegradation. This study aimed at investigating the effects of sub-aerial weathering on hydrocarbon distributions in oil sands and compares these effects with the biodegradation of oil occurring within the reservoir rock.

Biodegradation is the biochemical process that occurs in the reservoir at shallow depth and low temperature (< 80°C) where petroleum in the subsurface reservoir is biologically degraded by micro-organisms resulting to changes in the physical properties (. i.e., density, viscosity, acidity, sulphur content and API gravity) that determines well flow rate (Larter *et al.*, 2006) and chemical composition of oil either by aerobic or anaerobic process (Connan, 1984; Head *et al.*, 2003). Increasing level of biodegradation causes a decline in oil quality diminishing the value of oil thus oil becomes more viscous, richer in sulfur, resin, asphaltenes and metals (e.g., Vanadium and Nickel), has a higher total acid number and lower API gravity (Connan, 1984; Peters and Moldowan, 1993; Wenger *et al.*, 2002; Head *et al.*, 2003; Jones *et al.*, 2008). Biodegradation of crude oil could be under aerobic (Larter *et al.*, 2000) and anaerobic condition (Horstad *et al.*, 1992).

Sub- aerial weathering plays a significant part in the reduction of low molecular weight hydrocarbons. This weathering takes place under atmospheric air at the surface of the earth thus exposing sediments to the external environment for an extended period of time via physical processes. i.e., frost action and running water. It causes depletion in total organic carbon, decrease in extractable organic matter and alteration in hydrocarbon composition (Clayton and Swetland, 1978). There is an increase in the ratio of saturated to aromatic hydrocarbon and loss of *n*-alkanes relative to branched and cyclic alkanes when sediments are exposed to atmospheric air (Clayton and Swetland, 1978).

1.1 Study area

In this study, oil sand samples were collected from Athabasca tar sand and Paranà Basin located in Canada and Brazil respectively.

Athabasca oil sands are located in northeastern Alberta, where they underlie in an area in excess of 26,000km^2 between latitudes 55 and 58°N and longitudes 110 and 114°W. They outcrop extensively in the valleys of the Athabasca River and it tributaries north of the town of Fort McMurray Formation (

Figure 1). They hold the largest and most accessible reserves of bitumen with resources mainly in the McMurray Formation of the Lower Cretaceous Mannville Group (Barson *et al.*, 2001).

Figure 1A: Case study location (Athabasca oil sands)

Alberta's oil sands contain the biggest known accumulation of hydrocarbons in the world. An estimated 1.7 to 2.5 trillion barrels of oil are trapped in a complex mixture of sand, water and clay. It is a deposit of sand/clay heavily impregnated with semi solid or solid bitumen; it contains naturally occurring mixtures of sand/clay, water and bitumen (Fig 1 A). The oil sand is composed of approximately 70% sand and clay, 10% water, and from 0% to 18% of bitumen). The Athabasca Oil Sands are hydrophilic. The grains of the sand are surrounded by a film of water, which is then surrounded by oil

The second area where samples were collected is the tar sand of the Paranà basin. The Paranà basin is located in southern Brazil, where it covers an area of over 1,000,000km^2 and reaches neighboring countries such as Argentina, Uruguay, Paraguay with an additional area of 400,000km^2 (Figure 1). The basin is a large Ordovician – Cretaceous intracratonic basin filled by five major depositional sequences predominantly siliciclastic in nature (Zalàn *et al.*, 1990), the basin has a NNE-SSW- trending elliptical shape with two-thirds of its surface covered by Mesozoic basaltic lavas. The stratigraphic record of this basin exceeds 7,000m in thickness in the central depocentres (Milani and Zalàn, 1998). In the Paranà basin, tar accumulations are in the Lower Triassic sandstones along the eastern margin of the basin and the tars are derived from bituminous black shales of late Permian (Araújo *et al.*, 2000).

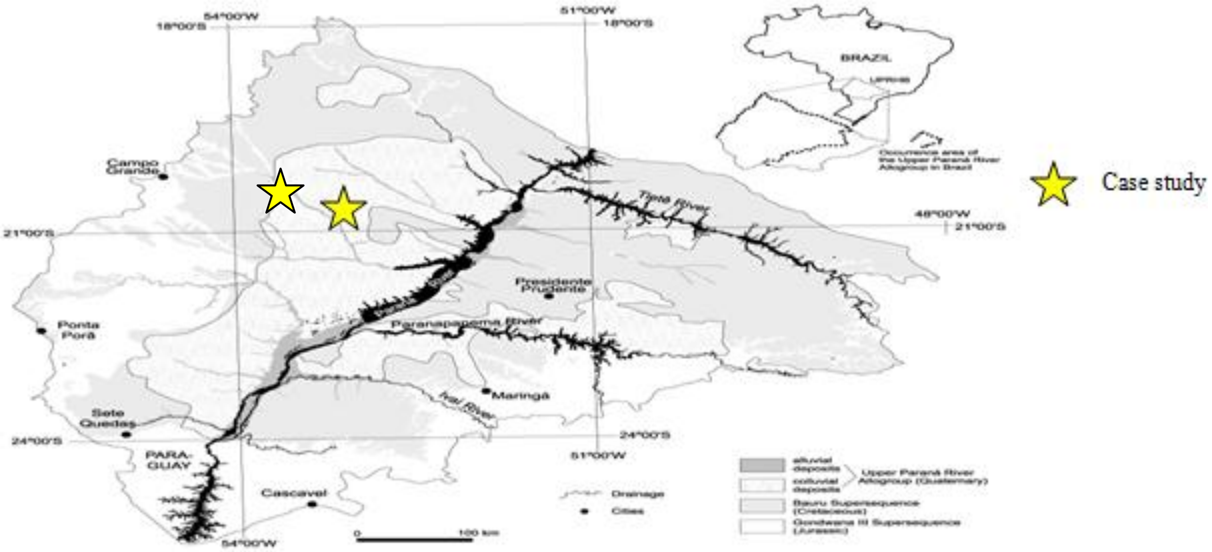

Figure 1B: Geologic map of the Paraná Basin showing case study (Sallun *et al.*, 2008).

2. Background Information

Several studies have shown that surface weathering of organic matter in outcrop samples can result in depletion of total organic matter content by as much as 50 to 60% and reduction in aromatic hydrocarbon relative to saturated hydrocarbons (Leythaeuser, 1973; Clayton and Swetland, 1978; Forsberg and Bjorøy, 1983). Studies by Leythaeuser (1973) showed that weathering results in the decrease in amount of organic matter, chemical composition and aromatic hydrocarbon.

Studies by Clayton and Swetland (1978) and Forsberg and Bjorøy (1983) also reveal that the ratio of saturated-to-aromatic hydrocarbons increase and *n*-alkanes are lost relative to branched and cyclic alkanes during weathering. Outcrops samples of Meade Peak Phosphatic Shale of the Permian Phosphoria Formation of northeastern Utah and shallow core samples of Mitten member of the Upper Cretaceous Pierre Shale of Colorado were analyzed and compared to determine the effects of weathering on the exposed outcrop samples.

Studies from Clayton and Ryder (1984); also showed effects of weathering on the relative amounts of the C_{19} to C_{21} tricyclic diterpanes. Thus, by comparing core samples and the weathered outcrop samples, which showed that the general distribution of tricyclic was similar throughout the core except shallow, weathered samples contain relatively low amounts of the C_{19} to C_{21} components relative to the C_{23} to C_{26} components (C_{19} component is completely lost). In terms of steranes, there is an evident loss of 20S diastereomer; thus, there is a low 20S/20S+20R ratio which is a maturity parameter to assess generation of petroleum (Seifert and Moldowan, 1981).

However, there have been limited published studies on the sub-aerial weathering effects on hydrocarbon distributions (with reference to aromatic hydrocarbon) and biomarkers where sediments have been exposed to atmospheric air.

3. Materials and Methods

3.1 Materials

The reagents included; Light petroleum spirit (petroleum ether), dichloromethane (DCM) and methanol. A suite of ten (10) oil sand samples were collected from two locations; the Athabasca tar sand deposit in Canada and the Parana Basin in Brazil. The samples were solvent extracted to get the extracts using Soxtec extraction and the following analyses were carried out in the laboratory; liquid column chromatography, gas chromatography (GC-FID) and gas chromatography-mass spectrometry (GC-MS).

3.2 Laboratory Techniques

Soxtec Extraction

The samples were solvent extracted using a Soxtec extraction apparatus. 130mL of an azeotropic mixture (93% distilled DCM and 7% methanol) mixture was used, along with activated copper turnings and anti-bumping granules. The samples were put in thimbles and covered with cotton wool along with the azeotropic mixture and were introduced into the Soxtec extractor; this was left to run at a temperature of 210°C for 4hours. The weight of the extractable organic matter was calculated and recorded.

Liquid Column Chromatography

The extract from the Soxtec extraction procedure was transferred to a 10mL measuring cylinder. 1ml of extract was taken and transferred to a 10mL vial. The column was washed and filled with petroleum ether and a slurry of silica in light petroleum ether was made and used to pack the column. A small quantity of alumina slurry was added to the bed of silica in the column and the weighed oil sample approximately 50mg was added to a small quantity of alumina in a 10mL vial. The alumina/oil sample was carefully added to the top of the column. The column was eluted with 70mL of petroleum ether ((Douglas *et al.*, 1991; Bennett and Larter, 2000) and the aliphatic hydrocarbon fraction was collected while the aromatic fraction was subsequently eluted using a similar volume of a 60:40

mixture of petroleum ether and dichloromethane (DCM) solvent. Both fractions were evaporated and 1mL was transferred to a GC vial and GC trace was then obtained.

Gas Chromatography (GC-FID)

GC-FID analysis of aliphatic and aromatic hydrocarbon fractions was performed on a Hewlett-Packard/Agilent (5890/6890/7890) GC in split-less mode, the injector at 280°C, FID at 310°C (Huang *et al.*, 2004). The data were acquired and stored on an Atlas laboratory data system. The sample (1ul) in Hexane/DCM was injected by an HP7673/7683 auto sampler and the split was opened after 1 minute. Separation was performed on a fused silica capillary column. The GC was temperature programmed from 40°C-300°C at 4°C min. The acquired data was stored on DVD for later data processing, integration and printing.

Gas Chromatography-Mass Spectrometer, GC-MS (Agilent 7890A)

GC-MS was used to identify and quantify biomarkers in the samples (e.g., Peters and Moldowan, 1993; Wang and Fingas, 2006). GC-MS analysis of the aliphatic and aromatic compounds was performed on an Agilent 7890A GC with split/split less injector (280°C). The sample (1ul) in hexane was injected by an HP7683B auto sampler and the split was opened after 1 minute. Separation was performed on an Agilent fused silica capillary column coated with phenyl-methyl polysiloxane (HP-5) phase (Huang *et al.*, 2004). The acquired data was stored on DVD for later data processing, integration and printing. Peaks were identified and labeled.

4. Results

The results of the effects of sub-aerial weathering on the distributions of hydrocarbons in oil sands are illustrated and shown below.

4.1 Gas chromatograms

These shows that the oil sand samples in the different locations are heavily degraded with the *n*-alkanes and isoprenoids having been consumed and with the presence of prominent humps indicating unresolved complex mixtures (UCM); Figure 2 is an example of gas chromatograms of oil sand hydrocarbon fractions showing heavy biodegradation and sub-aerial weathering effects on hydrocarbons causing removal of *n*-alkanes and isoprenoids.

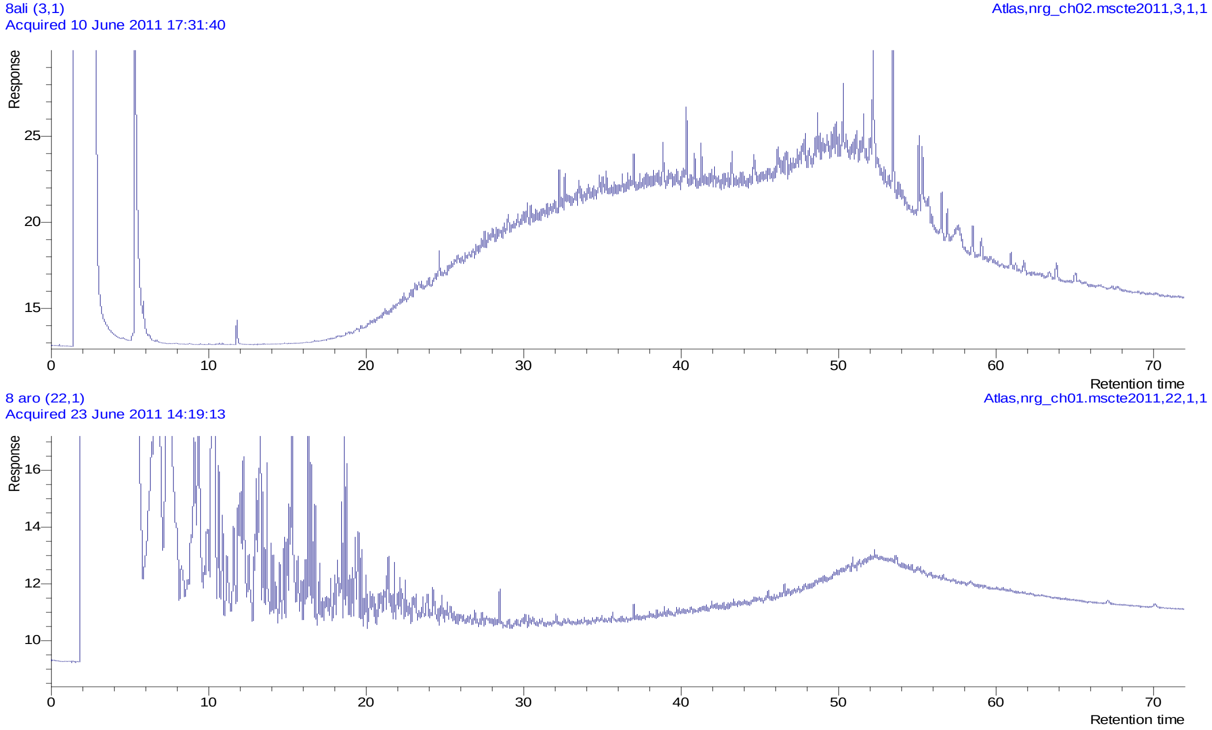

Figure 2: Gas chromatogram of aliphatic (top) and aromatic (bottom) hydrocarbon fractions of MTABA 1 (exterior) showing loss of *n*-alkanes and isoprenoids in the aliphatic hydrocarbons and alkyl-naphthalenes in the aromatic hydrocarbon fraction with presence of humps of unresolved complex mixtures

4.2 Gas chromatography mass spectrometry (GC-MS) results

4.2.1 Steranes

Sub-aerial and subsurface effects on steranes biomarkers were illustrated in the figures below to infer the level of degradation in-terms of abundance using ratios of peak heights and areas. These peak areas or heights were also used to determine maturity and depositional environment.

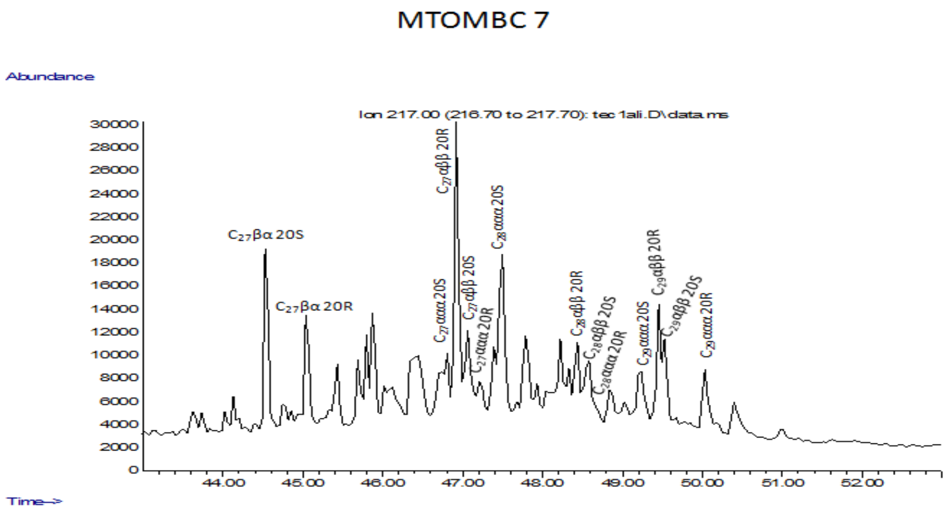

Figure 3: m/z 217 ion mass chromatogram for the aliphatic hydrocarbon fraction of sample MTOMBC 7 showing ααα as well as αββ steranes. Peaks identified properly in Table 1.

Table 1: Detailed peak assignments for sterane biomarkers.

Peak label	Peak name
C_{27}βα20S	C_{27} 13β(H), 17α(H)-diasteranes 20S
C_{27}βα20R	C_{27} 13β(H), 17α(H)-diasteranes 20R
C_{27}ααα20S	C_{27} 5α(H), 14α(H), 17α(H)-steranes 20S
C_{27}αββ20R	C_{27} 5α(H), 14β(H), 17β(H)-steranes 20R
C_{27}αββ20S	C_{27} 5α(H), 14β(H), 17β(H)-steranes 20S
C_{27}ααα20R	C_{27} 5α(H), 14α(H), 17α(H)-steranes 20R
C_{28}ααα20S	C_{28} 5α(H), 14α(H), 17α(H)-steranes 20S
C_{28}αββ20R	C_{28} 5α(H), 14β(H), 17β(H)-steranes 20R
C_{28}αββ20S	C_{28} 5α(H), 14β(H), 17β(H)-steranes 20S
C_{28}ααα20R	C_{28} 5α(H), 14α(H), 17α(H)-steranes 20R
C_{29}ααα20S	C_{29} 5α(H), 14α(H), 17α(H)-steranes 20S
C_{29}αββ20R	C_{29} 5α(H), 14β(H), 17β(H)-steranes 20R
C_{29}αββ20S	C_{29} 5α(H), 14β(H), 17β(H)-steranes 20S
C_{29}ααα20R	C_{29} 5α(H), 14α(H), 17α(H)-steranes 20R

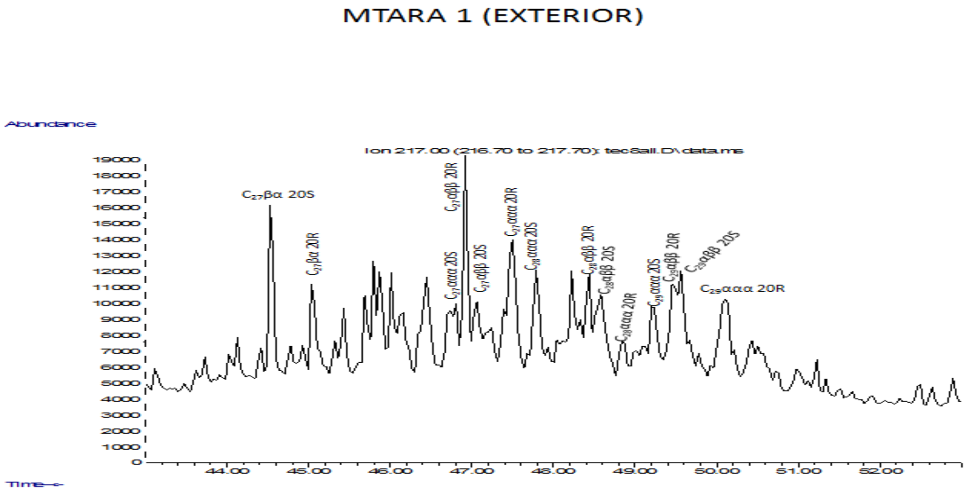

Figure 4: m/z 217 ion mass chromatogram for the aliphatic hydrocarbon fraction of sample MTABA 1 that has undergone sub-aerial weathering showing ααα as well as αββ steranes. Note: there is reduction in abundance of the C_{27-29} ααα20S isomer. Peaks identified properly in Table 1.

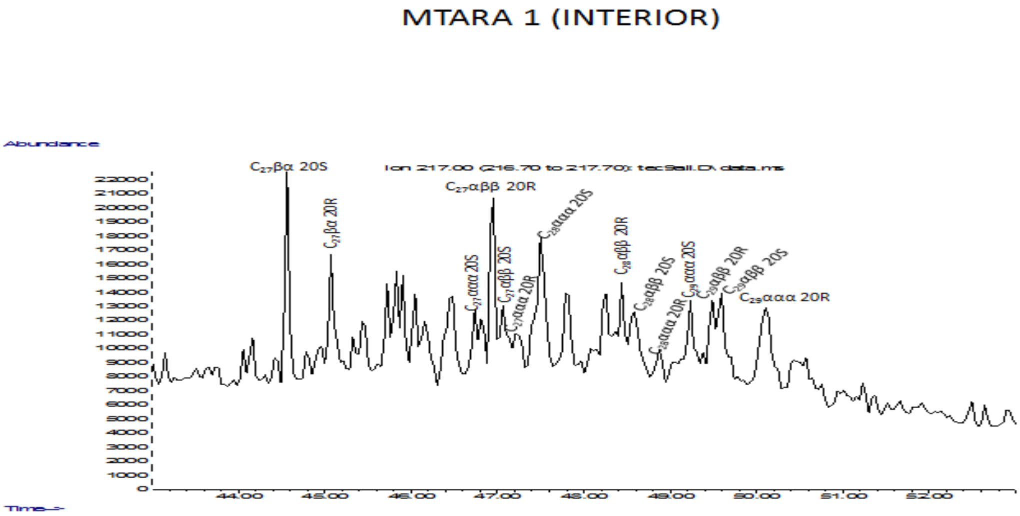

Figure 5: m/z 217 ion mass chromatogram for the aliphatic hydrocarbon fraction of the less weathered sample MTABA 1 showing ααα as well as αββ steranes. Note; the reduction in abundance of the ααα 20R isomer thus, $C_{27} > C_{28} > C_{29}$. Peaks identified properly in Table 1.

4.2.2 Hopane biomarkers

Sub-aerial and subsurface weathering effects on hopane biomarkers were illustrated in the figures below to infer the level of degradation and effects of sub-aerial weathering in-terms of abundance using ratios of peak heights or areas and to determine these effects on maturity and depositional environment parameters.

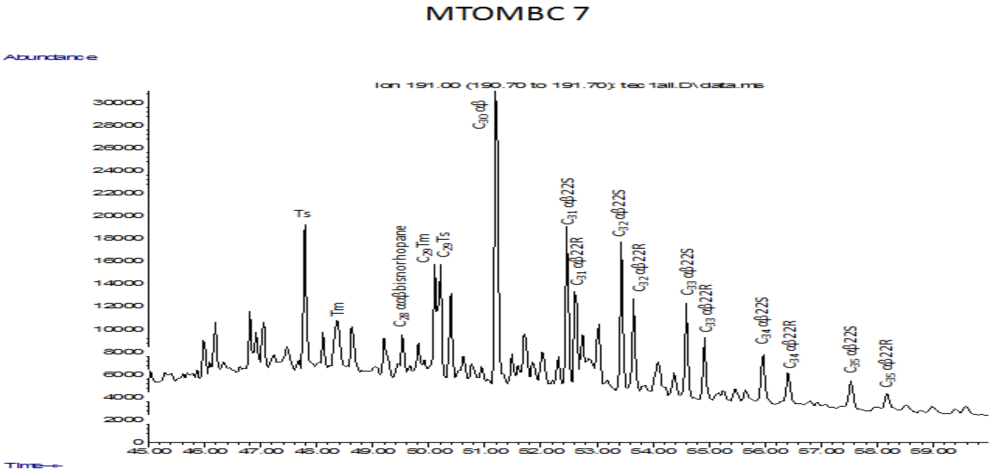

Figure 6: m/z 191 ion mass chromatogram for the aliphatic hydrocarbon fraction of sample MTOMBC 7 (oil seep) showing Ts, Tm, βα as well as αβ hopanes. Note: presence of Bisnorhopanes. Peaks identified properly in Table 2.

Table 2: Detailed peak assignments for hopane biomarkers.

Peak label	Peak name
Ts	C_{27}18α(H)-22,29,30-trisnorneohopane
Tm	C_{27}17α (H) 22, 29, 30-trisnorhopane
C_{28}ααβbnh	C_{28}17α(H),21β(H)-28,30bisnorhopanes
C_{29}Tm	C_{29} 17α(H),21β(H)-30-norhopane
C_{29}Ts	C_{29} 18α(H)-30-norneohopane
C_{30}αβ	C_{30} 17α(H),21β(H) hopane
C_{31}αβ22S	C_{31} 17α(H),21β(H) 22S hopane
C_{31}αβ22R	C_{31} 17α(H),21β(H) 22R hopane
30 Gamm	Gammacerane
C_{32}αβ22S	C_{32} 17α(H),21β(H) 22S hopane
C_{32}αβ22R	C_{32} 17α(H),21β(H) 22R hopane
C_{33}αβ22S	C_{33} 17α(H),21β(H) 22S hopane
C_{33}αβ22R	C_{33} 17α(H),21β(H) 22R hopane
C_{34}αβ22S	C_{34} 17α(H),21β(H) 22S hopane
C_{34}αβ22R	C_{34} 17α(H),21β(H) 22R hopane

C_{35}αβ22S	C_{35} 17α(H),21β(H) 22S hopane
C_{35}αβ22R	C_{35} 17α(H),21β(H) 22R hopane

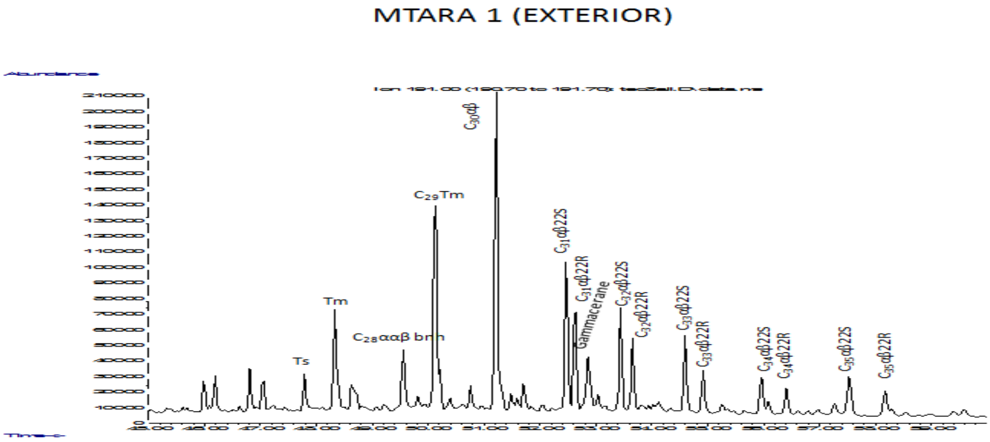

Figure 7: m/z 191 ion mass chromatogram for the aliphatic hydrocarbon fraction of sample MTABA 1 that has undergone sub-aerial weathering showing βα and αβ hopanes. Note: presence of low bisnorhopanes and gammacerane. Peaks identified properly in Table 2.

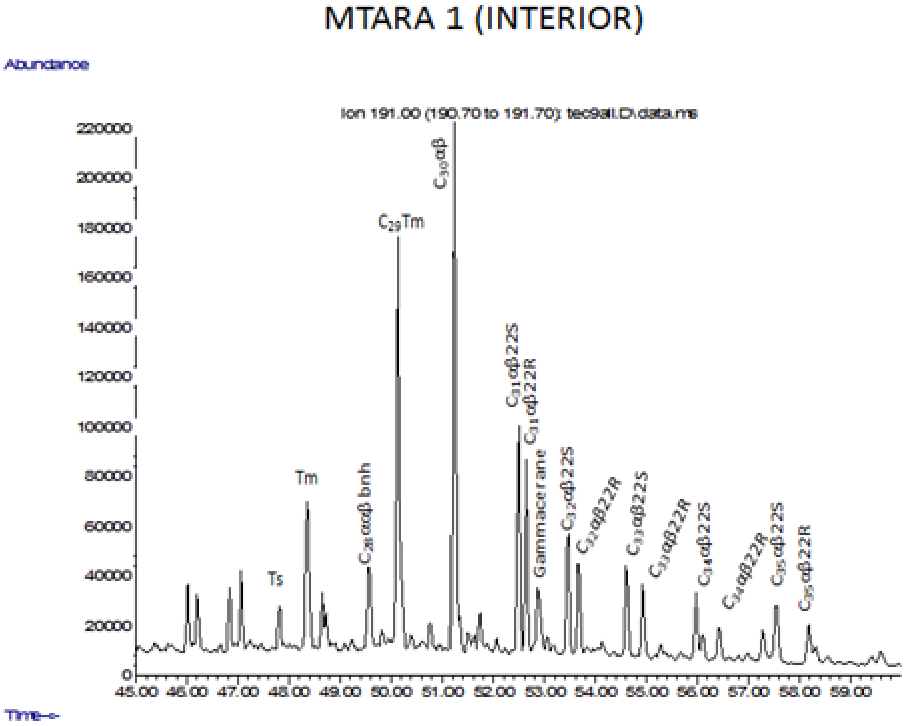

Figure 8: m/z 191 ion mass chromatogram for the aliphatic hydrocarbon fraction of the less weathered sample MTARA 1 showing βα and αβ hopanes. Note: presence of low bisnorhopanes and gammacerane. Peaks identified properly in Table 2

Table 3: Measured maturity indicating biomarker ratios.

SAMPLES	Maturity	
	HOPANES	STERANES
	22S/22S+22R (%)	20S/20S+20R (%)
MTOMBC 7	58.8	51.9
MTPBO 54 (interior)	55	49.2
MTPBO 54 (exterior)	55.9	48.8
MTARA 1 (exterior)	58.8	23.2
MTARA 1 (interior)	57.6	27.5
MTARA 2 (exterior)	59.6	30.1
MTARA 2 (interior)	52.8	42.8

From the different maturity parameters above, it shows that hopane maturity ratios increase with sub-aerial weathering while sterane maturity decreases with sub-aerial weathering.

Table 4: Measured depositional environment parameters.

Samples	Depositional Environment				
	HOPANES			STERANES	
	C_{35}/C_{34}	Gam/C_{30}	C_{29}/C_{30}	C_{27}/C_{28}	C_{27}/C_{29}
MTOMBC 7	0.79	0.099	0.31	0.86	0.62
MTPBO 54 (interior)	0.95	0.82	0.57	0.469	0.221
MTPBO 54 (exterior)	0.76	0.41	0.44	0.677	0.378
MTARA 1 (exterior)	1.28	0.22	0.84	4.775	1.45
MTARA 1 (interior)	1.18	0.2	0.91	1.14	0.247

MTARA 2 (exterior)	1.99	0.57	0.91	2.32	0.518
MTARA2 (interior)	1.63	0.39	0.83	0.816	0.285

5. Discussion of Results

In sub-aerial weathering, there is depletion of some saturated and aromatic hydrocarbons, biological markers and loss of low molecular weight aromatic steroidal compounds. These weathering effects results in variability in the ratios of saturated and aromatic hydrocarbons, which affect their interpretation for providing information on their maturity, sources and source depositional environments.

5.1 *n*-alkanes and isoprenoids

The oil sands located in the Athabasca tar sand and the Parana Basin are heavily-severely biodegraded (Brooks *et al.*, 1988; Larter *et al.*, 2000; Araújo *et al.*, 2000). As a result of this heavy biodegradation, the *n*-alkanes and isoprenoids in them have been totally consumed, so it is not possible to observe changes in the distributions of *n*-alkanes and isoprenoids in the sub-aerially weathered oil sand samples and the less weathered oil sand samples. Figure 2 show heavy biodegradation of oils from the total consumption of *n*-alkanes, branched alkanes, isoprenoids and with the presence of prominent humps. These humps consist of bio-resistant molecules like highly branched, cyclic saturates, aromatic and naphtha-aromatic that are not amenable to GC (Peters *et al.*, 2005b).

5.2 Biological markers

5.2.1 Steranes

Regular steranes biological markers are more susceptible to sub-aerial weathering and subsurface weathering relative to diasteranes and hopanes biomarkers (e.g., Seifert and Moldowan, 1979; Chosson *et al.*, 1991). Figure 4 shows that C_{27}, C_{28} and C_{29} steranes in sample MTARA 1 (exterior) are more depleted and have lower peak areas in the mass chromatograms when sub-aerially weathered compared to when less-weatheredin sample MTARA 1 (interior) in Figure 5. The diasteranes which have been recognized (e.g., Volkman *et al.*, 1983a; Connan, 1984) to be more resistant to subsurface weathering were not affected by sub-aerial weathering thus, diasteranes are preferentially bio-resistant with increasing carbon number and are rarely depleted in heavily biodegraded oil (Seifert and Moldowan, 1979). Depletion of C_{27-29} regular steranes in sub-aerially weathered sample relative to the less weathered sample could possibly be as a result of oxidation processes aiding aerobic bacteria for degradation (Seifert and Moldowan, 1979; Chosson *et al.*, 1991). Water washing that accompanies surface weathering has no effect on these biological markers due to the insolubility of steranes in water; however, these waters aid the presence of microbes that excrete enzymes which can react with biomarkers converting it to water soluble (Peters *et al.*, 2005b).

Another evident observation is the reduction in abundance of the C_{29} sterane 20S diastereomer relative to the 20R which results in a low 20S/20S+20R ratio (Table 1). This observation is consistent with Clayton and Swetland (1978) where they observed a low 20S/20S+20R ratio from the relative loss of 20S diastereomer during surface weathering in the Phosphoria Formation. The relative loss of the 20S diastereomer resulting to low 20S/20S + 20R ratio is opposite to the effect of bacterial degradation (e.g., Seifert *et al.*, 1981; Connan, 1984), where the 20R isomer is preferentially lost during biodegradation (subsurface weathering). This loss of the 20S configuration indicates that thermal maturity assessment based on steranes 20S/20S + 20R ratios would yield slightly low estimates for weathered samples compared to less weathered oil sand samples (Table 1) and this also suggests that bacterial oxidation might not be the major process during surface weathering of steranes.

5.2.2 Pentacyclic triterpanes

Hopane biomarkers are more resistant than steranes to biodegradation and weathering (Chosson *et al.*, 1991; Peters *et al.*, 2005). However, there are noticeable variations in hopane biomarker distributions of oil sands of MTARA 1 (exterior) and MTOMBC 7 exposed to sub-aerial weathering. It is observed from the mass chromatogram (Fig. 7) showed that sample MTABA 1 (exterior) has a lower peak area in hopane distributions when sub-aerially weathered than when less weathered (Fig 8) thus it shows a depletion in regular homohopanes (C_{35}>C_{34}>C_{33}>C_{32}>C_{31}) 22R relative to 22S. The same is observed for sampleMTOMBC 7 (Fig. 6). However, sample MTARA 1 (Fig. 7) showed higher peak areas of C_{30} hopane and C_{31-33} 22S isomers when sub-aerially weathered compared to when less weathered indicating that the relative susceptibility of hopanes and individual hopane isomers in degraded oils yield conflicting results. This infers that the relative degree of hopane biodegradation in oils might be reliant on the occurrences of certain factors. i.e., the population of microbes or some environmental dynamics aiding microbial processes (Peters *et al.*, 2005b). Furthermore, hopane parameters such as $C_{31}\alpha\beta$ 22S/22S+22R which is a sensitive maturity parameter changes during sub-aerial weathering resulting to a slightly higher ratio than the maturity ratio of the less weathered samples.

5.3 Effects of weathering on maturity parameters

Several maturity parameters of biomarkers (hopanes and steranes) were studied to check the effects of sub-aerial weathering on oil sands; parameters such as 22S/22S+22R (hopanes), 20S/20S+20R (steranes) were measured to determine the effect of sub-aerial weathering on maturity. The extent of isomerism of regular steranes and hopanes of the oil sands in the two locations infers that the oil sands show the same level of maturity though altered by sub-aerial weathering and biodegradation. It was observed that maturity ratios of hopanes (C_{31}22S/22S+22R) increased in sub-aerial weathered samples relative to less-weathered samples while steranes (C_{29}20S/20S+20R).

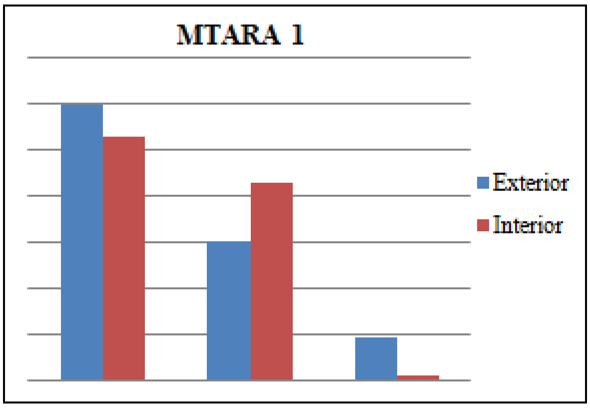

Figure 9: Effects of sub-aerial weathering on maturity parameters in sample MTARA 1. All maturity ratios increase with surface weathering except the 20S/20S+20R sterane ratio which decreases with weathering.

As a possible effect of water washing and oxidation processes in sub-aerial weathering, there is higher depletion of 22R relative to 22S diastereomer in hopanes resulting in higher maturity indicating ratios in the weathered samples relative to less weathered samples (Fig. 6 and 7).

5.4 Effects of weathering on depositional environment and source correlation parameters

Sub-aerial weathering has major evident effects on the interpretation of depositional environment when using various biomarkers and polycyclic aromatic hydrocarbons depositional environment indicators. Pentacyclic triterpanes parameters such as high C_{35}/C_{34}, Gam/C_{30} ratios and presence of 28, 30-bisnorhopanes; indicate anoxic depositional environments (Peters and Moldowan, 1991). The presence of abundant gammacerane infers hypersaline environments (Sinninghe-Damste *et al.*, 1995) and high relative presence of 28, 30-bisnorhopanes indicates reducing environment and possible carbonate lithology (Schoell *et al.*, 1992; Moldowan *et al.*, 1984).

The presence and relative abundance of these gammacerane and bisnorhopane biomarkers can be used in oil-source rock correlations. However, there are variations in the ratios of these indicators in weathered samples at the surface relative to less weathered samples which could result in a wrong interpretation of the depositional environment of the oil source (Table 4). There are also variations in depositional environment ratios using sterane parameters. e.g., C_{27}/C_{28} and C_{27}/C_{29} steranes. The variation results from preferential loss of 20S diastereomer relative to 20R of steranes in surface weathering; which infers high ratios of C_{27}/C_{28} and C_{27}/C_{29} steranes, thus, steranes ratios increase under the influence of sub-aerial weathering (Table 4, Fig. 3 and 4) (Moldowan *et al* 1984).

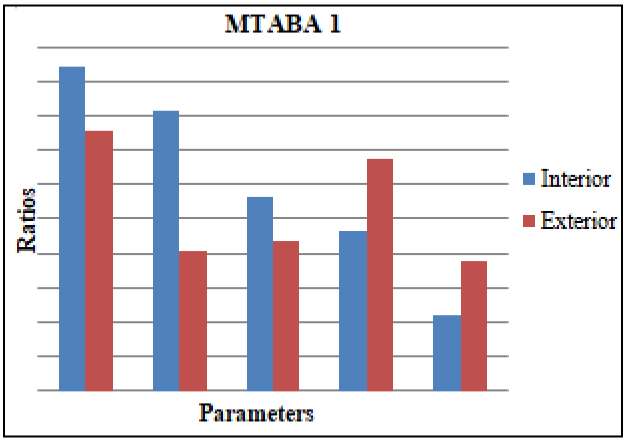

Figure 10: Variations in measured hopane (C_{35}/C_{34}, Gam/C_{30} and C_{29}/C_{30}) and sterane (C_{27}/C_{28} and C_{27}/C_{29}) depositional environment ratios in weathered (exterior) and less weathered (interior) MTABA 1 samples.

6. Conclusions

The extent of sub-aerial weathering induced changes in biomarkers and aromatic hydrocarbon distributions appeared to be variable, inconsistent and reliant upon a variety of factors. This investigation has thrown up potential windows of opportunity to discover more about the effect of sub-aerial weathering on oil sands in general and its bound biomarkers distribution and abundance. Aliphatic hydrocarbon biological markers were altered with preference to steranes which were depleted with loss of 20S diastereomer relative to 20R, a finding that is in contrast to the usually reported effects of biodegradation, but one that has been previously observed in a surface weathered shale. It is important to know the extent to which biomarkers are affected by exposure to atmospheric conditions, since biomarkers provide important information on the source depositional environment or thermal maturity of oil samples. An example can be seen from the measured C_{29}20S/20S+20R steranes maturity parameter and $C_{35}\alpha\beta/C_{34}\alpha\beta$ hopanes depositional environment parameters which showed variations during sub-aerial weathering. Indeed, sub-aerial weathering causes qualitative and quantitative alteration to the distribution of hydrocarbons and consequently changes parameters for assessing thermal maturation and environment of deposition which has great impact on the prospecting of petroleum. Thus, knowledge of the extent of surface weathering is useful for preliminary investigation in the evaluation of a basin in order to avoid costly errors prior to exploration process.

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