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Oil Biodegradation in Siliciclastic Reservoir: an Example from Paleogene, Oliva Block, North of Santos Basin, Brazil

Biodegradação de Óleo em Reservatório Siliciclástico: um Exemplo do Paleógeno, Bloco Oliva, Norte da Bacia de Santos, Brasil

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Abstract

For a petroleum company, the oil biodegradation is an important aspect to appraisal both exploration/production and economic perspective. Black to volatile oils require different materials and techniques in comparison to those used for heavy oils. Economically, biodegradable oils has a lower market value than the non-biodegradable oil. Following the presence and absence of a set of biomarkers observed in the chromatograms and fragmentograms, it is possible an interpretation and an indentification of different levels of biodegradation . This methodology comprises the main objective of this work. The oil studied lacks "n" and iso-alkanes, the major proportion of tricyclic on the pentacyclic, the presence of demethylated compounds, plus the major proportion of diasteranes on steranes, suggesting an advanced degree of biodegradation. According to this investigation, the degree 8 of biodegradation (Peter & Moldowan, 1993), records a huge process of bacterial attack happened into the reservoir in a range of temperature from 35^{0}C up to 50^{0}C, from the oil/water contact..

Keywords: Organic geochemistry; Biomarkers; Biodegradation

Resumo

Para as companhias de petróleo, o processo de biodegradação do óleo precisa ser caracterizado tanto na fase de exploração quanto de produção devido ao impacto econômico do projeto. Óleos não biodegradados requerem diferentes materiais e técnicas em relação aquelas utilizadas na investigação de óleos pesados. Economicamente, óleos biodegradados tem valor de mercado inferior aos não biodegradados. Através da presença ou ausência de um conjunto de biomarcadores identificados em cromatogramas e fragmentogramas torna-se possível a interpretação e identificação de diferentes graus de biodegradação. Essa metodologia investigativa constitui o objetivo principal deste trabalho. O óleo examinado nessa investigação apresenta ausência de *n*-alcanos e iso-alcanos, maior proporção de tricíclicos em relação a pentacíclicos, ocorrência de compostos desmetilados, além de maior proporção de diasteranos em relação aos esteranos,. Esses parâmetros geoquímicos permitiram caracterizar um elevado grau de biodegradação, de 8 na escala de Peters & Moldowan (1993), registrando um severo ataque bacteriano ocorrido a partir da interface do contato óleo/água, em temperaturas de reservatório entre 35^{0}C e 50^{0}C.

Palavras-chave: Geoquímica orgânica; Biomarcadores; Biodegradação

1 Introduction

The study of oil biodegradation process has been investigated by oil industry for a long time. Its importance lies in the fact that the biodegradation level defines what kind of explotation and refine techniques will be used. It also will need the appropriated industry installations to diferent levels of biodegradation.

This work aims the identification and characterization of the biodegradation that happens in the oil collected in the 1-BSS-0069-BS well, a siliciclastic reservoir of Paleogene age from Santos Basin.

2 Studied Area

The Santos Basin is located in the southeast portion of Brazilian continental margin, it is limited to the north by Cabo Frio Arch, to the south by Florianópolis Arch, to the east by bathymetry of 3000 m and to the west by Cretaceous hinge line. It has an overall area of 350.000 km^2 of extention (Mohriak, 2003).

2.1 Location of Area and Well

The well studied is located in the offshore portion of Santos Basin close to the border of Campos Basin (Cabo Frio High), in the Oliva Block (Figure 1).

2.2 Geology and Stratigraphy

Since the first discovery of hydrocarbon in Santos Basin made by Pecten (1980) (Merlusa Field), within turbidite sandstones of Itajai-Açu Formation, the exploratory studies have been intensified (Pereira & Macedo, 1990). With the Tubarão, Coral, Estrela do Mar and Caravela fields discoveries in the 1980 decade, Santos Basin has become a prominent area after the confirmation in the last years with the discoveries of Mexilhão, Tupi and Júpiter fields.

Latest estimates of Jones & Chaves (2015) shows a potential discovery of 179 billion barrels of recoverable oil (P90, it is igual to 90 % of occurence possibility) in pre-salt, and in the Tupi cluster only (Santos Basin) this volume is 139 billion barrels of recoverable oil (P90).

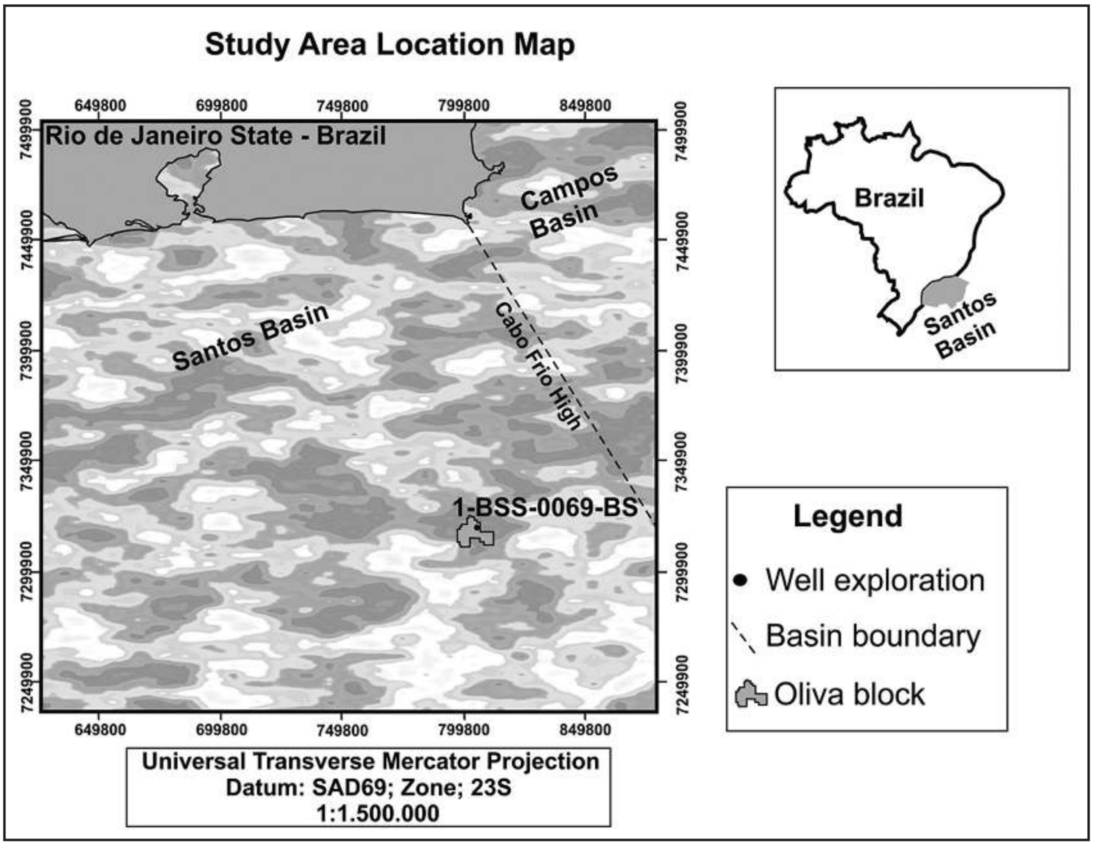


Figure 1 Location of well 1-BSS-0069-BS in Oliva Block, Santos Basin.

The basin genesis by Chang *et al*. (1990) and Moreira *et al.* (2007) is associated with extensional strains that led to the Gondwana break and the separation of South America and Africa as well as the others Brazilians east margin basins. This strain field was responsible for crustal thinning and sequential break. It has created the rifting of continental crust from Hauterivian to Albian. Landward facies (continental deposits - alluvial fans) shift to basinward facies (lacustrine and lagoon deposits) has filled the accommodation space. The post-rift phase (Aptian) is marked by tectonic quiescence with predominant thermal subsidence and deposits that are associated with conditions of stressful shallow waters (microbial, stromatolites and evaporites deposits). Because of drowning of evaporite deposits, the drift stage and the Atlantic Ocean installation have began. This stage develops until the present where shallow water, slope and deep waters deposits occur.

Studies of Pereira *et al.* (1986), Macedo (1989) e Moreira *et al.* (2007) subdivide the sedimentary packages in three tectonic stages: Rift (Valanginian - Lower Aptian), Post-Rift (Aptian) and Drift (Albian - Present). Moreira *et al.* (2007) have identified 25 second-order sequences which can be assembled in two cicles of retrogradation and progradation. It has been done with the help of Sequence Stratigraphy in the Santos Basin sedimentary package. The upper limits of these sequences are marked by erosion discontinuities and/or relative conformities (Figure 2).

3 Material and Methods

The oil studied in this paper was sampled in sandstone reservoir from the Oligocene – Middle

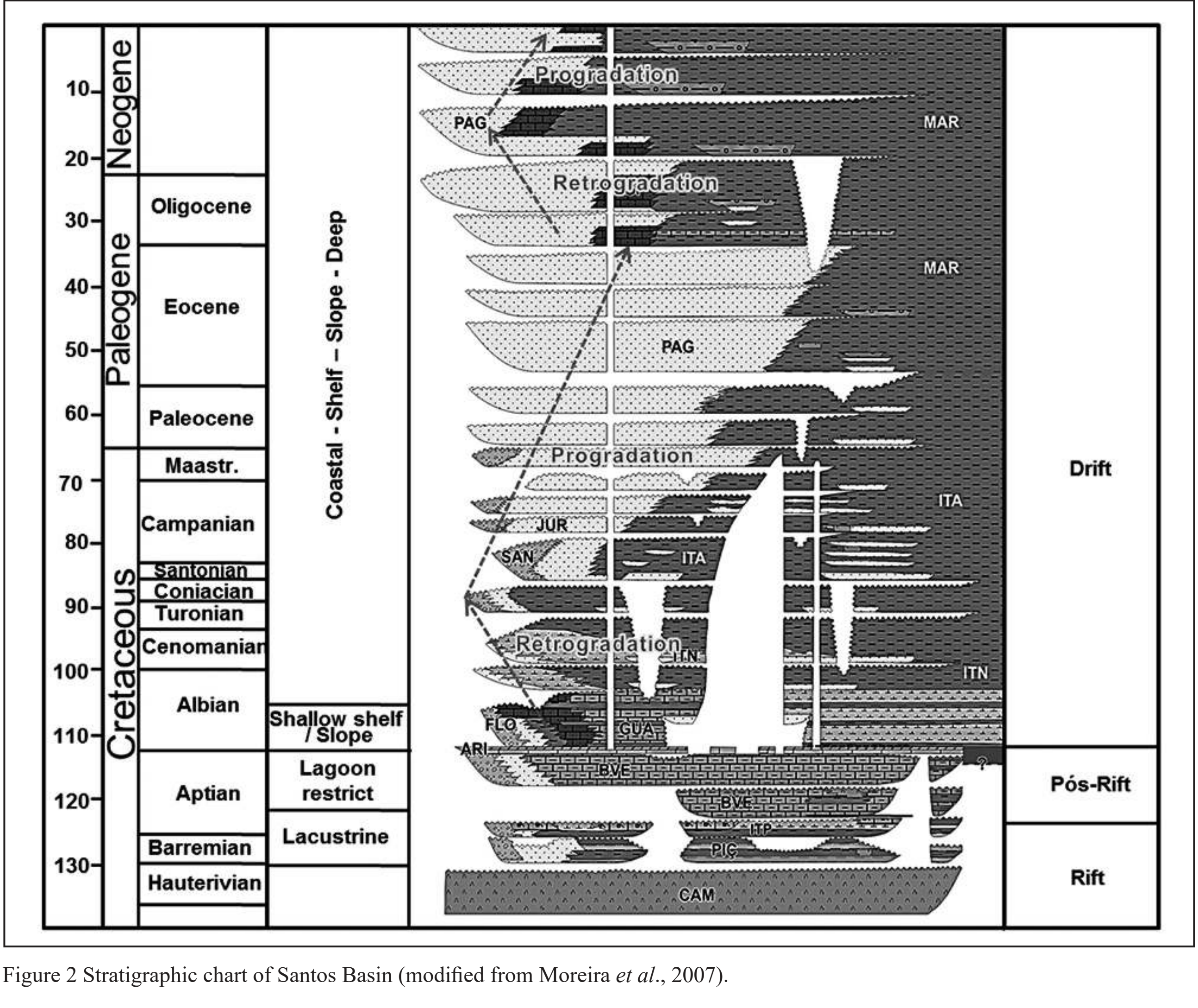


Figure 2 Stratigraphic chart of Santos Basin (modified from Moreira *et al*., 2007).

Miocene age. The data evaluated belong the well report from 1-BSS-0069-BS, within the geochemistry chapter wich was done in 11/29/1993. The results of biomarkers chromatogram and fragmentogram from the oil samples were analyzed and interpreted. This was provided by National Petroleum Agency (ANP) to carry out this avaliation.

The biomarkers are known as chemical fossils in the organic geochemistry branch. This term was created by Englinton & Calvin (1967) to describe the organic compounds found in rocks and oils; they are derived from organic matter deposited. Speers & Whitehead (1969) has used the biological markers as an expression. After a while, this term was replaced by molecular fossils. However, Seifert & Modowan (1986) have created the biomarkers term that is largely used in the current days.

Biomarkers are organic compounds which exist in all organic materials. Their structures can be related to the components of original material. Any change that occurs in the “carbon skeleton” of biomarker under the organic material deposition and burial within sedimentary record is limited by the stereochemical changes. Thus, accurate relationship between precursor/product has been established by many biomarkers classes (Philp, 1985).

For a compound to be considered a biomarker, it must satisfy the following characteristics (Peters *et al.*, 2005):

1. To show an indicative structure that has been a living organism component;

2. The precursor compound should be highly concentrated on the organisms and they must present wide distribution;

3. The main structural identification characteristics of the composites must be chemically stable under the recent sedimentation and burial.

The use of biomarkers as diagnosis elements and geologic interpretation is based on the fact that organic skeleton can be recognized even after it has been subjected to diagenesis processes and thermal maturation. The small rate of natural products (algae, plants and other organisms) which are resistant to extensive bacterial degradation between the organisms´ death and incorporation into sediments is a diagnostic of its biological origin (Hunt, 1996; van Aarssen *et al.*, 1999; Killops & Killops, 2005).

According to Mello *et al.* (1988), the biomarkers can assist with oil prospection providing information about: 1) Depositional environment, 2) Thermal maturation of source rock, 3) Source rock age, 4) Source rock characteristics, 5) Correlation oil/source rock, 6) Relative amount of oil/gas according to the kerogen type, 7) Secondary migration and 8) Biodegradation.

Since twenty-first century, the number of discoveries and used biomarkers in the geochemical studies increased significantly (Peters *et al.*, 2005). Mostly due to great advances in analytical techniques such as Gas Chromatography – Mass Spectrometry (GC-MS).

The greater or lesser absence of biomarkers from to chemical structures straight or cyclic is also an important aspect as it allows to establish different degree of oil and gas biodegradation. Bacterial action in general starts by linears compounds advancing to the cyclic (Peters & Moldowan, 1993). Full analysis of these compounds are essential to establish the degree of bacterial destruction of the hydrocarbon into reservoir conditions and consequently know the quality of oil and its economic profitability.

4.1 Saturated Biomarkers

4.1.1 Straight-Chain Alkanes

Straight-chain alkanes or *n*-alkanes are acyclic hydrocarbons which comprise a homologous series according to the formula CnH2n+2. Methane (CH_4) is the first in n-alkanes series.

The straight-chain alkanes analyzed by GC-MS can be monitored using Ion Mass Chromatogram m/z 85 (Figure 3).

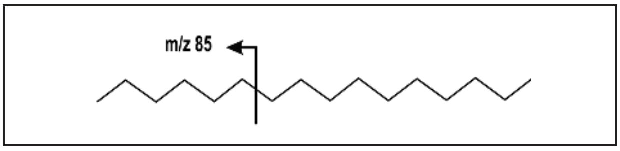


Figure 3 *N*-alkane molecular structure ($C_{16}H_{32}$).

Their mass spectrums show as a feature the occurrence of peak groups spaced 14 mass unit (corresponding to CH2 increase). Where CnH2n+1 peaks are abundant.

The application of derivatives parameters of chromatographic analysis includes:

1) Determination of thermal evolution of source rocks;

2) Organic matter origin;

3) Depositional environment.

According to Tissot & Welte (1984) organic matter samples with land plants contribution prevail *n*-alkanes between C_{25} and C_{33} (Figure 4), whereas samples deriving from marine organic matter prevail *n*-alkanes between C_{15} and C_{17} (Figure 5).

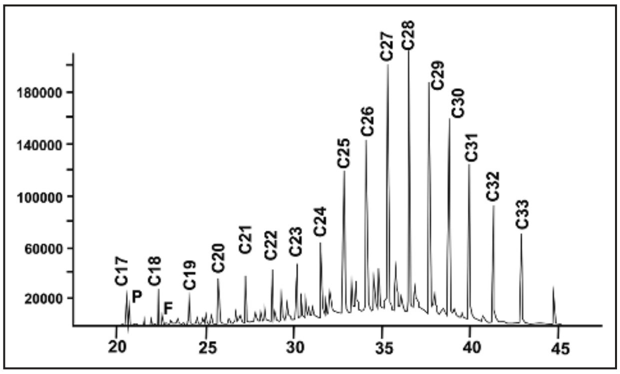


Figure 4 Example of terrestrial environmental chromatogram.

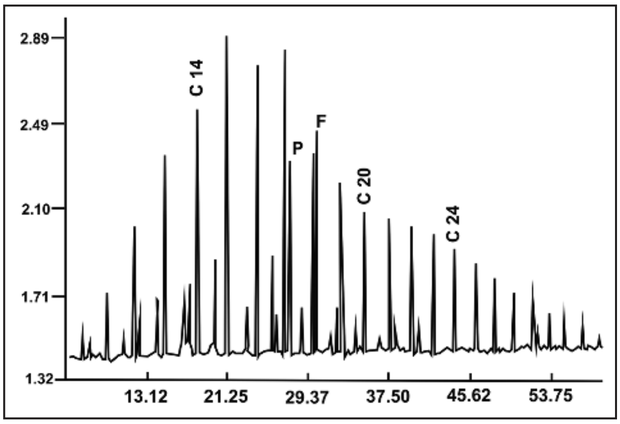


Figure 5 Example of marine environmental chromatogram.

According to these authors the presence of even a small portion of terrestrial organic matter (~10 %) defines the *n*-alkanes distribution.

The abundance of straight-chain saturated hydrocarbon with low molecular mass, predominantly alkanes between nC_{17} and nC_{18}, is usually associated with the organic matter from algae and/or cyanobacteria source (Hunt, 1996). While longer-chained alkanes which prevail unpaired hydrocarbons are generally assigned to higher plants (Schwab & Spangenberg, 2004 and references therein). However, the algae contribution shouldn´t be discarded.

With the increase of thermal evolution occurs cracking of high molecular weight hydrocarbons that cause a rise in the relative abundance of *n*-alkanes between C_{15} - C_{17}. It can compromise the environment interpretation.

In the biodegradation process the *n*-alkanes are the first compounds consumed by bacteria.

4.1.2 Branched-Chain Alkanes (Isoprenoids)

The isoprenoids belong to branched-chain alkanes group. They are formed from different combinations between isoprene units (methyl butadiene). As a result of these combinations, regular and irregular isoprenoids are created (Peters & Moldowan, 1993).

4.1.3 Acyclic Isoprenoids (Pristane and Phytane)

Both pristane and phytane (Fig. 6) are derived primarily from the lateral chain of chlorophyll phytol as well as the isoprenoids with fewer carbon atoms. This compound is present in phototrophic organisms (Didyk *et al.*, 1978; Brooks *et al.*, 1981).

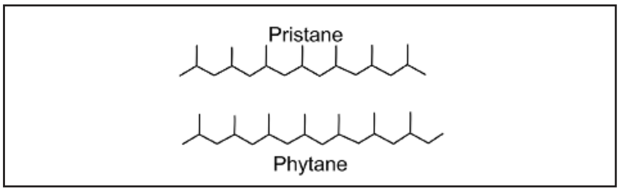


Figure 6 Generic structures of pristane and phytane isoprenoids.

Under anoxic conditions, the phytol lateral chain is cleaved. The phytol would be dehydrated and reduced to dihydrophytol which subsequently can be hydrogenated to phytane. Under oxidising conditions the phytol becomes phytenic, decarboxylated to pristeno and then reduced to pristane.

According to Mello *et al.* (1988) the low relationship between pristane and phytane (<1) is directly associated with hypersaline conditions, beside that this low relationship is predominantly from marine sources.

4.2 Cyclic (Unsaturated) Biomarkers

The terpanes consist of a biomarkers class of great importance in organic geochemistry. They are derived mainly from bacteria and used as an indicator of depositional and diagenetic conditions (Waples & Machihara, 1991).

The most ordinary terpanes in oil and sediments are tricyclic (A), tetracyclic (B) and pentacyclic (C) terpanes.

4.2.1 Tricyclic Terpanes

Many oils and rock extracts have a homologous series of tricyclic terpanes *cheilanthane* type within a range between C_{19} a C_{45}. Although, most abundance is found in homologous until C_{26}. They predominantly occur with 13β(H), 14α(H) configuration and from C_{25} homologous happen a mix of diastereoisomers in 22R e 22S position (Peters & Moldowan, 1993) (Figure 7).

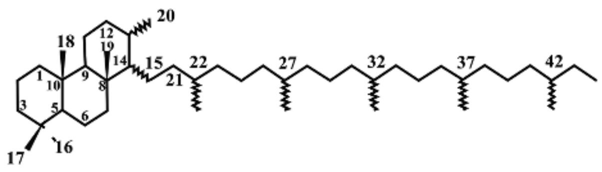


Figure 7 Chemical structure of tricyclic terpanes.

A proposed precursor for these compounds is tricyclohexaprenol which is formed from a universal constituent cell, the hexaprenol (Ourisson *et al.*, 1982). However, according to Simoneit *et al.* (1990) the tricylic terpanes can be originated from *tasmanaceas* algae which were abundant in Alasca and Tasmania during the Permian. These associations don´t prove the algae origin of these compounds after all, because the prokaryotic bacteria have been identified as possible tricyclic terpanes precursors (Ourisson *et al.*, 1982; Aquino Neto *et al.*, 1983; Peters & Moldowan, 1993).

4.2.2 Tetracyclic Terpanes

The tetracyclic terpanes constitute a more restricted series than tricyclic which has as the most commom compounds ranging between C_{24} and C_{27}.

The C_{24} tricyclic terpane abundance (Figure 8) is related to both carbonate and evaporite depositional environment (Conann *et al.*, 1986) but according to Waples & Machiara (1991), it is still not clear whether there is a unique origin from C_{24} tetracyclic, because C_{24} tetracyclic terpane is also associated to alginites or terrestrial organic matter.

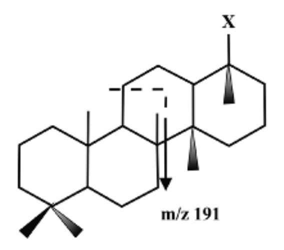


Figure 8 A characteristic fragmentogram (m/z 191) of the C_{24} tetracyclic terpane.

4.2.3 Pentacyclic Terpanes

The pentacyclic terpanes compose the most studied and used biomarker class between the cyclic biomarkers. The existence of a large number of chiral centers within their structures give to them a huge potential to create different stereochemical derivatives (Figure 9) which relatives abundances can be used as indicative parameters of depositional environment and/or thermal evolution and/or biodegradation level (Peters & Moldowan, 1993).

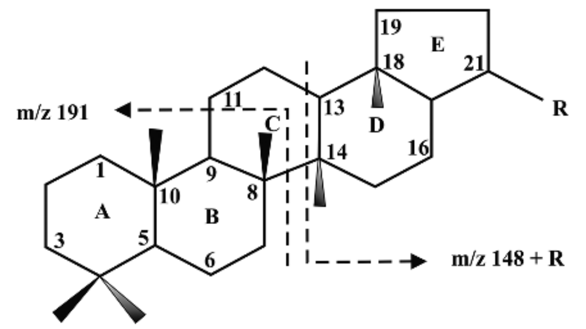


Figure 9 Hopane genetic structure.

There are hopanoids and non-hopanoids compounds in this class. Among the non-hopanoids pentacyclic terpanes, gammacerane and oleananes stand out (Figure 10).

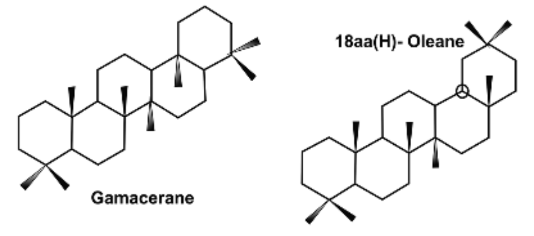


Figure 10 Non-hopanoide structure (gammacerane and oleanane).

The hopanes are the most plentiful terpenoids in sediments (Peters & Moldowan, 1993). The major precursor of these compounds is bacterio-hopanetetrol which is found in prokaryotic organism membranes. The original stereochemical arrangement of bacterio-hopanetetrol [17β(H),21β(H)] is thermodynamically unstable, the precursor change to more stable configurations like 17α(H), 21β(H)-hopanes and 17β(H), 21α(H)-moretanes consequently occurs (Tissot & Welt, 1984; Mello, 1988; Peters & Moldowan, 1993; Peters *et al.*, 2005, Figure 11).

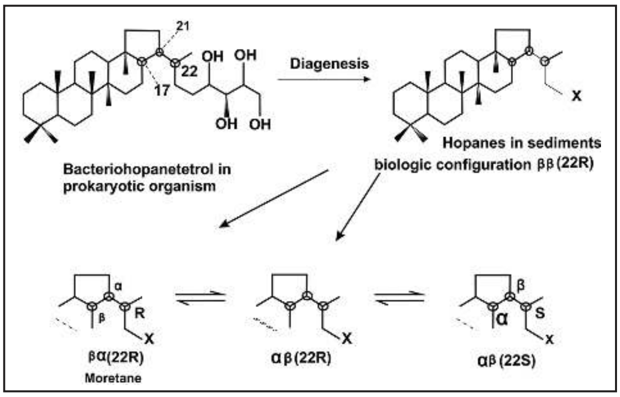


Figure 11 Precursor structure of the hopanes family.

4.2.4 Steranes

The steranes are the diagenetic process result of sterols. The sterols are found in most higher plants and algae and are uncommon in prokaryotic organism (Volkman, 1986; Waples & Machihara, 1991; Peters & Moldowan, 1993). They are important components of membrane and hormones in eukaryotic organisms (Waples & Machihara, 1991; Peters & Moldowan, 1993).

The four main precursors of sterols, including 27, 28, 29 and 30 carbon atoms, are identified in many photosynthetic organisms. These sterols originate four different regular steranes under diagenesis process. They can be called homologous or member of homologous series, because they differ only by addition of methylene (CH_2) in the molecule (Figure 12).

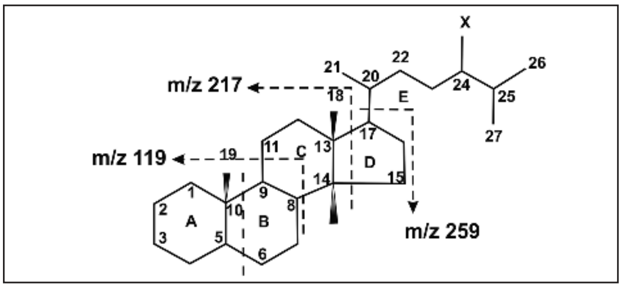


Figure 12 Sterane genetic structure.

The C_{27}, C_{28} and C_{29} compounds are denominated cholestane, ergostane and sitostane respectively. The C_{28} and C_{29} also can be named methy-cholestane and ethy-cholestane (Waples & Machihara, 1991).

The steranes complex distribution is affected by two major factors: origin and thermal evolution. The predominant steranes in sediments and oils are C_{27}, C_{28} and C_{29}, but may occur compounds from C_{18} to C_{30} (Mackenzie et al., 1981).

Huang & Meinschein (1978) proposed that the preponderance of C_{29} sterane can indicate a strong terrestrial contribution whereas the C_{27} sterane dominance imply that marine phytoplankton is prevalent. The C_{28} sterane is usually found in smaller relative quantities. However, their abundance can indicate lake algae contribution.

4.3 Oil Biodegradation

The petroleum is a complex mix of hydrocarbons and others organic compounds including some organometallic constituents such as nickel and vanadium (van Hamme et al., 2003). The hydrocarbon can constitute substrates as well as products from microbial metabolism (Bushnell & Hass, 1941; Ehrlich, 2001). Microorganisms have enzymatic arsenals able to use oil as a source of carbon and energy (van Hamme et al., 2003). This is the reason of the general move research in biochemistry, molecular biology and microbiology to determine the species involved and their activities under in situ oils.

According to Hunt (1996), White et al. (2003) and Head et al. (2003) the biodegradation effects in composition and physico-chemical properties of crude oils and natural gas are well known. The bacterial action reduces saturated hydrocarbon content and the API gravity (American Petroleum Institute) besides increasing the density and sulfur content, acidity, viscosity and metals which influence the oil production by reducing the flow rate and refinery operation. The oil oxidation induces the loss of its economic value and damage in explotation and refine of oil.

The biodegradation results from anaerobic processes, typically methanogenic degradation from native microbials communities that occur in the water zone of oil accumulations (Aitken *et al.*, 2004; Jones *et al.*, 2008). This conclusion is based on field data characteristic metabolites measures anaerobic oil degradation (Aitken *et al.*, 2004), in a comparative analysis of degraded oil from oilfields with degraded oils in incubations in the laboratory and isotopic analysis gas field and the one modeled by the Rayleigh fractionation (Jones *et al.*, 2008). The intensity of biodegradation is controlled by critical factors such as temperature (Aitken *et al.*, 2004; Jones *et al.*, 2008), the geometry and thickness of the reservoir, the supply of nutrients in the water zone which is a microcosm of the bacteria. The temperature is considered one of the major critical factors in the occurrence of biodegraded oils in the reservoir (Adams *et al.*, 2006). As the rate of biodegradation is controlled by the temperature, with increased temperature intensifies the metabolic activity and increases the rate of biodegradation, which reaches maximum activity around 40°C (Larter *et al.*, 2003). From 40°C to 80°C, metabolic microbial activity, decreases, becoming inactive at temperatures higher than 80°C, when the reservoir undergoes a sterilization process, since above this temperature occurs reservoir pasteurization with thermal destruction of communities autochthonous bacterial (Wilhelms *et al.*, 2001; Head *et al.*, 2003).

Peters & Moldowan (1993) determined qualitative indicators to appoint the degree of oil biodegradation based on petroleum compositional change from the study of their biomarkers (Figure 13).

According to Mohriak *et al.* (1990) the oil biodegradation within turbidite reservoirs of the Cretaceous and Tertiary in the offshore basins of Brazilian East Coast seems to be related to rainwater infiltration in contact with oil reservoirs.

The aerobic theory that dominated up to the last two decade was replaced by anaerobic one mainly in marginal basins.While biodegradation by fresh water percolation can proceed aerobically with high degradation rates, some studies of environmental plus aquifers suggest that slow anaerobic processes dominate the hydrocarbon degradation in subsurface which envolves multiple oxidation steps, metal reduction and methanogenesis (Zengler *et al.*, 1999).

5 Results and Discussion

Analyzing the oil chromatogram of Figure 14 it is possible to observe that there is a lack of *n*-alkanes and iso-alkanes which indicate a advanced stage of biodegradation (Figure 14).

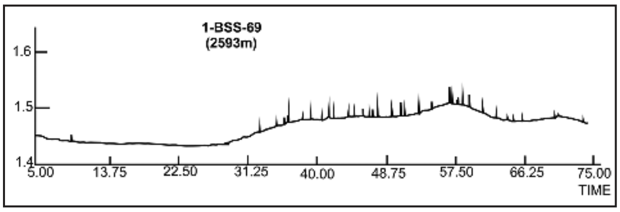


Figure 14 Oil sample chromatogram from depth 2593 m, 1-BSS-0069-BS well.

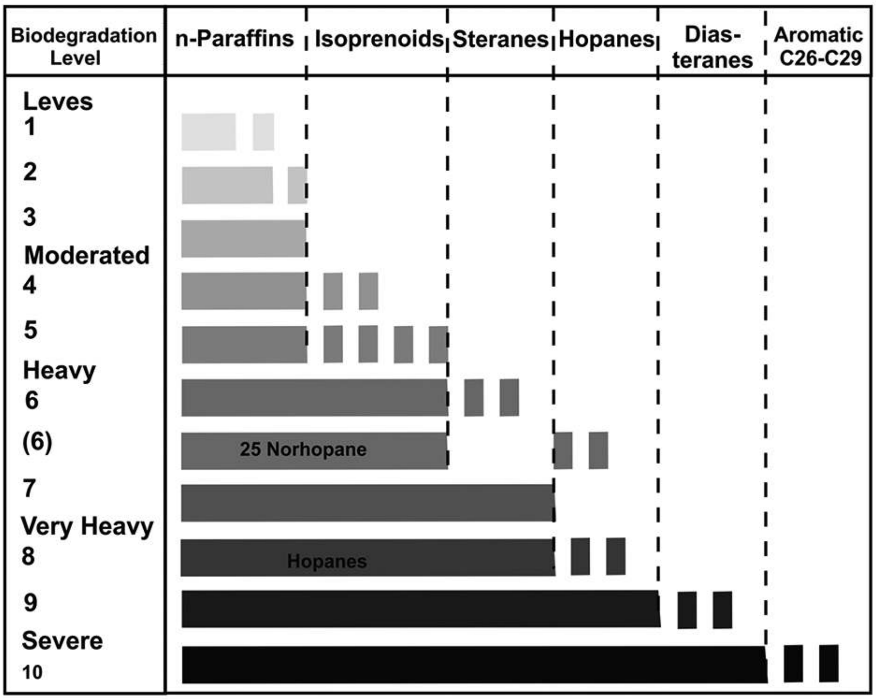


Figure 13 Scale of biodegradation listed from 1 to 10, according to Peters & Moldowan (1993). 1= Some *n*-paraffins homologues depletion, 2= *n*-paraffins biodegradation, 3= Only remaining *n*-paraffins traces, 4= Intact acyclic isoprenoids, 5= Lack of acyclic isoprenoids, 6= Partially degraded steranes, 7= Degraded steranes and intact steranes, 8= Partially degraded hopanes, 9= Lack of hopanes and degraded diasteranes and 10= Degraded C_{26}-C_{29} aromatics.

Analysing the m/z 191 fragmentograms (Figs. 15 and 16) show that the tricyclic terpanes proportion is bigger than the pentacyclic terpanes proportion (ratio C23/C30 =2.1). This happens because tricyclic terpanes are more resistent to biodegradation process than pentacyclic terpanes (hopanes).

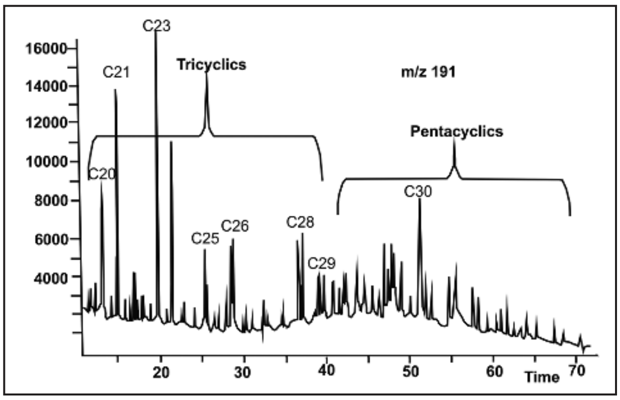
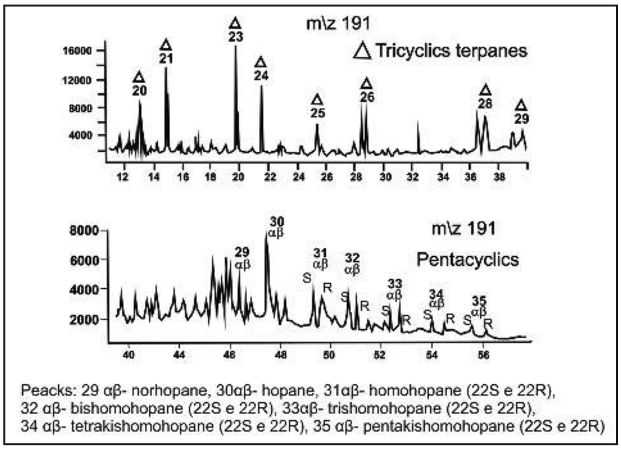


Figure 15 m/z 191 fragmentogram of the oil sample from depth 2593 m, 1-BSS-0069-BS well showing terpanes, tricyclics bigger than pentacyclics proportion.



Peacks: 29 αβ- norhopane, 30αβ- hopane, 31αβ- homohopane (22S e 22R),
32 αβ- bishomohopane (22S e 22R), 33αβ- trishomohopane (22S e 22R),
34 αβ- tetrakishomohopane (22S e 22R), 35 αβ- pentakishomohopane (22S e 22R)

Figure 16 Detail from figure 15 of m/z 191 fragmentogram of the oil sample from depth 2593 m, 1-BSS-0069-BS well, and terpanes peaks identification.

Following the biodegradation scale proposed by Peters & Moldowan (1993), it was interpreted that the oil investigated can be ranked as level 8 of biodegradation due to partial consume of hopanes. The other evidence of biodegradation stage is the presence of demethylated compounds which is shown on m/z 177 fragmentogram (Figure 17).

The m/z 177 fragmentogram (Figure 17) shows that the C28 D (demethylated) is bigger than C_{29} norhopane ($C_{28}D/C_{29}$norhopane= 1.7which can be related to biodegradation process because the disteranes are more resistant to decomposition by bacteria. This could be an additional factor to ratify the biodegradation stage of this oil.

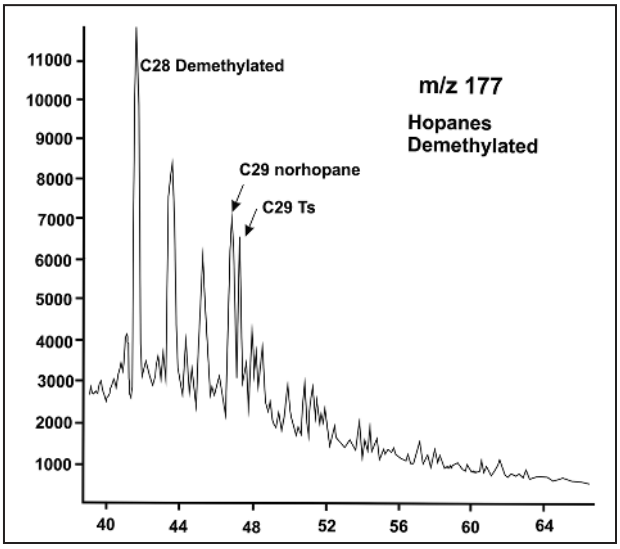


Figure 17 m/z 177 fragmentogram of the oil sample from the depth 2593 m,1-BSS-0069-B well, showing the demethylated compounds.

Due to the high degree of biodegradation (level 8), it is estimated that the reservoir (2593 m) was subjected to temperatures below 80°C probably between 35°C up to 50°C), suggesting an average geothermal gradient less than 30°C/km, being coherent with Cardoso & Hamza (2014) that calculated a range of 25°C/km to 30°C/km - in this region. This range of temperature from 35°C up to 50°C is considered the best condition for high biodegradation rate (Aitken *et al*., 2004). According to Larter *et al.* (2003), at this biodegration level (8) more than 50% of oil mass is consumed during the bacterial attack.

6 Conclusion

Considering the fragmentogram and chromatrogram data is it possible conclude that the oil from Paleogene sandstone sampled in the 1-BSS-0069-BS well shows evidence of advanced degradation stage, level 8, which was certificated by lack of n-alkanes and iso-alkanes, greater tricyclic terpanes proportion related to pentacyclic terpane, the presence of demethylated compounds and bigger diasteranes proportion than steranes. This high level of biodegrational is suggestive that during the process of oil filling, the temperature in the reservoir ranged from 35°C up to 50°C, interval of severe bacterial attack.

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8 References

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