

COMPARISON OF CRUDE OIL SOURCE-RELATED INDICATORS BASED ON C₁₅₋, C₁₅₊ AND C₄₀₊ PARAMETERS

*COMPARACIÓN DE INDICADORES DE FUENTE DE CRUDOS
BASADOS EN PARÁMETROS DE C₁₅₋, C₁₅₊ Y C₄₀₊*

*COMPARAÇÃO DE INDICADORES DE FONTE DE ÓLEOS CRUS EM
PARÂMETROS DE C₁₅₋, C₁₅₊ Y C₄₀₊*

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ABSTRACT

This work presents a comparative study of source-related indicators based on parameters determined in the C₁₅₋, C₁₅₊ and C₄₀₊ fractions in oil from the Barinas sub-basin, Venezuela. The objective was to determine whether the results obtained from High Temperature Gas Chromatography (HTGC-C₄₀₊) for the definition of organic facies and maturity, along with obtained by Whole-Oil Gas Chromatography (WOGC-C₁₅₋), to define maturity and secondary processes at the reservoirs are comparable with those obtained from biomarkers (GCMS-C₁₅₊). WOGC detected the presence of *n*-C₅ to *n*-C₉ alkanes, benzene and toluene, and the lack of these components indicates water washing. Oils from Caipe, La Victoria, Silvan, and Guafita not show biodegradation or water washing; Sinco show water washing and La Victoria and some from Guafita and Silvan oils presented evidence of evaporative fractionation. Biomarkers indicates that the oils derived from marine, algal and bacterial organic matter with variation in terrigenous organic matter input generated by a mature source rock with different lithofacies (siliciclastic-carbonatic). Based on CPI^o (C₄₂-C₄₆) five oils have values > 1, which is associated with marine depositional environments. However, 21 samples have CPI^o ≈ 1, which considered typical of freshwater lacustrine environments, which differs from those determined in previous works based on biomarkers and isotopic studies.

Keywords: Biomarkers, Organic facies, Sedimentation environment, Gas chromatography, Marine deposits, Crude oils.

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RESUMEN

Este trabajo presenta un estudio comparativo de indicadores de fuente basados en el estudio de parámetros determinados en las fracciones C_{15-} , C_{15+} y C_{40+} en crudos de la sub-cuenca de Barinas, Venezuela. El objetivo fue determinar si los resultados obtenidos a partir de cromatografía de alta temperatura (CGAT- C_{40+}) para la definición de facies orgánicas y madurez, junto con los de cromatografía de crudo total (CGCT- C_{15-}), para definir madurez y procesos secundarios en el yacimiento son comparables con los obtenidos de biomarcadores (CGEM- C_{15+}). CGCT detectó alcanos entre $n-C_5$ a $n-C_9$, benceno y tolueno, y la ausencia de estos compuestos indicó lavado por aguas. Los crudos de Caipe, La Victoria, Silvan y Guafita no presentan biodegradación o lavado por aguas, Sinco presenta lavado por aguas y La Victoria, y algunos de Guafita y Silvan presentan fraccionamiento evaporativo. Los biomarcadores indicaron un origen de materia orgánica marina, algal y bacterial; con variaciones en el aporte de materia orgánica terrígena, en una roca fuente madura con distintas facies litológicas (siliciclásticas-carbonáticas). Basado en CPI^a ($C_{42}-C_{46}$), cinco crudos tienen valores > 1 , asociado a ambientes de sedimentación marinos. Sin embargo, veintiún (21) crudos tienen $CPI^a \cong 1$, relacionado a ambientes lacustres de aguas dulces, lo que difiere de estudios previos basados en biomarcadores e isótopos.

Palabras clave: Biomarcadores, Facies orgánicas, Ambiente de sedimentación, Cromatografía de gases, Depósitos marinos, Crudos.

RESUMO

Este trabalho apresenta um estudo comparativo de indicadores de fonte baseados na apreciação de parâmetros determinados nas frações C_{15-} , C_{15+} e C_{40+} em crus da sub-bacia de Barinas, Venezuela. O objetivo foi determinar se os resultados obtidos com base na cromatografia de alta temperatura (CGAT- C_{40+}) para a definição de fácies orgânicas e maturidade e processos secundários na jazida são comparáveis com aqueles obtidos pelo uso de biomarcadores (CGEM- C_{15+}). CGCT possibilitou a detecção de alcanos entre $n-C_5$ a $n-C_9$, benzeno e tolueno, e a ausência destes compostos foi indicação de lavagem por águas. Os óleos de Caipe, La Victoria, Silvan e Guafita não apresentam biodegradação ou lavagem por águas, Sinco apresenta lavagem por águas e La Victoria, e alguns de Guafita e Silvan apresentam fracionamento evaporativo. Os biomarcadores indicaram uma origem de matéria orgânica marina, algal e bacteriana; com variações no aporte de matéria orgânica terrígena, em uma roca fonte madura com diferentes fácies litológicas (siliciclásticas-carbonáticas). Baseado no CPI^a ($C_{42}-C_{46}$), cinco óleos crus têm valores > 1 , sendo associados a ambientes de sedimentação marinhos. No entanto, vinte e um (21) óleos crus têm $CPI^a \cong 1$ associados a ambientes lacustres de águas doces, o que difere com os levantamentos prévios baseados em biomarcadores e isótopos.

Palavras-chave: Biomarcadores, Fácies orgânicas, Ambiente de sedimentação, Cromatografia de gases, Depósitos marinhos, Óleos Crus.

1. INTRODUCTION

Analysis of crude oils based on biomarkers (e.g. Peters & Moldowan, 1993; Hunt, 1996; Peters, Walters & Moldowan, 2005; Armstroff *et al.*, 2006; Gaimes, Eglinton & Rullkötter, 2009; Silvan, Datta & Singh, 2008; Abogilila *et al.*, 2010; Nytoft, Kildahl-Andersen & Olukayode, 2010, El Diasty & Moldowan, 2012; Sinninghe Damsté, Schouten & Volkman, 2014; Wang, Chang, Wang & Simoneit, 2015; and reference therein), isotopic composition (Sofer, 1984a; 1984b; Abogilila *et al.*, 2010) and trace elements such as V/Ni ratio (Al-Shahristani & Al-Thyia, 1972; López, Lo Mónaco, Espinoza & Blanco, 1991; López *et al.*, 1995; López, Lo Mónaco & Richardson, 1998; Frankenberger *et al.*, 1994; Alberdi, López & Galarraga, 1996; López & Lo Mónaco, 2004, López & Lo Mónaco, 2010) provides information about organic matter types, paleoenvironmental sedimentation conditions and maturity. Furthermore, biomarkers are used to determine the level of biodegradation of oils (Volkman *et al.*, 1983a; Volkman, Alexander, Kagi & Woodhouse, 1983b; Volkman *et al.*, 1984; Tissot & Welte, 1984; Peters & Moldowan, 1993; Hunt, 1996; Wenger, Davis & Isaksen, 2002; Huang, Bowler, Oldenburg & Larter, 2004; Larter *et al.*, 2006; Bennett & Larter, 2008; Haeseler, Behar, Garnier & Chenet, 2010; Larter *et al.*, 2012; Zhang *et al.*, 2014). Other crude oil studies include the analysis of Low Molecular Weight Hydrocarbons (LMWHC: C₁₅₊) by Whole Oil Gas Chromatography (WOGC) (Leythaeuser, Schaefer & Weiner, 1979; Philippi, 1981; Thompson, 1983; 1987; Odden, Patience & Van Graas, 1998; Odden, 1999; Odden & Barth, 2000; Jarvie, 2001; Cañipa-Moralesa, Galán-Vidal, Guzmán-Vega & Jarvie, 2003; Thompson, 2006; Hill *et al.*, 2007). In this case, a set of relationships using compounds such as benzene, toluene, xylene, n-alkanes (< n-C₈) and methylcycloalkanes (< C₈) furnishes information about maturation of oils and secondary processes in the reservoir, such as evaporative fractionation, water washing and biodegradation. This technique has also been used to determine organic matter types in correlation studies and oil mixtures assessments (Leythaeuser *et al.*, 1979; Philippi, 1981; Thompson, 1979; 1983; 1987; 1988; Mango, 1987; 1990a; 1990b; 1994; 1997; ten Haven, 1996; Odden *et al.*, 1998; Odden, 1999; Odden & Barth, 2000; Jarvie, 2001; Jarvie, Morelos & Han, 2001; Cañipa-Moralesa *et al.*,

2003; Thompson, 2006; Hill *et al.*, 2007). The analysis of High Molecular Weight Hydrocarbons (HMWHC: C₄₀₊) using High Temperature Gas Chromatography (HTGC) is another widely used technique (Heath, Lewis & Rowland, 1997; Mueller & Philp, 1998; Thanh, Hsieh & Philp, 1999; Hsieh & Philp, 2001; Huang, Larter & Love, 2003; Hong *et al.*, 2003; Tuo & Philp, 2003; Zhou, Li & Jiang, 2005). HMWHC are a complex mixture of alkyl-cycloalkanes, methylbranched alkanes, and alkyl-aromatic hydrocarbons (Hsieh & Philp, 2001; Huang *et al.*, 2003). Detailed oil studies indicate the presence of homologous series of branched hydrocarbons, including mono methylalkanes, n-alkylcyclohexanes, methyl- and n-alkylcyclohexanes, n-alkylcyclopentanes, n-alkylbenzenes, n-alkyltoluenes and n-alkylxylenes (Del Rio, Philp & Allen, 1992; Carlson *et al.*, 1993; Carlson, Jacobsen, Moldowan & Chan, 1994; Carlson, Dias & Schoell, 1997; Del Rio & Philp, 1999; Hsieh, Philp & Del Rio, 2000; Hsieh & Philp, 2001; Jarvie *et al.*, 2001; Tuo & Philp, 2003; Philp & Hsieh, 2004). The CPI based on alkylcyclopentanes (CPI^a) in the range C₄₂-C₄₆ is used as indicator of paleoenvironmental sedimentation conditions. CPI^a (C₄₂-C₄₆) > 1 with odd/even predominance pattern indicates marine oils, CPI^a (C₄₂-C₄₆) << 1 with high even/odd predominance pattern indicates oils from saline lacustrine environment, and CPI^a (C₄₂-C₄₆) ≈ 1 with low even/odd or no clear predominance has been considered to indicate freshwater lacustrine environment (Hsieh & Philp, 2001). Therefore, it appears that the study of C₁₅₊ and C₄₀₊ fractions in crude oils may provide information about the organic matter source, paleoenvironmental sedimentation conditions, maturity and secondary processes in the reservoir.

The Barinas sub-basin (Figure 1), the third most important petroleum basin in Venezuela, contains a series of oil fields, in which organic matter types, paleoenvironmental sedimentation conditions and maturity have been determined, based on the study of biomarkers, V/Ni ratio and isotopic composition in saturated and aromatic hydrocarbons fractions (Labrador, López & Galarraga, 1995; Gil, Chigne & Mello, 1996; Gil, 1998; López *et al.*, 1998; Lo Mónaco, López & Labastida, 1999). In the Barinas sub-basin, crude oils were derived from marine organic matter, with a variable contribution of terrigenous organic matter. Oils from La Victoria and Guafita (Apure fields), have

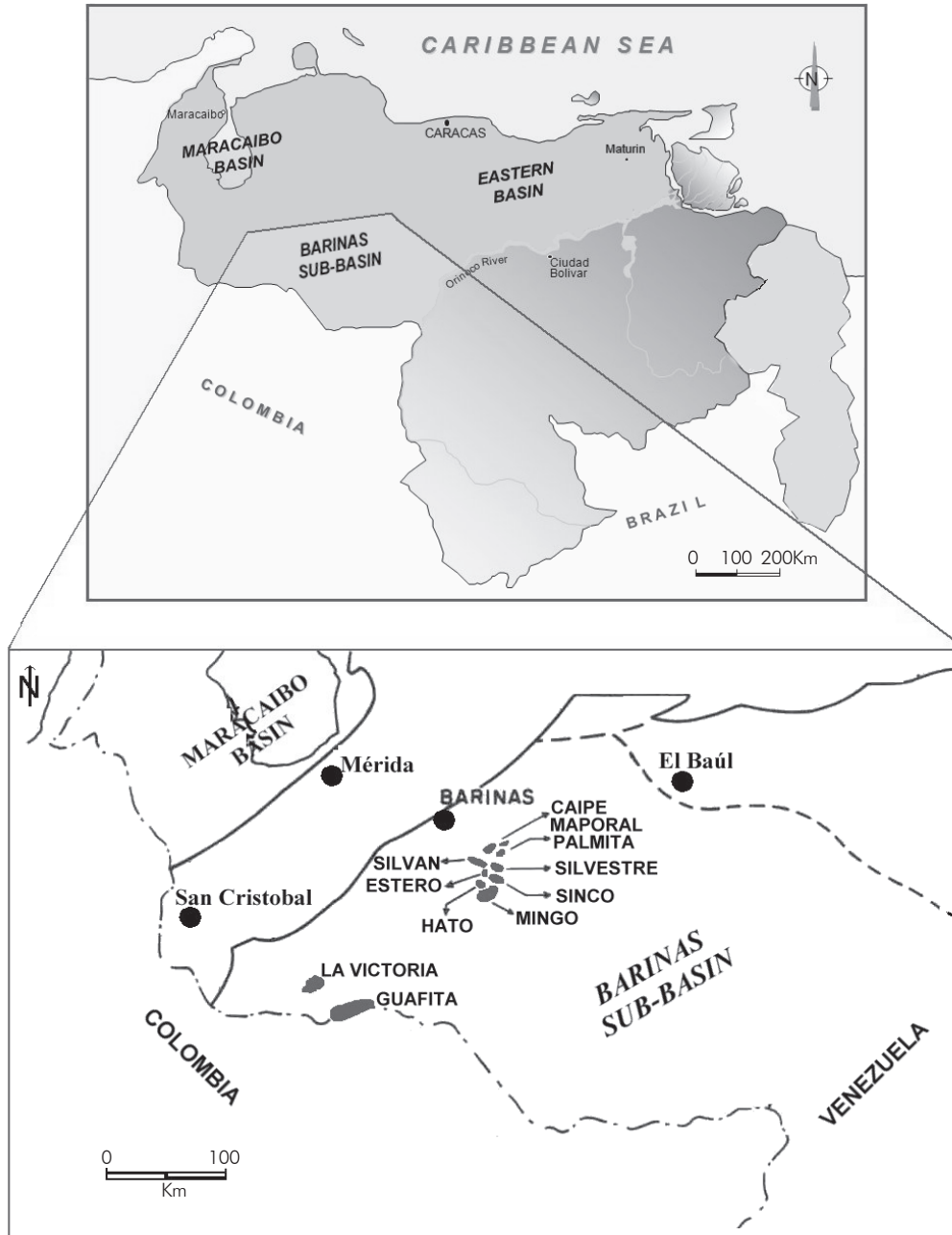


Figure 1. Map of Venezuela showing the location of the fields in Barinas sub-basin, Venezuelan.

a higher contribution of terrigenous organic matter in a more siliciclastic and less mature source rock. Crude oils from Caipe, Silvestre, Sinco, Silvan, and Palmita fields (Barinas fields) show lower contribution of terrigenous organic matter, and are originated by carbonatic facies and a more mature source rock (López *et al.*, 1998). In crude oils with these compositional variations, it is interesting to integrate biomarkers with LMWHC and HMWHC data to define depositional environment of petroleum source rock. For this reason, this work

is intended to use C_{15-} and C_{40+} fractions in crude oils from the Barinas sub-basin as indicators for determining organic matter types, paleoenvironmental sedimentation conditions and maturity, and then compared them to those parameters based on biomarkers (C_{15+}), V/Ni ratio and isotopic composition analyzed in previous works (López *et al.*, 1998). Some aspects related to secondary process in the reservoir, such as biodegradation and water washing, are considered. With this purpose, results obtained from the investigation of the C_{40+} fraction of

the studied oil samples are compared to those obtained from biomarkers, in order to make interpretations related to source rock sedimentation environment (marine or lacustrine environments). The oil C₁₅₋ fraction is used to identify secondary processes in the reservoir, such as biodegradation, water washing and/or evaporative fractionation, including the Thompson (1979; 1983; 1987) parameters.

2. EXPERIMENTAL METHODOLOGY

Sampling

Thirty-three oil samples from seven oil fields from Barinas sub-basin Venezuela (Figure 1) were collected in amber glass bottles at wellhead. The sampling points are located in Guafita, La Victoria, Caipe, Silvestre, Sinco, Silvan and Palmita fields. The best samples for GC analysis are those collected at reservoir temperature and pressure (bottom hole sample). Unfortunately, sampling oil in this way is expensive and requires the use of sophisticated pressure vessels (Harriman, 1994). Because of this, many samples are collected at the wellhead under atmospheric pressure.

SARA Composition and Sulfur Content

Crude oil were separated into maltene and asphaltene fractions, using n-heptane (1/40 w/v), and the asphaltenes fraction was rinsed with cold n-heptane (10 °C). Maltene fractions were separated by silica gel, open column, liquid chromatography to quantify saturated and aromatic hydrocarbons and resins fractions. The saturated hydrocarbons were eluted with n-pentane and aromatic hydrocarbons with n-hexane. Sulfur was analyzed in a LECO equipment.

Analysis of C₁₅₋, C₁₅₊ and C₄₀₊ Fractions

Twenty two crude oils were examined through whole-oil gas chromatography (C₁₅₋ fraction), using HP 6890 Series GC-FID system with a 25 m, Ultra 1, methyl siloxane capillary column by automatic injection. In thirty-three oil samples, gas chromatography (GC) of the saturated hydrocarbon fractions was carried out on a 5890 Series Plus using a Flame Ionization Detector (FID) and type CP-SIL fused capillary columns (50 m, 0.25 mm, 0.25 μm). Saturate and aromatic biomarker analyses were performed on HP 5890 Series II GC systems coupled with HP 5970 MSDs. The GC system was equipped with DB-5 fused silica capillary column (30 m, 0.25 mm, 0.25 μm). The monitored ions were

$m/z = 191, 177$ (terpanes), 217, 218 (steranes and diasteranes), and $m/z = 178$ (phenanthrene), 192 (methylphenanthrenes), 184 (dibenzothiophene), 198 (methyl-dibenzothiophenes), 253 and 231 (mono- and tri-aromatic steroids). Humble Geochemical Services performed HTGC on twenty-six samples. In these analyses, a standard from C₁₂ to C₆₀ was used to identify C₄₀₊ compounds.

Elemental Composition

Trace elements (V and Ni) were analyzed by inductively coupled plasma mass spectrometry (ICP/MS, Thermal Jarrel Ash ENVIRO II). Sulfur content was determined using a LECO SC-432 sulfur analyzer (López *et al.*, 1998; Lo Mónaco *et al.*, 2002; López & Lo Mónaco, 2004).

3. RESULTS AND DISCUSSION

Crude Oils Classification

Table 1 presents API gravities, sulfur content and SARA composition for the analyzed oils (López *et al.*, 1998). Oils API gravity ranged from 25-32° and they can be classified as intermediate to light crude oils. Exceptions for API gravity values were observed in some oils from Caipe, Sinco and Silvan (12-15 API), which were classified as heavy crude oils. Concentrations of saturated hydrocarbons in the crude oil range from 30-64%, aromatic hydrocarbons are between 25-41%, and NSO compounds (resins + asphaltenes) between 5-42%. Total sulfur (St) content shows values between 0.4-2.1 %. Based on saturated, aromatic, NSO compounds, and St content, oils from La Victoria and Guafita are classified as paraffinic-naphthenic, and oils from Caipe, Silvestre, Sinco, Silvan, and Palmita fields are classified as aromatic (Tissot & Welte, 1984).

Low-Molecular-Weight Hydrocarbons (C₁₅₋)

WOGC for selected samples (Figure 2) indicate different fingerprints for the investigated oils. In crude oils from Caipe, La Victoria, Silvan and Guafita, the *n*-alkanes C₁₅₋ fraction is present together with cycloalkanes and low-molecular-weight aromatics, such as toluene and benzene (Figure 2a and 2b). These results indicate that these oils are not biodegraded and have not been subject to water washing. However, the chromatograms are characterized by lifting the baseline, resulting in a hump or unresolved complex

Table 1. Parameters indicators of organic matter types, redox sedimentation conditions, source rock lithofacies and maturity (¹ López *et al.*, 1998).

Geochemical parameter	La Victoria, Guafita Siliciclastic-rich lithofacies	Caípe, Silvestre, Sinco, Silvan, Palmita Carbonate-rich lithofacies
API	Light and intermediate oil	Intermediate oils
SARA composition (wt%) Saturated (± 1)	La Victoria (4)*: 44–64 Guafita (13): 47–59	Caípe (4): 31–43 Silvestre (6): 30–43 Sinco (2): 31–33 Silvan (2): 43–48 Palmita (1): 42
Aromatic (± 2)	La Victoria (4): 25–29 Guafita (13): 25–32	Caípe (4): 29–41 Silvestre (6): 25–35 Sinco (2): 30–32 Silvan (2): 29–37 Palmita (1): 37
Resins + Asphaltenes (± 1)	La Victoria (4): 5–12 Guafita (13): 10–22	Caípe (4): 19–27 Silvestre (6): 22–42 Sinco (2): 36 Silvan (2): 20–23 Palmita (1): 21
Sulfur concentration ¹	< 0.6	> 0.6
CPI ^{a1}	0.9–1.1 Mature oils	0.9–1.1 Mature oils
CPI ^a (C ⁴² -C ⁴⁶) ^b	La Victoria (4): 0.8 Guafita (13): 0.8–1.3	Caípe (2): 1.2–1.3 Silvestre (4): 0.7–1.5 Sinco (1): 0.8 Silvan (2): 0.8 Palmita (1): 0.7
Moretanes/Hopanes ^c	0.10–0.15 Less mature La Victoria (4): 0.14–0.15 Guafita (13): 0.10–0.14	0.08–0.11 More mature Caípe (4): 0.09–0.10 Silvestre (6): 0.08–0.11 Sinco (2): 0.10 Silvan (2): 0.08–0.09 Palmita (1): 0.08
%C ₂₉ 20S ^{d1}	38–44 Less mature	45–50 More mature
%C ₂₉ $\beta\beta$ ^{e1}	36–43 Less mature	44–50 More mature
Triaromatic steroids (TAS) ^{f1}	0.12–0.16 Less mature	0.12–0.23 More mature
Monoaromatic steroids (MAS) ^{g1}	0.6–0.8 Less mature	0.12–0.17 More mature
PP-1 _{modified} ^{h1}	La Victoria (4): 0.80–1.18 Guafita (13): 1.18–1.30	Caípe (4): 1.16–1.18 Silvestre (6): 1.28–1.46 Sinco (2): 1.12–1.16 Silvan (2): 1.39–1.46 Palmita (1): 1.44
Waxiness index ⁱ	Range: 0.30–0.39 Average: 0.34	Range: 0.32–0.39 Average: 0.35
Gammacerane index (%) ^{j1}	La Victoria (4)*: 22 Guafita (13): 28 \pm 1	Caípe (4): 27 \pm 1 Silvestre (6): 26 \pm 1 Sinco (2): 28 \pm 1 Silvan (2): 29 \pm 1 Palmita (1): 29
Oleanane index (%) ^{k11}	La Victoria (4)*: 12 \pm 1 Guafita (13): 14 \pm 1	Caípe (4): 10 \pm 1 Silvestre (6): 10 \pm 1 Sinco (2): 12 Silvan (2): 10 Palmita (1): 10

Table 1. Parameters indicators of organic matter types, redox sedimentation conditions, source rock lithofacies and maturity (¹ López *et al.*, 1998).(Continuación)

Geochemical parameter	La Victoria, Guafita Siliciclastic-rich lithofacies	Caípe, Silvestre, Sinco, Silvan, Palmita Carbonate-rich lithofacies
Pr/Ph ¹¹	> 1 La Victoria (4): 1.42 ± 0.08 Guafita (13): 1.29 ± 0.05	≈ 1 Caípe (4): 1.00 ± 0.02 Silvestre: 1.09 ± 0.03 Sinco (2): 1.184 ± 0.001 Silvan (2): 1.09 ± 0.01 Palmita (1): 1.08
Diasteranes/steranes ^{m1}	0.42–0.50	≈ 0.50
MeDBT distribution ⁿ¹	4-MeDBT > 2,3-MeDBT < 1-MeDBT	4-MeDBT > 2,3-MeDBT > 1-MeDBT
V/Ni ratio ^{o1}	Range: 0.23–0.38 Average: 0.30	Range: 0.51–3.54 Average: 2.9

*number of well for fields and analyzed samples.

^a CPI = Carbon Preference Index (Bray and Evans, 1961).

^b CPI^o (C₄₂-C₄₆) = $\frac{2(C_{42}-C_{45})}{(C_{44}-C_{46})+(C_{42}+C_{44})}$ The CPI for alkylcyclopentanes (CPI^o) in the C₄₂-C₄₆ range. Hsieh and Philp (2001).

^c Moretanes/Hopanes = C₃₀17β(H),21α(H)-moretane/ C₃₀17α(H),21β(H)-hopane (Seifert and Moldowan, 1980).

^d %C₂₉20S: C₂₉20S/(C₂₉20S + C₂₉20R) steranes. ^e %C₂₉αβ: C₂₉ββ/(C₂₉ββ + C₂₉αα) steranes (Seifert and Moldowan, 1978; Mackenzie, P Hoffmann & Maxwell, 1981).

^f TAS = $\frac{\sum(C_{20}-C_{21})/\sum(C_{20}-C_{21})+\sum(C_{26}-C_{28})}{\sum(C_{21}-C_{22})/\sum(C_{21}-C_{22})+\sum(C_{27}-C_{29})}$ (Seifert and Moldowan, 1980; Mackenzie *et al.*, 1980).

^g PP-1_{modified} = (1MP+9MP)/(2MP+3MP) (Cassani *et al.*, 1988).

^h Waxiness index = $\frac{\sum(n-C_{21}-n-C_{31})/\sum(n-C_{15}-n-C_{20})}{\sum(n-C_{21}-n-C_{31})/\sum(n-C_{15}-n-C_{20})}$ (El Diasty and Moldowan, 2012).

ⁱ Gammacerane index = [gammacerane/(gammacerane + 17α,21β-C₃₀hopane)]*100 (Moldowan *et al.*, 1985).

^k Oleanane index = $\frac{[(18\alpha(H)-oleaneane)/(18\alpha(H)-oleaneane + 17\alpha,21\beta-C_{30}hopane)] \times 100}{[(18\alpha(H)-oleaneane)/(18\alpha(H)-oleaneane + 17\alpha,21\beta-C_{30}hopane)] \times 100}$ (Moldowan *et al.*, 1994).

^l Pr/Ph = Pristane/Phytane (Tissot and Welte, 1984).

^m Diasteranes/steranes (Peters *et al.*, 2015).

ⁿ MeDBT distribution = Methylbenzothiophene distribution (Hughes, 1984).

^o V/Ni ratio = vanadium/nickel ratio.

mixture of compounds. The presence of a full suite of n-alkanes distributed across the UCM are interpreted to be a recharge of hydrocarbons after initial biodegradation. Additionally, crude oils from Silvestre and Sinco are characterized by the presence of traces of 25-norhopanes, common in severe biodegraded oils (Peters & Moldowan, 1993). These results may suggest that two oil charges occurred in the reservoirs. During the first event, the crude oils were biodegraded, and many susceptible biomarkers changed. Other oils from Silvestre and Sinco fields show variable amounts of LMWHC. For those compounds that are water-soluble (benzene, toluene), variations in concentration may be a consequence of alteration processes (Figure 2c), such as water washing (López *et al.*, 1998). Based on LMWHC distribution, peak ratios or compound class comparison are used to define oil types (Mango, 1987; Jarvie, 2001).

The measured peak heights for LMWHC, i.e. n-pentane (n-C₅), n-hexane (n-C₆), n-heptane (n-C₇), methylcyclopentane (MCP), methylcyclohexane (MCH), benzene (Bz) and toluene (Tol) are shown in Figure 3. Thompson (1983; 1987) proposed the use of hydrocarbons ratios for oil components in the fraction C₁₅₋ to define oils as being biodegraded, normal, mature

or over mature, or having undergone an evaporative fractionation process. Some of the studied oils (Figure 4) show low aromaticity (except oil S-B from Sinco field), as shown by the variation in the Bz/n-C₆ and Tol/n-C₇ ratios (Thompson, 1983; 1987). The ratios CH/MCP and n-C₇/MCH have low values for La Victoria and Silvan oils, clearly differentiating these fields from the others (Figure 4). Additionally, in the ternary diagram showing the relative proportions of methylcyclohexane, toluene and n-heptane, crude oils separate into two groups (Figure 5). La Victoria (LV) and Silvan (SNW) are located in the field of lower n-heptane (31-39%), higher methylcyclohexane (41-45%) and toluene intermediate (21-27%). Crude oils from Guafita (GF), Caípe (CA), Silvestre (SSW) and Palmita (SPW) are grouped with high n-heptane (49-59%), low methylcyclohexane (10-14%), and again with toluene intermediate (31-43%). One of the samples from La Victoria constitutes an exception, with 9 % in toluene and 74 % in n-heptane. This diagram does not separate the crude oils from Barinas sub-basin based on organic matter input or source rock lithology, as has been observed in other basins (Hill *et al.*, 2007). The differentiation in this case may indicate secondary processes in the reservoir, rather than origin of crude oils. Analyzed oils appear to follow the trend proposed by Thompson (1987) for evaporative

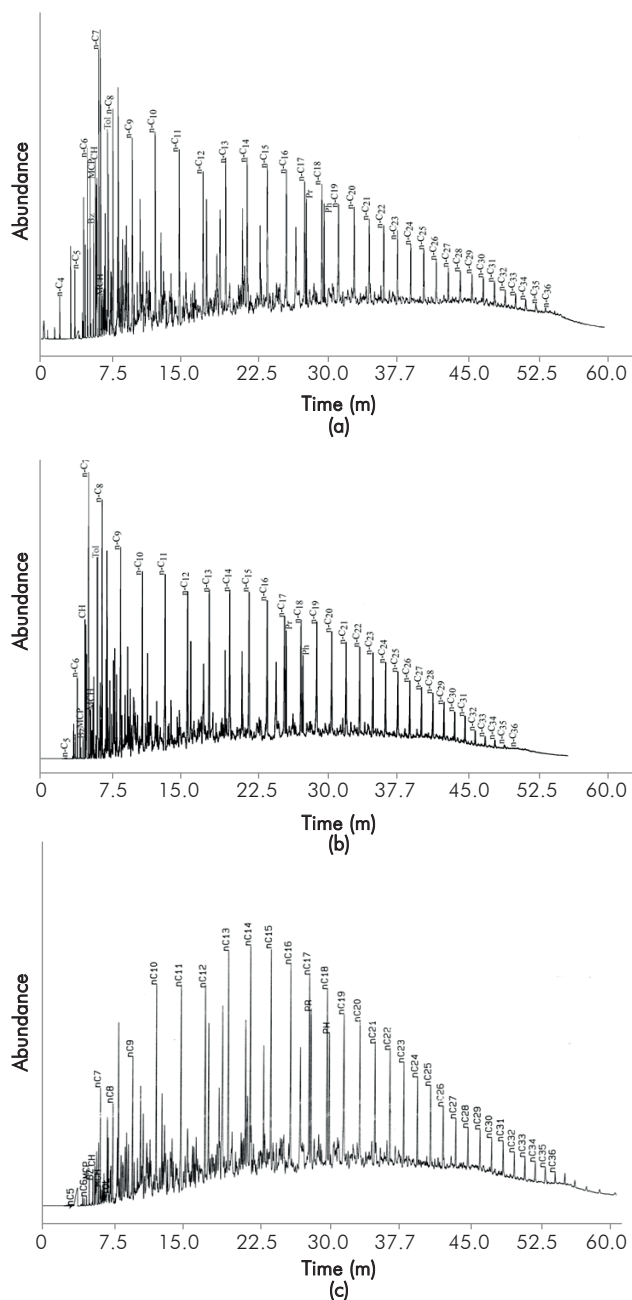


Figure 2. Representative whole-oil gas chromatography. Samples from Guafita (a), La Victoria (b) and Sinco (c) fields.

fractionation, whereas other oils roughly follow the maturation trend (Figure 6). The graph of aromaticity index: toluene/*n*-heptane (Tol/*n*-C₇) vs. paraffinicity index: *n*-heptane/methylcyclohexane (*n*-C₇/MCH), in terms of the alteration vectors proposed by Thompson (1983; 1987) represents oil types based on maturation or evaporative fractionation (Thompson, 1987). Figure 6 shows some crude oils that appear to be altered by evaporative fractionation, including those from La

Victoria (LV), Silvan (SNW) and Guafita (GF-J) fields, suggesting some compositional fractionation due to gas separation processes in the reservoir. Although we do not have sufficient geological information of the reservoirs for determining the distribution of the components of LMWHC by evaporative fractionation, Tol/*n*-C₇ and *n*-C₇/MCH ratio suggest the loss of light components by post-emplacement alteration. Oils from La Victoria (LV), Guafita (GF), Caípe (CA), Silvestre (SSW), Silvan (SNW) and Palmita (SPW) are located in the graph area for oils generated from a mature source rock. However, the difference in maturity of oils from Guafita and La Victoria compared to the rest of the fields was suggested by previous studies where maturity was determined using biomarkers (López *et al.*, 1998). Some parameters suggested differences of maturity (Table 1) among the investigated oils from Barinas-Apure. Maturity was assessed based on carbon preference index (CPI), moretane/hopane ratio (C₃₀17β(H),21α(H)-moretane/C₃₀17α(H),21β(H)-hopane), C₂₉ sterane isomerization ratios (C₂₉20S and C₂₉αββ), methylphenanthrene index and monoaromatic and triaromatic steroids ratios (Table 1). We were not able to assess maturity differences based on Ts/(Ts+Tm) ratio since this parameter is maturity and source rock lithology dependent (Seifert & Moldowan, 1978; Peters *et al.*, 2005), and these ratio should be used with caution in settings where hydrocarbons may be generated from source rocks with variable lithofacies; which is the case for the studied oils. The maturity parameters studied indicate that La Victoria and Guafita oils were generated in a less mature stage compared to a more mature stage of generation for oils from Caípe, Silvestre, Sinco, Silvan and Palmita fields. Additionally, all oils are classified as paraffin-rich oils based on toluene/*n*-heptane ratio < 1.0 (Jarvie, 2001).

***n*-Alkanes Distribution and Biomarkers (C₁₅₊)**

Crude oils from the Barinas sub-basin contain *n*-alkanes in the range *n*-C₉ to *n*-C₄₀, with unimodal distribution, with maximum values between *n*-C₁₃ and *n*-C₁₇ (Figure 7a). The high wax content in crude oils has been associated with terrigenous organic matter. Crude oils characterized by a high proportion of HMWHC present high waxiness index (El Diasty & Moldowan, 2012). Waxiness index for crude oils from the Barinas sub-basin has values between 0.30 and 0.39 (Table 1). Oils from La Victoria and Guafita range from 0.30-0.39 (average: 0.34), and Caípe, Silvestre, Sinco, Silvan, Palmita range from 0.32-0.39 (average: 0.35). This ratio

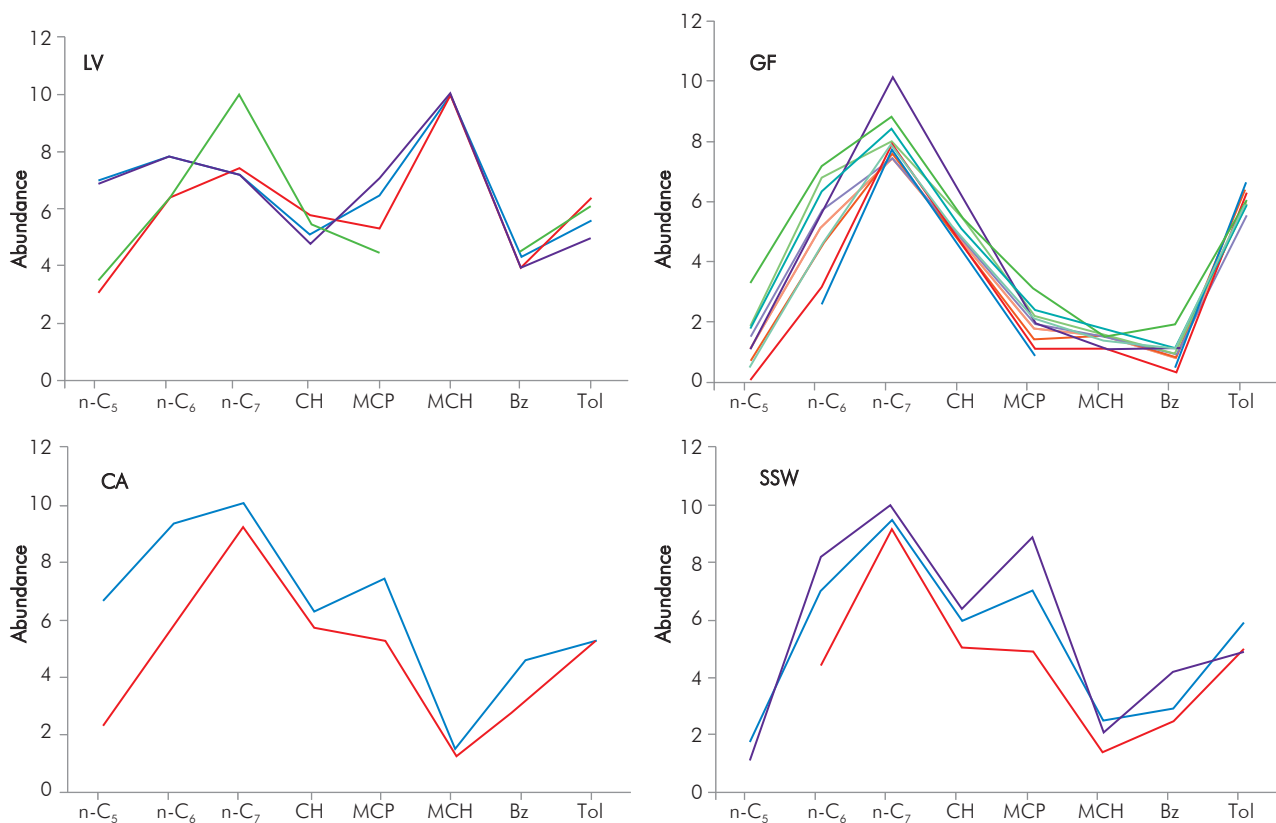


Figure 3. Distribution of low-molecular-weight hydrocarbons. *n*-pentane (*n*-C₅), *n*-hexane (*n*-C₆), *n*-heptane (*n*-C₇), cyclohexane (CH), methylcyclopentane (MCP), methylcyclohexane (MCH), benzene (Bz) and toluene (Tol). Oils from La Victoria (LV), Guafita (GF), Caípe (CA) and Silvestre (SSW) fields.

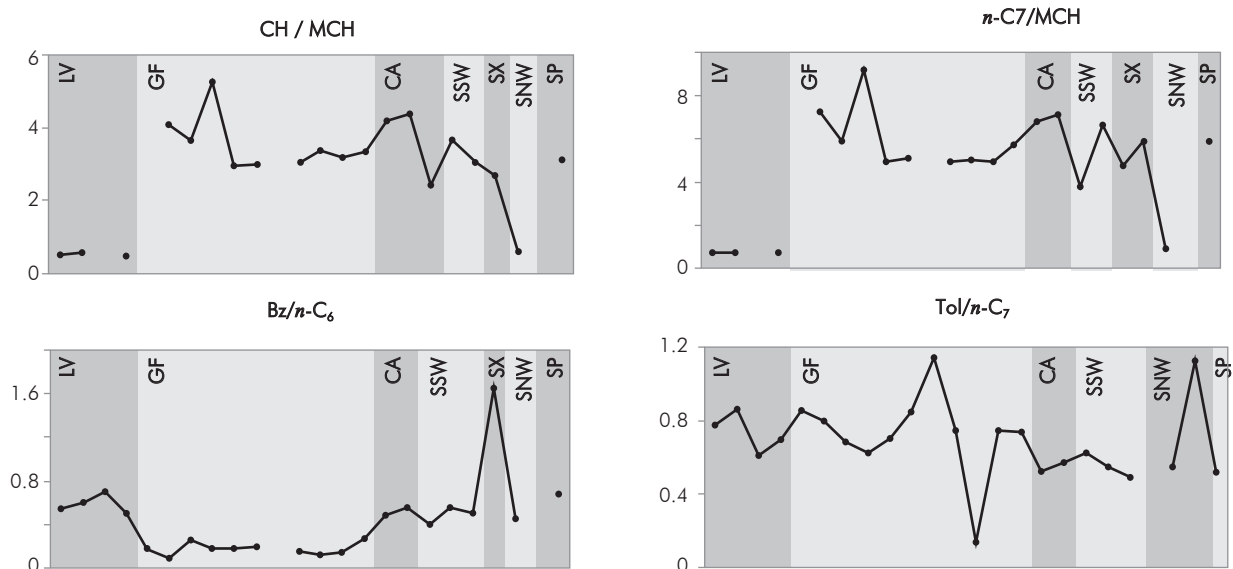


Figure 4. Thompson's ratios for oils from the Barinas sub-basin cyclohexane/methylcyclohexane (CH/MCH), *n*-heptane/methylcycloheptane (*n*-C₇/MCH), benzene/*n*-hexane (Bz/*n*-C₆), toluene/*n*-heptane (Tol/*n*-C₇). La Victoria (LV), Guafita (GF), Caípe (CA), Silvestre (SSW), Silvan (SNW), Sinco (S) and Palmita (SP).

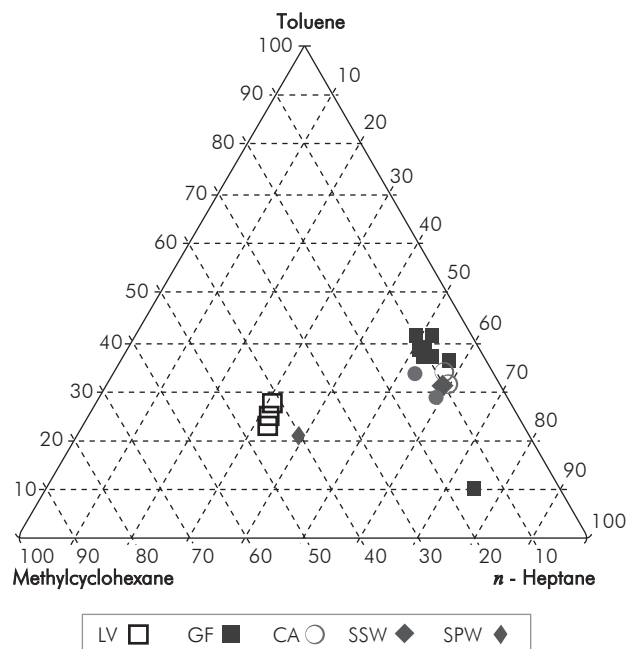


Figure 5. Ternary diagram showing the relative abundance of methylcyclohexane, toluene and n-heptane (Hill *et al.*, 2007) in crude oils from Barinas-Apure.

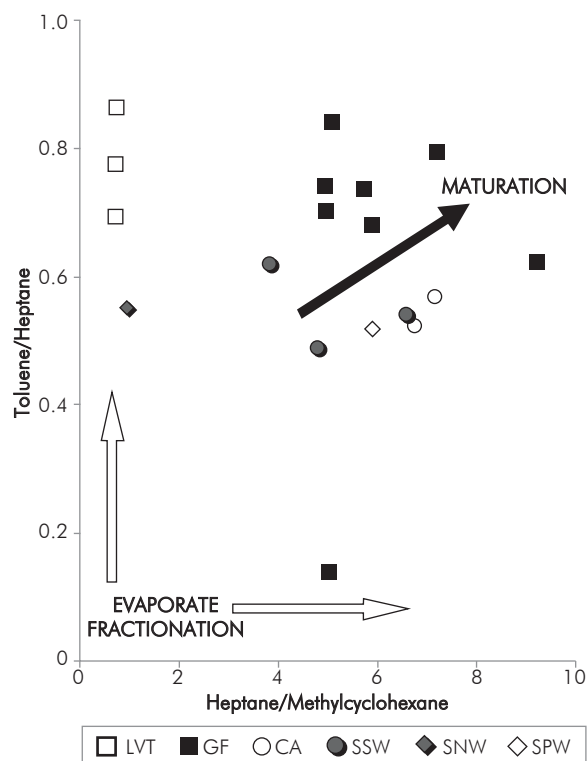


Figure 6. Diagram of alteration vectors of oils types (Thompson, 1987) for oils from Barinas sub-basin.

does not differentiate crude oils from different fields in the Barinas sub-basin.

On a previous study (López *et al.*, 1998; López, Lo Mónaco & Olivares, 2002), a detailed investigation of biomarkers in the terpane mass chromatogram ($m/z = 191$) indicated the presence of gammacerane and $18\alpha(H)$ -oleanane (Figure 7b, López *et al.*, 1998), so the oleanane $[\text{oleanane}/(\text{oleanane}+17\alpha,21\beta\text{-C}_{30}\text{hopane})\times 100]$ and gammacerane $[(\text{gammacerane}/(\text{gammacerane} + 17\alpha,21\beta\text{-C}_{30}\text{hopane}))\times 100]$ indexes were calculated. The gammacerane index range from 22 – 29% (Table 1), these values may be related to low stratification in water column during source rock sedimentation. Moldowan, Seifert & Gallegos, 1985; Sinnighe Damsté *et al.*, 1995; Peters *et al.*, 2005).

The oleanane index range from 10 to 14 (Table 1), all related to low higher-plant input during organic matter deposition (Peters *et al.*, 2005). Predominance of marine organic matter was determined by the relatively high abundance of tricyclic terpanes (maximum in C_{23-3}) (Figure 7b), the higher relative abundance of C_{27} sterane is associated with C_{29} (Figure 7c), and the presence of C_{30} sterane (López *et al.*, 1998).

The oleanane index and the pristane/phytane ratio are used to assess the regional variations in marine and terrigenous organic matter input, and redox sedimentation conditions (Table 1). This piece of data separates the oils into two groups: La Victoria and Guafita show higher oleanane index and pristane/phytane ratio. This suggests a greater contribution of terrigenous organic matter during sedimentation of organic facies that originated oils from Guafita and La Victoria, as compared to that of the other fields. Moreover, the higher pristane/phytane ratio for oils from Guafita and La Victoria suggests more oxic sedimentation conditions (López *et al.*, 1998). Figure 8 is a cross-plot of pristane/ $n\text{-C}_{17}$ versus phytane/ $n\text{-C}_{18}$ ratios that can be used to infer oxicity and organic matter type in the source-rock depositional environment (Connan & Cassou, 1980; Peters *et al.*, 1999; Gürgey, 2003). According to Figure 8, the oils from La Victoria and Guafita and some oils from the other fields are located in the area of mixed organic matter (mixed type-II-III kerogen), but most of these oils are located at the borderline with the marine area.

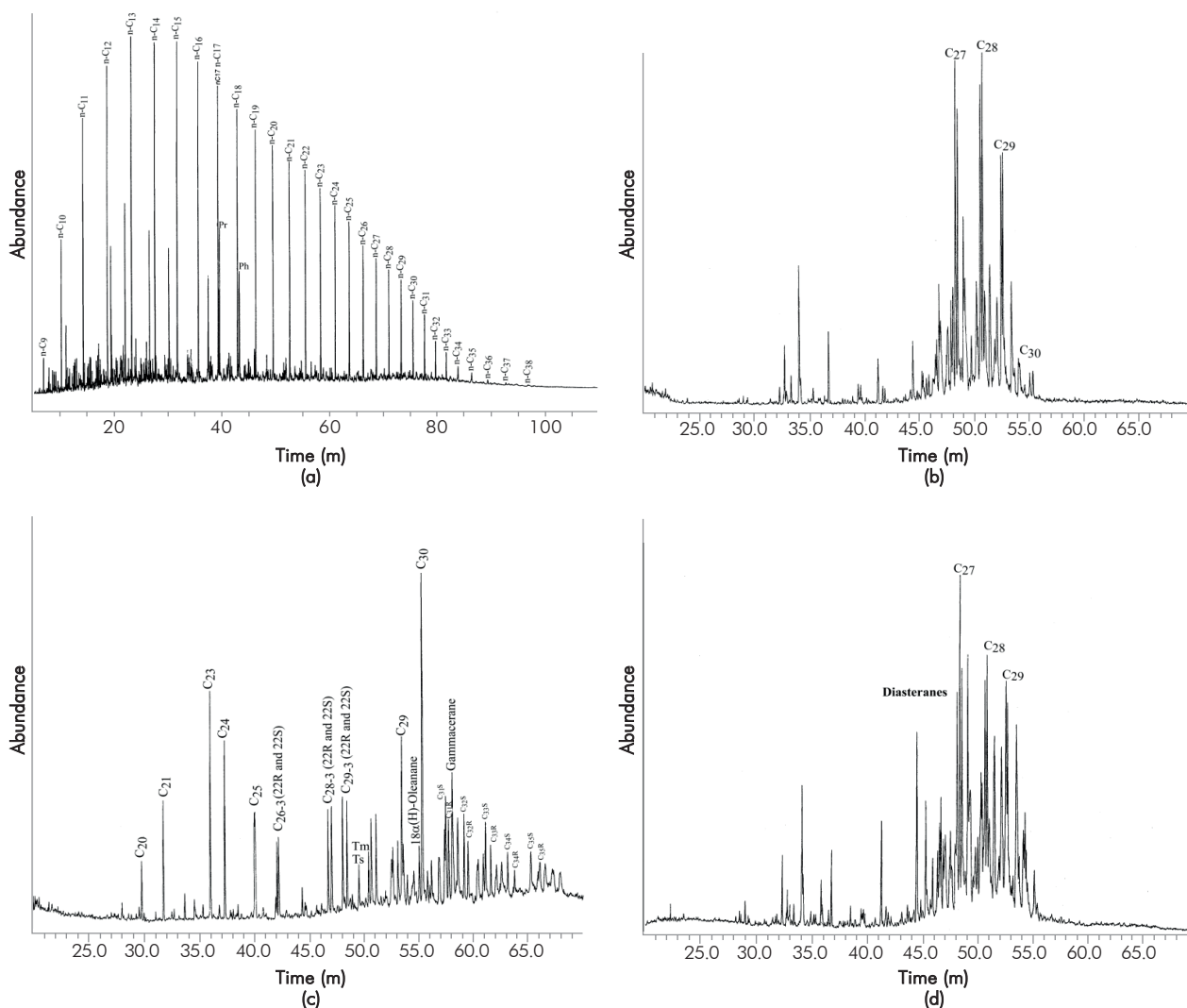


Figure 7. Representative gas chromatographs (a), and mass fragmentograms for terpanes (b): $m/z = 191$ and steranes (c): $m/z = 218$ and (d): $m/z = 217$ of the saturated hydrocarbon fractions extracted from oil GF-A. Pristane (Pr) and phytane (Ph).

The greater contribution of terrigenous organic matter to oils of the Apure fields was determined in a previous work using a C₃₀-sterane index (C₃₀-sterane/(C₂₇ to C₃₀ steranes) vs. oleanane index plot. The presence of C₃₀ sterane was corroborated by GC-MSMS (López *et al.*, 1998). The oils from Caipe, Silvestre, Sinco, Silvan and Palmita fields have higher sterane index and lower oleanane index than the oils from La Victoria and Guafita fields. These observations suggest a higher contribution of terrigenous organic matter in the oils from La Victoria and Guafita fields as compared to the others oils. Another group of geochemical parameters such as V/Ni ratio, $\delta^{13}\text{C}$ of the saturated and aromatic fractions, and the other group of biomarkers (López *et al.*, 1998) also suggest a greater contribution of terrigenous organic matter.

Additional information on source rock lithofacies derived from the isomer distribution pattern of methylbenzothiophenes (MeDBT). The Me-DBT isomer distribution pattern from La Victoria and Guafita fields corresponds to 4-MeDBT > 2,3-MeDBT > 1-MeDBT, which is normally associated with siliciclastic source rocks (Hughes, 1984). For Caipe, Silvestre, Sinco, Silvan and Palmita oils, the pattern corresponds to 4-MeDBT > 2,3Me-DBT < 1Me-DBT, associated with carbonate-rich source rocks (López *et al.*, 1998; Hughes, 1984). Table 1 presents a summary of the characteristics that determine the differences in lithofacies and depositional conditions of the rock source for oils under analysis (López *et al.*, 1998; Lo Mónaco *et al.*, 1999). In general, based of methylbenzothiophene (MeDBT) distribution and diasterane/sterane ratio was

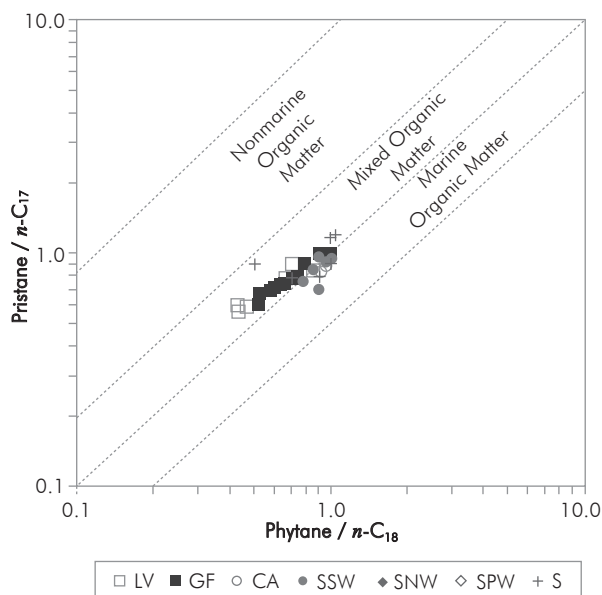


Figure 8. Cross-plot of pristane/ n -C₁₇ versus phytane/ n -C₁₈ relationships (Connan & Cassou, 1980) for analyzed oils. Forty-seven samples of crude oils from seven fields are represented in the graph.

possible to determine that crude oils from La Victoria, Guafita were generated by siliclastic-rich lithofacies and oil from Caipe, Silvestre, Sinco, Silvan, Palmita by carbonate-rich lithofacies. Maturity parameters such as moretanes/hopanes, %C₂₉20S, %C₂₉ββ, triaromatic steroids (TAS), monoaromatic steroids (MAS) and PP-1_{modified} allow determining that the oils from La Victoria and Guafita have less mature relation when compared to oils from Caipe, Silvestre, Sinco, Silvan and Palmita.

High-Molecular-Weight Hydrocarbons (C₄₀₊)

Figure 9 shows the distribution of HMWHC for two crude oils from Barinas sub-basin. It is worth mentioning that the whole set of oils exhibits very low relative intensities in the C₄₀₊ interval, which is associated with crude oils with low waxy index. Only SSW-B (Silvestre), SNW-B (Silvan), CA-A (Caipe), and GF-D (Guafita) oils are characterized by higher intensities in the interval corresponding to the C₄₂-C₅₀ (Figure 9). The carbon preference index CPI^a (Hsieh & Philp, 2001). f high-molecular weight alkylcyclopentanes was determined in the C₄₂-C₄₆ interval (Table 1). This parameter provides information on the original sedimentation environment; and it is considered not to depend on age, maturity and oil biodegradation, thus, being a very useful geochemical parameter (Hsieh & Philp, 2001). Values of CPI^a (C₄₂-C₄₆) \cong 1 have been associated with freshwater lacustrine environments; CPI^a (C₄₂-C₄₆) \ll 1 are related to saline lacustrine environments; and CPI^a

(C₄₂-C₄₆) $>$ 1 are associated with marine environments. In particular, a CPI^a(C₄₂-C₄₆) $>$ 1 for alkylcyclopentanes appears to reflect a marine depositional environment (Hsieh & Philp, 2001). CPI^a(C₄₂-C₄₆) in the analyzed oils (Table 1) show values from 0.7 to 1.5 but do not differentiate oils from different fields. Most of the crude oils analyzed show CPI^a(C₄₂-C₄₆) values ranging from 0.7-0.9 and only five oils have values $>$ 1. These results do not match with the different groups obtained in previous studies, based on biomarkers, isotopes and V/Ni ratio, which indicate a marine depositional environment for the source rock of these oils (López *et al.*, 1998). Therefore, in analyzed oils from the Barinas sub-basin, the CPI^a(C₄₂-C₄₆) ratio is not a good indicator to differentiate crude oils generated by source rocks with variations in lithology (carbonate-siliclastic), and organic matter input (marine-terrestrial); or it is necessary to have a larger number of samples and HMWHC analysis in crude oils from Barinas sub-basin in order to identify similarities or differences in these crude oils based on CPI^a(C₄₂-C₄₆) ratio.

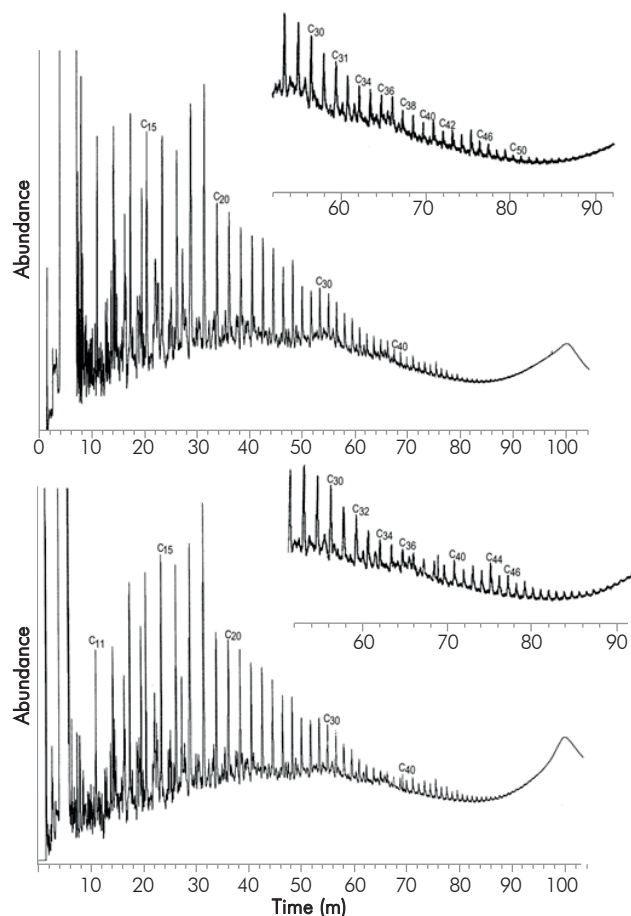


Figure 9. High-temperature gas chromatography for selected oils from the Barinas sub-basin. Oils GF-A (A) and CA-A (B).

4. CONCLUSIONS

- In this study, results of oil fingerprinting by WOGC suggest different processes may be affecting crude oil in the reservoirs, based on relations in the C₁₅₋ fraction associated with paraffinity and aromaticity. The crude oils studied from Caipe, La Victoria, Silvan, and Guafita did not undergo biodegradation and/or water washing processes. Silvestre crude oils appear to have been subject to biodegradation and water washing and those from Sinco only to water washing. WOGC in hydrocarbons, according to toluene/n-heptane (Tol/n-C₇) vs. n-heptane/methylcyclohexane (n-C₇/MCH), indicate that studied oils from Guafita, Caipe, Silvestre and Palmita were generated from a mature source rock, also showing that oils from La Victoria and some from Guafita and Silvan may have undergone evaporative fractionation. For a set of samples, the results obtained for the CPI^a(C₄₂-C₄₆) are not compatible with other parameters used as environmental indicators suggested by the biomarkers and isotopic studies (López *et al.*, 1998). It is necessary to analyze a larger number of samples and compare source parameters obtained from CPI^a(C₄₂-C₄₆) with those obtained by biomarkers to determine whether these two kinds of results are comparable in interpreting crude oil source-related parameters.

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