

# ASSESSMENT OF TERRIGENOUS AND MARINE SOURCED OILS MIXTURES: LOS MANUELES FIELD, MARACAIBO BASIN, VENEZUELA

## EVALUACIÓN DE MEZCLAS DE CRUDOS DE ORIGEN TERRÍGENO Y MARINO: CAMPO LOS MANUELES, CUENCA DE MARACAIBO, VENEZUELA

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### ABSTRACT

Seven crude oil samples from Los Manueles field, Maracaibo Basin, Venezuela, were analyzed to evaluate oil mixtures associated with different oil charges into the reservoirs. Analyses of the bulk physicochemical parameters suggest variations in the API gravity, the concentration of saturated and aromatic hydrocarbons, NSO compounds + asphaltenes, sulfur, vanadium, nickel, and the biomarkers distribution. The oils were divided in two groups: G-I with high saturated hydrocarbons and low NSO compounds + asphaltenes, sulfur, vanadium and nickel, a bimodal distribution of *n*-alkanes, high Pr/Ph and oleanane index, low steranes index, low abundance of tricyclic terpanes and  $C_{35}S/C_{34}S < 0.54$  and G-II with low saturated hydrocarbons and high NSO compounds+ asphaltenes, sulfur, vanadium and nickel, an unimodal distribution of *n*-alkanes with low Pr/Ph and oleanane index, high steranes index, abundance of tricyclic terpanes and  $C_{35}S/C_{34}S > 0.70$ . G-I has a higher contribution of terrigenous organic matter compared to G-II, characterized by a higher contribution of marine organic matter. Source rock lithology biomarker indicators suggest marine shale as the source rock for oils of terrigenous origin. The results indicate that oils were generated by two independent source rocks, La Luna Formation and a secondary source rock with terrigenous organic matter, probably represented by the Capacho Formation.

### RESUMEN

Se analizaron siete muestras de crudos del campo Los Manueles de la Cuenca de Maracaibo, Venezuela, para evaluar las mezclas de crudos debido a las diferentes cargas a los yacimientos. El análisis de los parámetros fisicoquímicos indican variaciones en la gravedad API y la concentración de hidrocarburos saturados y aromáticos, compuestos NSO + asfaltenos, azufre, vanadio y níquel y en la distribución de biomarcadores. Los crudos se dividieron en dos grupos: G-I altos hidrocarburos saturados y bajos en compuestos NSO + asfaltenos, azufre, vanadio y níquel, con distribución bimodal de *n*-alcanos, alto índice de Pr/Ph y oleanano, bajo índice de esteranos, baja abundancia de terpanos tricíclicos y  $C_{35}S/C_{34}S < 0,54$  y G-II bajos en hidrocarburos saturados y altos en compuestos NSO+ asfaltenos, azufre, vanadio y níquel, con distribución unimodal de *n*-alcanos bajo índice Pr/Ph y oleanano, alto índice de esteranos, abundancia de terpanos tricíclicos y  $C_{35}S/C_{34}S > 0,70$ . G-I tiene una mayor contribución de materia orgánica terrígena comparada con el G-II, caracterizado por mayor contribución de materia orgánica marina. Los indicadores de litología de la roca fuente basados en los biomarcadores, sugieren lutitas marina para los crudos de origen terrígeno. Los resultados indican que los crudos fueron generados por dos rocas fuente independientes, la Formación La Luna y como roca fuente secundaria, con materia orgánica terrígena probablemente representada por la Formación Capacho.

### KEYWORDS / PALABRAS CLAVE

Mixed oil | Terrigenous oil | Marine oils | La Luna Formation | Capacho Formation | Maracaibo Basin | Los Manueles field.

Mezcla de crudos | Crudos terrígenos | Crudos marinos | Formación La Luna | Formación Capacho | Cuenca de Maracaibo | Campo Los Manueles.

### AFFILIATION

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## 1. INTRODUCTION

Oil exploration studies conducted in the Maracaibo Basin, northwest of Venezuela, have determined that La Luna Formation (Cenomanian-Coniacian) is the main source rock for most of the oil accumulated in reservoirs (1-4). However, towards the southwest of the Maracaibo Basin, there are several oil fields with different geochemical characteristics as compared with those reported for La Luna Formation and which origin is not entirely defined, e.g., Los Manueles field. Previous studies of these oils suggest their terrigenous origin (2,4,5), and might be considered a product of generation from single source rocks containing both marine and terrigenous organic matter or by the mixture of oils from two source rocks with different organic matter. Considering that La Luna Formation, the main source rock of the Maracaibo basin, is characterized by marine organic matter (1,2,3,6), the terrigenous components found in crude oils from Los Manueles suggest that a secondary source rock, associated with the Maracaibo basin, has also contributed to the generation of these oils (7). Located in the southwestern of the Maracaibo Basin is the hypothetical Orocué petroleum system, represented by a coaly source rock containing type III kerogen. This hypothetical petroleum system is associated to terrigenous oils and oil mixtures (marine and terrigenous), which

are associated to both, Orocué and La Luna (8,9). Other possible source rock is the Capacho Formation, with siliciclastic source rock from marine origin (7,10). Both formations have also been proposed as source rocks for mixed marine-terrigenous oils in the Catatumbo Basin (Colombia), which is located in the southwestern edge of the Maracaibo Basin (10). The Capacho Formation is subdivided into three members: Guayacan (limestones), Seboruco (clastic shales) and La Grita (limestone and calcareous shale), and characterized by kerogen II in La Grita Member (11)], or II /III (7,10). However, as regards a terrigenous source rock, the origin of Los Manueles field is not well established. Therefore, we describe a series of parameters such as SARA composition (saturate and aromatic hydrocarbons, NSO compounds and asphaltenes), sulfur, vanadium and nickel concentration, V/Ni ratio, and biomarkers; measured in seven crude oils from different oil wells in Los Manueles field, to present evidences of oils mixtures, to provide insights into the characteristics of the possible terrigenous source rocks (e.g., lithology, organic-matter input, redox depositional conditions and thermal maturity) and, based on these interpretation, show the geological formation that could contribute as a secondary source rock of terrigenous origin.

## 2. GEOLOGY AND GEOCHEMISTRY

Los Manueles field is located in the Maracaibo Basin, Venezuela, near the limit between Venezuela and Colombia (Figure 1). This field, together with Las Cruces and El Cubo, are grouped under the name of Tarra, located in the anticline of the same name (12). Los Manueles field belongs to the Orocué hypothetical petroleum system, which is restricted to the southwest of the Maracaibo Basin. The oils in this petroleum system come from non-marine source rocks with input of terrigenous organic matter in mixtures with oils from a marine organic matter from La Luna Formation. The Orocué petroleum system is considered hypothetical, due to the lack of a clear determination of oils-source rock correlations that would allow to properly establish the origin of these oils (8,9). Additionally, the influence of oil mixture over the quality of oils in the reservoirs has not been established.

Based on sulfur and vanadium content, *n*-alkane distribution, and biomarkers, three oil types were detected in the Maracaibo Basin. These types include marine, terrigenous, and a third group derived

from the mixture of both. The marine oils are distributed throughout the basin, while the terrigenous and those originated by mixtures are present only in the southwestern part of the Basin, in Los Manueles (Eocene), Tarra Oeste (Paleocene) and Las Cruces (Paleocene Eocene) fields (2,5,13). Although it has been determined that La Luna Formation is the main source rock of marine oils, the source rock of the terrigenous oils has not been established, suggesting an origin from the Eocene coals of the Carbonera Formation (5), characterized by the presence of terrigenous organic matter. On the other hand, the V/Ni and V/(V+Ni) ratios are similar to those obtained from other fields in the Maracaibo Basin (e.g., Lagunillas field), but the biomarkers of these oils are mainly distinguished by the presence of  $18\alpha$ (H)-oleanane, which marks the terrigenous contribution of angiosperms plants (2,4). Therefore, a detailed study on the variations in the contribution of marine and terrigenous organic matter in oils from Los Manueles field is necessary to understand the origin and oils mixtures.

## 3. LOS MANUELES THERMAL MODELING

Thermal modeling considers a Jurassic rifting event in different areas of northern South America (14). The effect of the extension along the Central Cordillera of Colombia was estimated as five lithosphere stretching pulses during the Mesozoic (15). The thermal effect, a higher heat flow for a beta stretching factor of 1.3, is decreasing exponentially to the present-day estimation of heat flow in several wells in Colombia (Figure. 2A). Maturity parameters are measured with the vitrinite reflectance and the Tmax value during pyrolysis of rock samples (10). Modeling of the heat flow history and the thickness of eroded sediments fit maturity parameters.

Thermal modeling for a pseudo well at the SE of Los Manueles field

(7), projected to a W-E seismic line across the field, fit the maturity trends in Colombia. It corresponds to a deep point of the draining area at the kitchen of Cretaceous source rocks. Hydrocarbons generated migrate to Los Manueles field along faults at Cretaceous shallower sites, as is shown in the sketch corresponding to the interpretation of the seismic line. The source of the hydrocarbons is the Cretaceous La Luna, calcareous with a clastic content up to 30%, and a Type II kerogen, and the Capacho Formation, just below, with Type II/III organic matter (10).

The generation and expulsion history of the bottom of La Luna Formation (Figure 2C) starts at 70 Ma with a peak (R<sub>t</sub>) of 20 mg Oil/g

TOC \* Ma for the oil generation rate at the Paleocene in contrast to the average of 2 mg Oil/g TOC \* Ma from the Eocene onwards. The peak corresponds to the maximum generation pressure rate, genetically associated with the change from solid kerogen to a lower density hydrocarbon fluid. Expulsion of oil (primary migration) starts at the Early Oligocene (Ex). A generated oil saturation threshold triggers fluid expulsion when a continuous thread of oil forms through the rock. Saturation correlates to a higher TOC, thermal maturity, and the kinetics of the transformation of the kerogen into hydrocarbons. Nevertheless, expulsion and eventually secondary migration to the Eocene-Oligocene carrier bed, reservoirs in Los Manueles field, will need the sealing restriction at the reservoir top, which are the shales of the Oligocene formations. The sedimentation of those shales ends at Mid-Miocene (RS), before the peak on the volumes of expelled oil and gas and corresponds to maturity of the source rock slightly above 1% Ro at the bottom of La Luna (Figure 2C). The present-day configuration of structural traps is given by the uplifting inverse faults shaping the Maracaibo basin and related to the growing mountains ranges to the West (Perijá) and East (Andes). The seismic interpretation (Figure 2B) records this event at the upper right corner. The evolution of the Capacho Formation is similar, with slight differences in the event ages, because of a higher maturity reached. Nevertheless, the expelled volume calculated from Capacho is less than 10% of the total by both source rocks, mainly because of the lower effective thickness and TOC. There are also Cretaceous reservoirs below that compete for receiving the hydrocarbons from both source rocks.

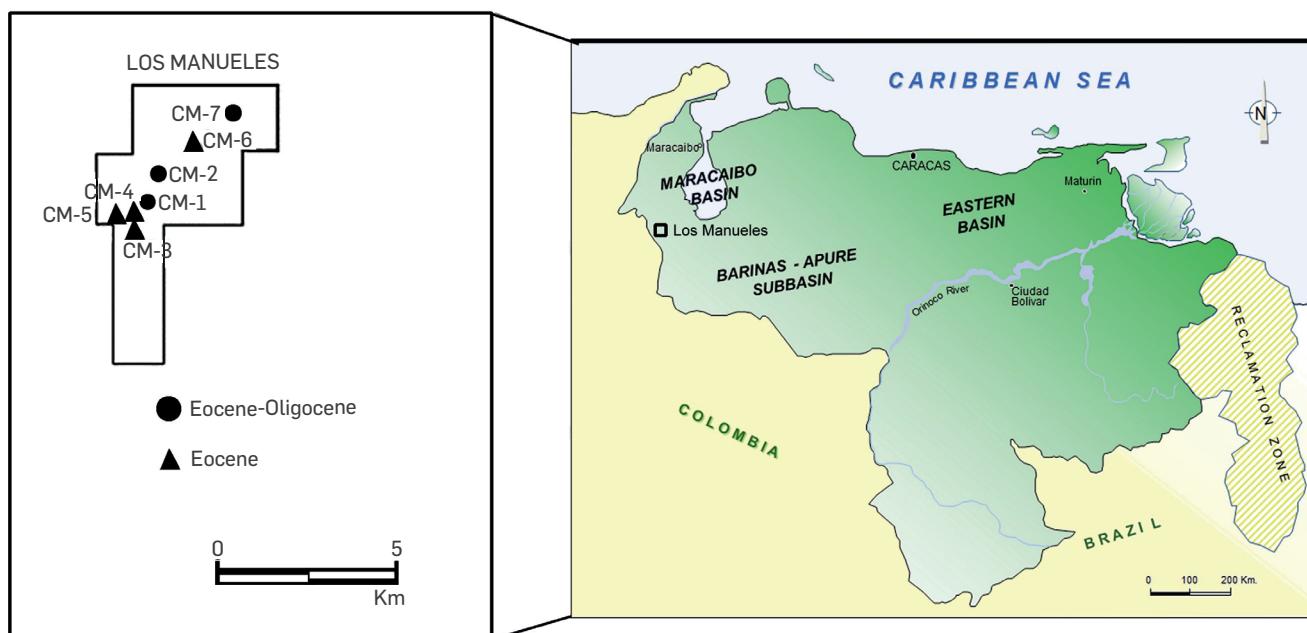
## 4. EXPERIMENTAL DEVELOPMENT

Seven samples of crude oil from Los Manueles field (Table 1) were fractioned into saturate, aromatic, NSO and asphaltenes by means of adsorption chromatography, using packed columns (20

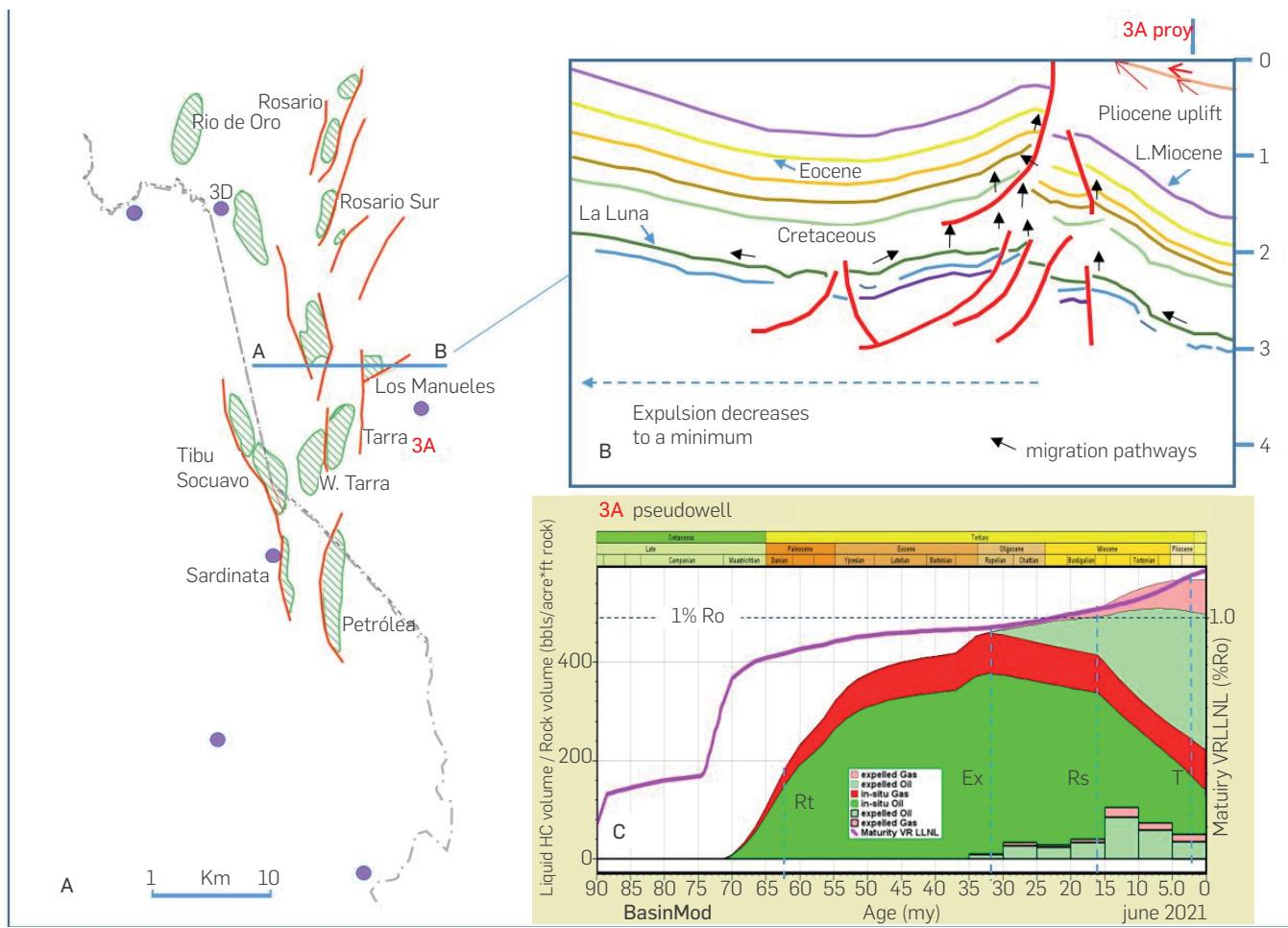
cm long and 1.5 cm i.d.) with alumina as the stationary phase (20 g). Saturated hydrocarbons were eluted with *n*-hexane (30 mL), and the aromatic hydrocarbons with toluene (20 mL). The NSO + asphaltene percentage weight (wt. %) was determined by difference [% (NSO + asphaltenes) = 100% - (% saturated + % aromatic)]. Prior to the biomarkers analysis, the saturated hydrocarbon fraction was purified twice by liquid chromatography using packed columns as described above.

Trace elements (V and Ni) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Jobin-Yvon JY-24). The sulfur content was determined using a LECO SC-432 sulfur analyzer. Before the analysis of S, V and Ni in crude oils, samples were mixed with toluene (2:1, v:v) followed by centrifugation (20 min at 5000 rpm) to separate water and sediment; subsequently, the solvent was removed by evaporation under reduced pressure. This was intended to decrease the possible contamination by trace elements present in sediment or water associated to oil (16,17).

Gas chromatography (GC) of the saturated hydrocarbon fractions was conducted on a 6890N Agilent Technologies Network gas chromatograph using a flame ionization detector (FID) and DB-1 fused capillary columns (0.25  $\mu$ m film thickness  $\times$  0.25 mm i.d., and 60 m length). Detailed analyses of the saturated and aromatic compounds were performed by gas chromatography - mass spectrometry (GC-MS) by coupling the gas chromatograph to a 5975 Agilent Technologies mass spectrometer operated in single ion monitoring mode. The GC system was equipped with DB-1 or DB-5 fused silica capillary columns (0.25  $\mu$ m film thickness  $\times$  0.25 mm i.d., and 60 m length) to analyze the saturated and aromatic fractions, respectively. Samples were analyzed in selected ion monitoring (SIM) mode, the mass-to-charge ratios were *m/z* = 191 (terpanes), 412 (18 $\alpha$ (H)-oleanane, gammacerane), 217, 218 (steranes), 231 (triangular steroids), 178 (phenanthrene), 192 (methylphenanthrenes), 184 (dibenzothiophene + tetramethylnaphthalenes), and 198 (methyldibenzothiophenes).



**Figure 1.** Map of Venezuela showing the location of Los Manueles field in the Maracaibo Basin, Venezuela.



**Figure 2.** **A** Catatumbo's oil fields (Colombia/Venezuela). Wells with stratigraphic and maturity data (10). **A-B** seismic line and Pseudo wells locations from (7). **B** Seismic line (7) sketch interpretation. Migration pathways for La Luna and Capacho expelled oil and gas. **C** Age diagram for the cumulative generated and the expelled hydrocarbon volume from La Luna source rock and its thermal maturity evolution. Events Age: Rt-Oil generation rate peak, Ex-tart of oil and gas expulsion, RS-Tertiary reservoir/seal existence, T-Tertiary structural traps genesis.

## 5. RESULTS AND DISCUSSION

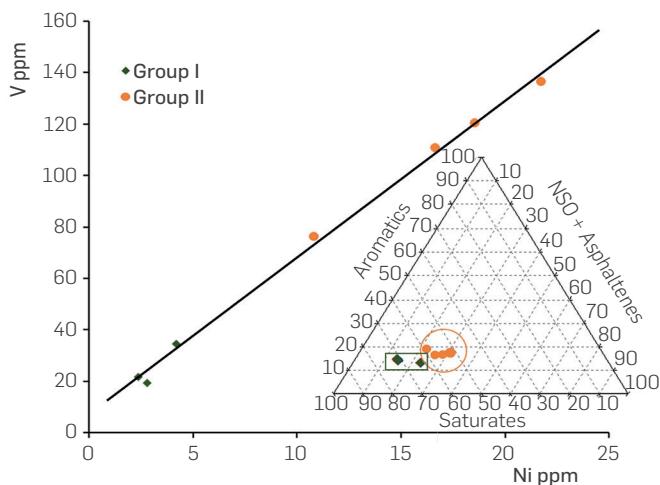
### BULK GEOCHEMICAL PARAMETERS

Table 1 shows the API classification and SARA composition of the analyzed oils. All the oils are medium to light with API gravity ranging from 26 to 39. They have a high content of saturates (52-71 %), and low content of aromatic (13-19%) and NSO-compounds + asphaltenes (14-31%). According to the bulk SARA composition, all oils can be classified as paraffinic naphthenic. A detailed analysis in SARA composition reflects differences between oils. CM-1, CM-2 and CM-3 are characterized by saturate hydrocarbons  $\geq 64\%$ , aromatic hydrocarbons between 4 to 17% and NSO and asphaltenes between 14 to 23%, while the samples CM-4, CM-5, CM-6 and CM-7 have saturated hydrocarbons  $\leq 59\%$ , aromatic hydrocarbons between 16 to 19% and NSO + asphaltenes in the range of 22 to 31%. Table 1 also shows the concentrations of sulfur, vanadium, and nickel, together with V/Ni and V/(V+Ni) ratios. Samples CM-1 to CM-3 present lowest sulfur, vanadium and nickel concentration,

compared with CM-4 to CM-7. However, the V/Ni and V/(V+Ni) ratio is in the same range of values for all crude oils.

The different oil types are specified in the SARA composition, sulfur, vanadium, and nickel concentrations. These differences are used to divide oils in two groups:

- a) Group I, characterized by sulfur ranging from 0.43 to 0.52 %, vanadium from 19.3-34.3 ppm, nickel from 2.4-4.2 ppm, saturated hydrocarbons  $\geq 64\%$ , aromatic hydrocarbons between 13 and 15 % and NSO + asphaltenes between 14 and 23 % (Figure 3), and
- b) Group II, this group have sulfur from 0.97 to 1.08 %, vanadium from 76.6-136.8 ppm, nickel from 10.8-21.7 ppm, saturated hydrocarbons  $\leq 59\%$ , aromatic hydrocarbons from 16 to 19 % and NSO + asphaltenes between 22 and 31 % (Figure 3). This variability in crude oil composition may be the result of different source rocks and oil mixtures in the reservoir. With the aim of determining the origin of these oils, detailed analyses based on molecular parameters, together with SARA composition and vanadium, nickel and sulfur concentrations are discussed in the following section.



**Figure 3.** Relationships between V and Ni concentrations and ternary diagram showing the bulk SARA (saturated, aromatic, resins and asphaltenes) composition of crude oil from Los Manueles field.

## ORGANIC MATTER TYPE AND SEDIMENTATION ENVIRONMENT

Figure 4 shows examples of the distributions of *n*-alkanes and acyclic isoprenoids (GC-FID) that are representative of the two oil groups. The *n*-alkanes in the range of *n*-C<sub>13</sub> to *n*-C<sub>38</sub> show two different distributions, and also a different Pr/Ph ratio: (a) bimodal *n*-alkane distribution maximizing at *n*-C<sub>17</sub> and *n*-C<sub>27</sub> (samples CM-1 to CM-3), with Pr/Ph ≈ 2.3; (b) unimodal *n*-alkane distribution maximizing at *n*-C<sub>17</sub>, with Pr/Ph ≈ 1.1 (samples CM-4 a CM-7) (Table 2). These distributions in oils from Group I are usually associated to mixed (terrigenous + marine) organic matter input during sedimentation in dysoxic conditions. Oils from Group II are associated to marine organic matter deposited under suboxic conditions (18,19). The cross-plot of pristane/*n*-C<sub>17</sub> versus phytane/*n*-C<sub>18</sub> ratios was used to infer the organic matter type (20,21). According to Figure 5, all samples are characterized by mixed organic matter with different input of terrigenous organic matter and variations in redox sedimentation conditions.

**Table 1.** API gravity, SARA composition, sulfur, vanadium, nickel concentration, and V/Ni and V/(V+Ni) ratios for oils from Los Manueles field.

Oil Group	Well	Producer interval	API gravity	Saturates wt. %	Aromatics wt. %	NSO+Asph <sup>1</sup> wt. %	S wt. %	V ppm	Ni ppm	V/Ni	V/(V+Ni)
Group I	CM-1	Carbonera Fm <sup>2</sup> .	26	71	15	14	0.48	21.5	2.4	8.5	0.8952
	CM-2	Carbonera Fm.	36	64	13	23	0.43	34.3	4.2	8.2	0.8909
	CM-3	Mirador Fm <sup>3</sup> .	30	71	14	15	0.52	19.3	2.8	6.9	0.8730
Group II	CM-4	Mirador Fm.	28	52	17	31	0.97	136.8	21.7	6.3	0.8631
	CM-5	Mirador Fm.	34	56	16	29	1.07	120.8	18.5	6.5	0.8672
	CM-6	Mirador Fm.	----	59	19	22	1.08	110.9	16.6	6.7	0.8698
	CM-7	Mirador Fm.	39	57	16	27	1.03	76.6	10.8	7.1	0.8764

NSO+Asph: NSO compounds + Asphaltenes

Fm: Formation<sup>2</sup>Carbonera Fm: Carbonera Formation Eocene-Oligocene

<sup>3</sup> Mirador Fm: Mirador Formation Eocene

----: Data not available

**Table 2.** Saturated hydrocarbon biomarker source parameters for oil from the Los Manueles field.

Oil Group	Well	Pr/Ph <sup>1</sup>	Pr/n-C <sub>17</sub> <sup>1</sup>	Pr/n-C <sub>18</sub> <sup>1</sup>	OI <sup>2</sup>	GI <sup>3</sup>	SI <sup>4</sup>	%C <sub>27</sub> <sup>5</sup>	%C <sub>28</sub> <sup>5</sup>	%C <sub>29</sub> <sup>5</sup>	Ster/Hop <sup>6</sup>
Group I	CM-1	2.3	0.71	0.33	20	7	3.5	35	30	35	0.18
	CM-2	2.2	0.78	0.34	20	5	3.8	36	28	37	0.18
	CM-3	2.3	0.71	0.33	23	6	3.2	35	30	35	0.17
Group II	CM-4	1.1	0.69	0.68	6	7	4.7	38	31	31	0.35
	CM-5	1.1	0.69	0.69	6	8	4.3	38	32	31	0.36
	CM-6	1.1	0.68	0.68	6	6	4.1	39	31	31	0.38
	CM-7	1.2	0.72	0.66	8	7	4.1	38	31	31	0.35

<sup>1</sup>Pr/Ph = Pristane/Phytane Pr/n-C<sub>17</sub> = Pristane/n-C<sub>17</sub> Ph/n-C<sub>18</sub> = Phytane/n-C<sub>18</sub>(18,20).

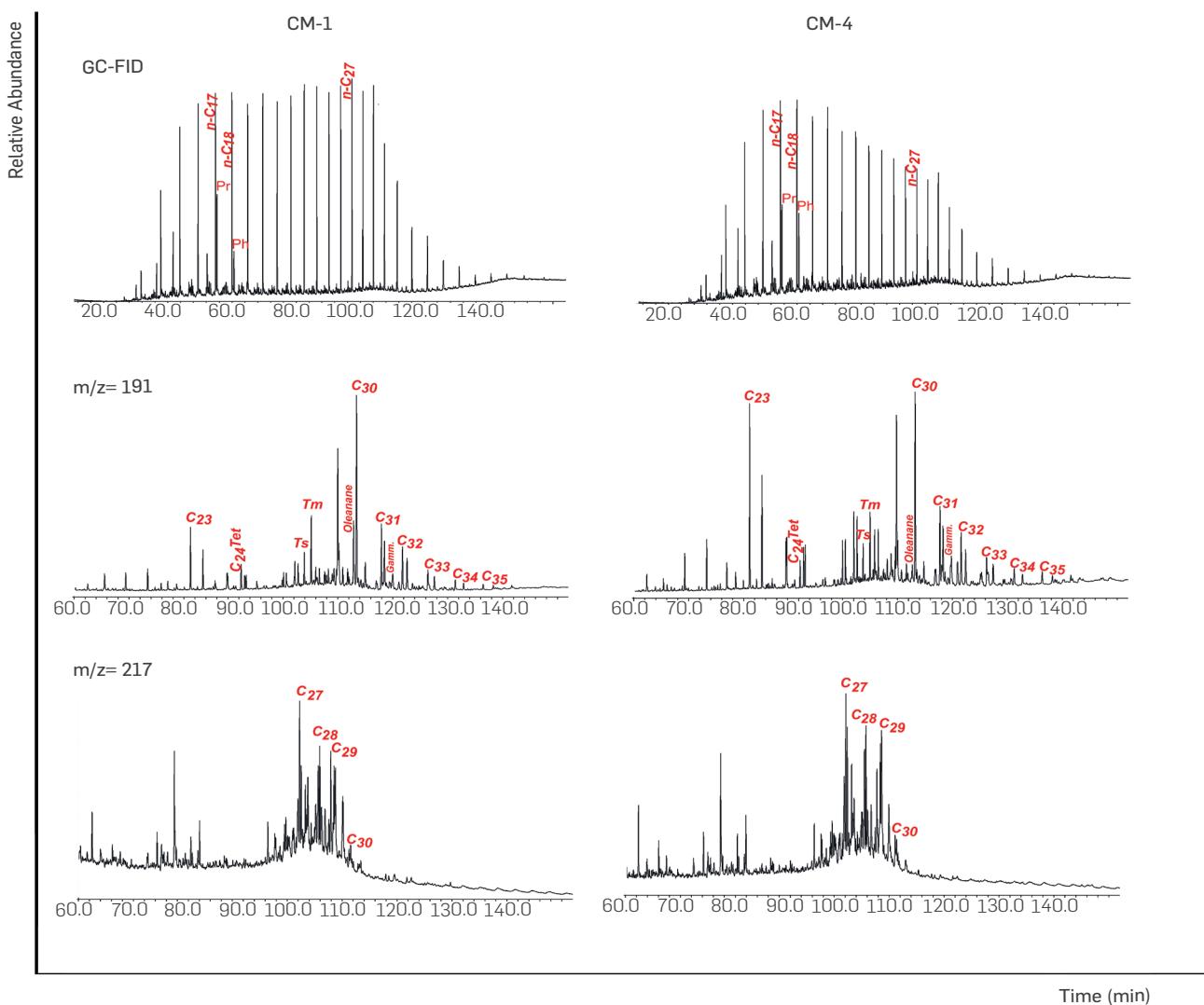
<sup>2</sup>OI Oleane Index = [(18α(H)-oleane)/(18α(H)-oleane + 17α,21β-C<sub>30</sub>hopane)] X 100 (22).

<sup>3</sup> GI = Gammacerane Index = [gammacerane/gammacerane + 17α,21β-C<sub>30</sub>hopane] x 100 (23).

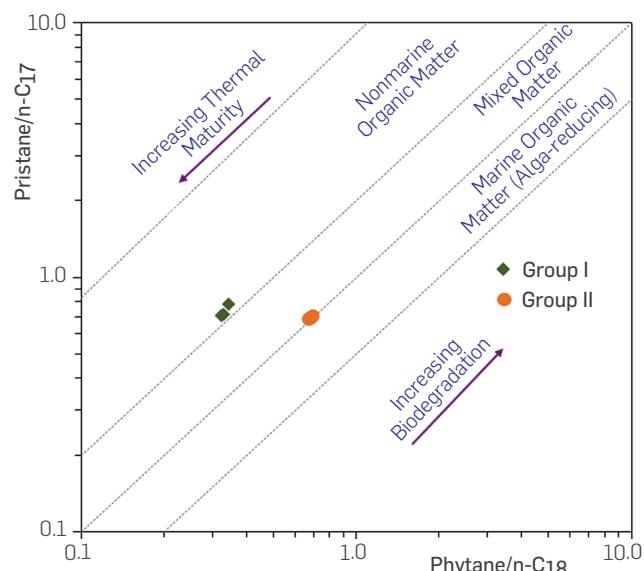
<sup>4</sup> SI = Steranes Index = C<sub>30</sub> [ααα (20S + 20R) + αββ (20S + 20R)] / Σ C<sub>27</sub> - C<sub>30</sub> [ααα (20S + 20R) + αββ (20S + 20R)] (24).

<sup>5</sup>Sterane proportions = %C<sub>27</sub> = [C<sub>27</sub>/Σ(C<sub>27</sub> to C<sub>29</sub>) X 100; %C<sub>28</sub> = [C<sub>28</sub>/Σ(C<sub>27</sub> to C<sub>29</sub>) X 100; %C<sub>29</sub> = [C<sub>29</sub>/Σ(C<sub>27</sub> to C<sub>29</sub>) X 100 (24).

<sup>6</sup>Steranes/Hopanes = Steranes ΣC<sub>27</sub> - C<sub>29</sub> [ααα (20S + 20R) + αββ (20S + 20R)]/Hopanes [C<sub>29</sub> + C<sub>30</sub> + [Σ C<sub>31</sub> - C<sub>33</sub> (S + R)]] (23).



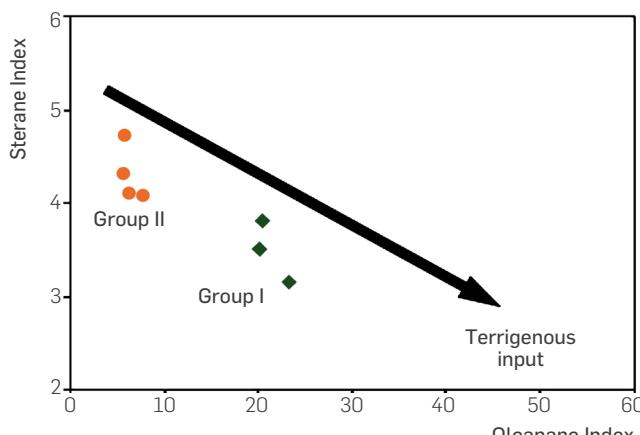
**Figure 4.** Representative *n*-alkanes and acyclic isoprenoid alkane pristane (Pr) and phytane (Ph) gas chromatograms (GC-FID) and mass fragmentograms of terpanes (*m/z* = 191) and steranes (*m/z* = 217) for two selected oil samples.



**Figure 5.** Pristane/*n*-C<sub>17</sub> versus phytane/*n*-C<sub>18</sub> for crude oils from the Los Manueles field.

Figure 4 also shows terpanes and steranes distribution (GC-MS *m/z* 191 and 217 respectively) for representative oils. The terpane distributions of oils CM-1 to CM-3 exhibit low abundance of tricyclic terpanes (cheilanthanes) and high abundance of tetracyclic terpane (C<sub>24</sub>Tet) and 18 $\alpha$ (H)-oleanane compared to pentacyclic terpanes (hopanes) abundance. Opposite trends are observed in oils CM-4 to CM-7, with tricyclic terpanes more abundant compared to pentacyclic and lower abundance of tetracyclic terpane (C<sub>24</sub>Tet) and 18 $\alpha$ (H)-oleanane. These results also suggest a mix for both groups of oils, with greater contribution of terrigenous organic matter for Group I. Gammacerane was also detected in all analyzed oils; a similar gammacerane index (GI between 5 to 8%) suggests slight variations in stratification conditions in water column (25). On the other hand, the pregnanes (pregnane C<sub>20</sub> and homopregnane C<sub>21</sub>) and C<sub>27</sub>, C<sub>28</sub>, C<sub>29</sub> and C<sub>30</sub> regular steranes are observed in all the samples. The steranes distribution is characterized by C<sub>27</sub> > C<sub>28</sub> > C<sub>29</sub>. These distributions and the presence of C<sub>30</sub> sterane are commonly associated with marine organic matter input (26). Based on the graphic representation of the oleanane index (OI) vs. the steranes index (SI) (Table 2, Figure 6), differences in the input of terrigenous organic matter are observed. Oils from Group I have higher OI and lower SI index, which suggests more terrigenous

input. In Group II, the tendency is opposed, suggesting a source with major contribution of marine organic matter. Additionally, the steranes/hopanes ratio (25), which is an organic matter source parameter frequently used to compare the compounds from higher plants or algal sources (eukaryotic organism) with those from bacterial source (prokaryotic organism) (19,26), yielded values in the range of 0.17-0.18 and 0.35-0.38 for oils from groups I and II respectively (Table 2). This suggests a significant contribution of terrigenous and/or microbial reworked organic matter for oils from Group I compared to Group II. It should be noted that, considering the source of mixed organic matter for the oils from Los Manueles field, it is not possible to have a single origin from the main source rock of the Maracaibo Basin, La Luna Formation, which is characterized mainly by marine organic matter from limestones deposited in an anoxic environment (2,8).



**Figure 6.**  $C_{30}$  steranes index [ $C_{30}/(C_{27} \text{ to } C_{30})$ ] vs. oleanane index [ $18\alpha(\text{H})\text{-Oleanane}/(18\alpha(\text{H})\text{-Oleanane} + C_{30}\text{-hopane})$ ].

To infer lithology and depositional environment of source rocks, some tricyclic and pentacyclic terpane ratios were used (Table 3). The  $C_{24}/C_{23}$ ,  $C_{22}/C_{21}$  and  $C_{26}/C_{25}$  tricyclic terpane ratios, and the  $C_{31}22R/C_{30}\text{Hop}$  ratio can be used to distinguish source rock lithology of crude oils (carbonate, marine shale, lacustrine, marl or carbonate source rocks) (26). Figure 7 shows the graph of  $C_{24}/C_{23}$  vs.  $C_{22}/C_{21}$  ratios, which indicates a lithology of marine shales, evaporates or marls for Group I oils and marls for Group II. Similarly, the  $C_{35}\text{S}/C_{34}\text{S}$ ,  $C_{29}/C_{30}\text{-hopane}$ ,  $C_{26}/C_{25}$  tricyclic terpanes and  $C_{31}22R/C_{30}\text{-hopane}$  ratios, also relate the oil of the Group I to marine shales, evaporites or marls, and Group II to carbonates or marls. Likewise, the relative abundances of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  steranes in the ternary diagram (Figure 8), evidence the contribution of mixed organic matter for both groups, with a source rock whose lithology is associated to marine shales, carbonates, and non-marine shales. However, based on the geological history of the Maracaibo Basin (12,27,28) it is possible to rule out sedimentation in non-marine shales as it is not a reported environment for this basin. Another characteristic observed on the  $m/z = 217$  (Figure 4) is the lower abundance of diasteranes related to regular steranes ( $C_{27}$ ,  $C_{28}$  and  $C_{29}$ ), typical of source rocks with lithology poor in clay minerals (26). Furthermore, other parameter

**Table 3.** Saturated and aromatic hydrocarbon lithology and redox conditions parameters in source rocks from Los Manueles field

Oil Group	Well	$C_{24}-C_{23}^1$	$C_{22}-C_{21}^1$	$C_{26}-C_{27}^1$	$C_{31}22R/C_{30}\text{Hop}^2$	$C_{35}\text{S}-C_{34}\text{S}^3$	$\text{DBT/Ph}^4$
Group I	CM-1	0.6	0.4	0.95	0.23	0.54	0.38
	CM-2	0.6	0.4	0.93	0.24	0.49	0.35
	CM-3	0.6	0.3	0.93	0.24	0.49	0.36
Group II	CM-4	0.5	0.5	0.87	0.27	0.78	0.51
	CM-5	0.5	0.5	0.87	0.26	0.80	0.53
	CM-6	0.5	0.5	0.87	0.25	0.71	0.48
	CM-7	0.5	0.6	0.87	0.25	0.70	0.46

<sup>1</sup> $C_{24}/C_{23}$ ,  $C_{22}/C_{21}$ , <sup>2</sup> $C_{26}/C_{25}$  = tricyclic terpane ratios (26).

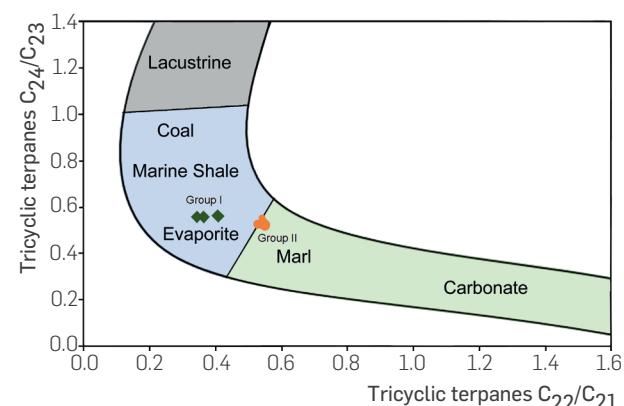
<sup>2</sup> $C_{31}22R/C_{30}\text{Hop}$  =  $17\alpha,21\beta\text{-homohopane (22R)}/C3017\alpha,21\beta\text{-hopane}$  (26).

<sup>3</sup> $C_{35}\text{S}/C_{34}\text{S}$  = homohopane index (30).

<sup>4</sup> DBT/F = Dibenzothiophene/Phenanthrene (29).

to infer lithology and depositional environment in source rocks is present in graph of DBT/PHE versus Pr/Ph ratios (29) (Figure 9). The plot indicates that samples may be originated from marine shale environment, with suboxic or dysoxic conditions.

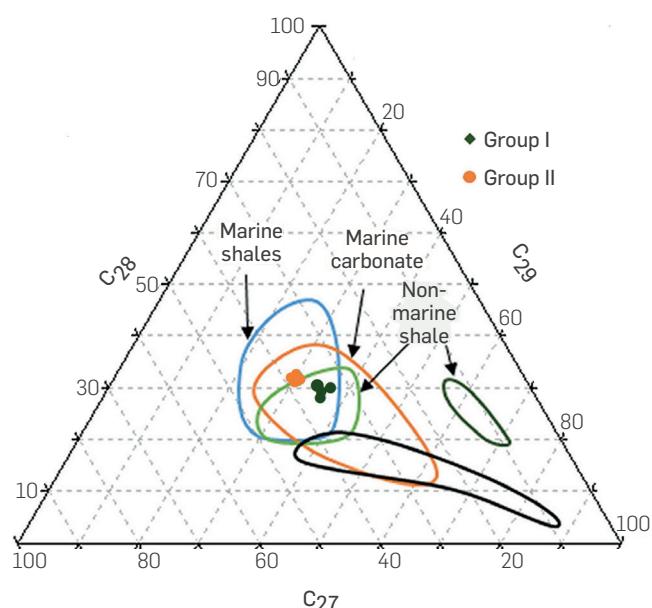
The homohopane index ( $C_{35}\text{S}/C_{34}\text{S}$ ) can be used to infer redox sedimentation, when  $C_{35} < C_{34}$  the deposition occurred in suboxic to dysoxic conditions. Samples have  $C_{35}\text{S}/C_{34}\text{S}$  ratio  $\leq 1$  (Table 3), associated to suboxic or dysoxic conditions (30). In addition, it is possible to suggest variations in these conditions, being a more dysoxic environment for Group I ( $C_{35}\text{S}/C_{34}\text{S}$  from 0.49 to 0.54) and towards more suboxic for Group II ( $C_{35}\text{S}/C_{34}\text{S}$  from 0.71 to 0.80) (Table 3). However, all oils present a  $V/(V+Ni)$  ratio  $> 0.8$  (Table 1), typical of anoxic conditions and may be related to marine marls or carbonatic source rocks (4). These results cannot be associated to the redox conditions of a single source rock, and can indicate oils mixtures from different source rocks.



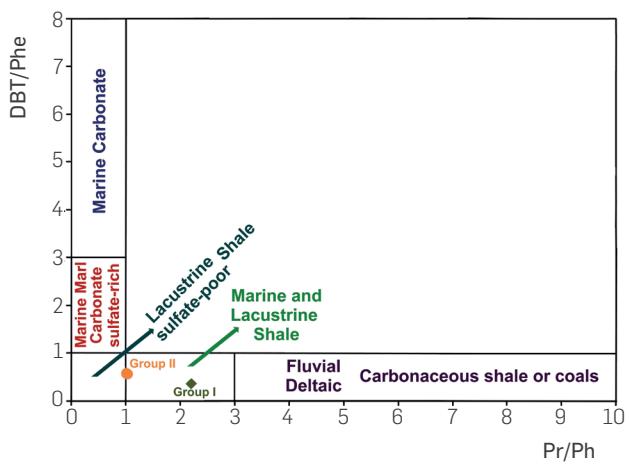
**Figure 7.** Cross-plot of the  $C_{24}/C_{23}$  and  $C_{22}/C_{21}$  ratios used to infer source rock lithology (26).

## OILS MATURITY

Table 4 shows the parameters used to determine maturity of oils. The values of homohopane isomerization index  $22S/(22S+R)$  in  $C_{32}17\alpha\text{-hopanes}$  (29,30) used for immature to early oil generation, are in the range from 0.57-0.58 and 0.60-0.61 for oils from groups



**Figure 8.** C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub> steranes ternary diagram showing their relative abundance and the relation with organic matter input and source rock lithology (28).



**Figure 9.** Cross-plot of the dibenzothiophene/phenanthrene (DBT/Phe) and pristane/phytane (Pr/Ph) ratios to infer source rock lithology and depositional environment (27).

I and II respectively (0.55-0.62 = equilibrium), indicating that in all samples, the epimerization is at equilibrium and that the early phase of oil generation has been reached (24).

Another maturity parameter used was the ratio of Mor/Hop [C<sub>30</sub>17 $\beta$ ,21 $\alpha$ (H)-moretane/(C<sub>30</sub>17 $\beta$ ,21 $\alpha$ (H)-moretane + C<sub>30</sub>17 $\beta$ ,21 $\alpha$ (H)-hopane], which decreases with increasing maturity from 0.8 in immature rocks to < 0.15 in mature stage, with a minimum of 0.05 (24). The Mor/Hop ratio varied between 0.13-0.15 (Group I) and 0.09-0.10 (Group II) suggesting maturity near the peak of the oil window, with higher maturity for Group II oils. In regards to Ts/(Ts + Tm) ratio, with average values of 0.33 and 0.36 for Group I and Group II oils respectively, its use as an indicator of

maturity is limited because the Ts/(Ts + Tm) ratio depends on the lithology (24), and there are evidence of variations in lithology of source rock of these oils.

The C<sub>29</sub> sterane isomerization (29) presents maturity levels with values close to equilibrium (Table 4), with %C<sub>29</sub>20S from 45-48% and %C<sub>29</sub> $\beta\beta$  from 40-53% (C<sub>29</sub>20S 52-55% and C<sub>29</sub> $\alpha\beta$  67-71% equilibrium values). The values for these ratios indicate that the end point has not been reached and suggest that the crude oils were generated by source rocks near the peak of the oil window. Similarly, when comparing the maturity between the oil groups, it can be noted that %C<sub>29</sub>20S shows values in the same range for all oils, but %C<sub>29</sub> $\beta\beta$  values suggest that the oils from Group II are more mature. Other factors, such as organofacies differences, can affect C<sub>29</sub>20S sterane isomerization ratios, while the C<sub>29</sub> $\beta\beta$  ratio appears to be independent of source organic matter input (24). It has been suggested that C<sub>29</sub>20S sterane isomerization ratios can vary with the source rock lithology (31). Considering that oils from Los Manueles field present variations in sedimentation environments and inorganic facies, the values of C<sub>29</sub>20S isomerization ratio may be the consequence of other factors than maturity.

Maturity parameters based on aromatic hydrocarbons (Table 4) were determined using the triaromatic steroid (TAS), phenanthrene (PHE), methylphenanthrene (C<sub>1</sub>-PHE), methyl dibenzothiophene (C<sub>1</sub>-DBT) and tetramethylnaphthalenes (C<sub>4</sub>-NAPH) (32).

The triaromatic steroids ratio TAS ( $(\Sigma C_{20}-C_{21}) / (\Sigma C_{25}-C_{28})$ ) (20) shows values from 0.41-0.43 (Group I) and 0.30-0.42 (Group II), suggesting that these oils were generated from source rock near the peak of the oil window. Differences in TAS ratio also suggest that the oils of Group I are relatively more mature.

Variations in the distribution of MethylPhe are used as maturity indicator based on more abundance of 1-MethylPhe and 9-MethylPhe ( $\alpha$ -substituted isomers) in immature oils, relate to 2-MethylPhe and 3-MethylPhe isomers ( $\beta$ -substituted isomers) more abundant in mature oils (33-36). In analyzed oils, there is predominance of 9-MethylPhe and 1-MethylPhe for Group II and 2-MethylPhe and 3-MethylPhe for Group I. Hence, the ratio MPI-1 and MPI-1<sub>(modified)</sub> indicates that the oils from Group II are less mature than those of Group I (Table 4).

Maturity determined using the calculated vitrinite reflectance (33,37) shows Rc values between 0.63 to 0.66 (Table 4). Also, the ratios calculated for C<sub>4</sub>-NAPH (Table 4) (37,38,39), are in the same range of values for both oil groups. These maturity parameters also indicate that the oils from Los Manueles were generated by source rocks near the peak of the oil window, and do not suggest different maturity between groups I and II. Contrary to the Rc values and C<sub>4</sub>-NAPH ratios, the methyl dibenzothiophene ratio (MDR = 4-MethylDBT/1-MethylDBT), based on the lower thermal stability of 1-MethylDBT ( $\alpha$ -substituted isomer) compared to 4-MethylDBT ( $\beta$ -substituted isomer) (34), yields values between 4.4-4.7 and 2.3-2.4 for groups I and II, respectively (Table 4), suggesting again variable maturity. Here, the highest MDR values are obtained in more mature oils from Group I.

Based on maturity parameters, it was determined that the crude oils from Los Manueles field were generated from source rock near the peak of the oil window. However, some maturity parameters differ in the relative maturity assigned to groups I and II. This result may be a consequence of oil mixtures with different maturity.

## ORIGIN OF OILS FROM LOS MANUELES FIELD

The geochemical characteristics of Los Manueles oils are presented in Tables 1 to 4. Seven oil samples are classified in two oil groups. Three oils have low sulfur, vanadium, and nickel, high saturates, low asphaltenes, a bimodal distribution of *n*-alkanes, high Pr/Ph ratio, high oleanane index, low steranes index, low tricyclic terpanes (cheilanthanes) and  $C_{34}/C_{35} < 0.54$ . These characteristics suggest that the principal contribution is from a terrigenous source rock. These oils are located in the northwest to southwest area of the field; in a reservoir with an age range from Eocene to Eocene-Oligocene (Figure 1). The other four oils have higher sulfur, vanadium, nickel, low saturates, high asphaltenes, a unimodal distribution of *n*-alkanes, low Pr/Ph ratio, low oleanane index, high steranes index and abundant tricyclic terpanes, which maximize at  $C_{23}$  and  $C_{34}/C_{35} > 0.70$ . These characteristics suggest a principal contribution from marine source rock. These oils are located in the northeast to southwest area of the field in Eocene reservoirs (Figure 1).

Geochemical data in this study suggest that the seven oils studied from Los Manueles field are derived from terrigenous organic matter deposited under dysoxic conditions and marine organic matter deposited under suboxic conditions. The results also suggest that these oils might have variable contribution from both marine and terrigenous source. Oils from Group I have a major contribution of terrigenous organic matter than the oils of Group II, characterized by a major contribution of marine organic matter. Probably, marine shale and limestone with oil-generating potential have contributed to the oils accumulated in Los Manueles field. However, the maturity of oils present inconsistencies, as a consequence of the mixture of oils derived from source rocks with different lithology and kerogen type.

In the Maracaibo basin, La Luna Formation is the main source rock (1,2,8). In this formation,  $18\alpha(H)$ -oleanane is not detected in bitumen extracts and is not commonly observed in crude oils from the Maracaibo Basin (40). Only in some areas of the Maracaibo Basin, specifically in the central field of the Bloque V-Centro, the Bolívar Coastal field (38) and La Luna Formation outcropping in the Perijá Range (41),  $18\alpha(H)$ -oleanane was detected in low quantities. Therefore, it is likely that La Luna Formation was the main source rock for the marine oils in Los Manueles field. Therefore, the contribution of terrigenous organic matter has another source rock. For example, other rocks have been proposed such as the coals and coally shales from Orocué Group (Catatumbo, Barco, and Los Cuervos formations) or the Carbonera Formation, where  $18\alpha(H)$ -oleanane was detected (5). Furthermore, Los Manueles field has been found in the Orocué petroleum system, which is restricted to the southwest of the Maracaibo basin (8,42). The oils in this petroleum system were originated from non-marine source rocks with terrigenous organic matter, or from the mixture of these oils with others of marine origin from La Luna Formation. The Orocué petroleum system is considered hypothetical, as the oil-source rock correlation studies have not allowed to completely establish the origin of oils, due to the fact that a possible source rock with terrigenous organic matter has not been determined (8). Nonetheless, according to the results obtained through the study of biomarkers, it seems that the source rock are shales from marine environments, which input of organic matter was mainly terrigenous organic matter. This is based on:

- 1) The redox sedimentation conditions from dysoxic to suboxic, and  $\text{Pr/Ph} < 2$ , lower than the values reported for Barco, Los Cuervos and Carbonera formations, with values ( $> 2$ ) (5,9). High  $\text{Pr/Ph} (>$

- 3) indicates terrigenous organic matter input under oxic conditions (24,43,45). Additionally,  $\text{Pr/Ph}$  may be higher ( $> 6$ ) in coals (27).
- 2) Source rock lithology indicators, based on terpanes, suggest marl and shale source rocks.
- 3) DBT/Phenanthrene vs.  $\text{Pr/Ph}$  ratios located the oils towards source rocks with lithologies typical of shale and marl (27).
- 4) Steranes are characterized by  $C_{27} > C_{29}$  regular steranes and presence of  $C_{30}$  sterane, typical of marine organic matter from La Luna Formation. The most terrigenous Group I oils present  $C_{27} > C_{29}$  and the most marine Group II present  $C_{27} > C_{29}$  (44).
- 5) Gammacerane is only detected in some samples from La Luna Formation with gammacerane index from 9-21% (4). GI have similar values in oils from groups I and II and suggest a single source of gammacerane, probably La Luna Formation.
- 6) Los Cuervos-K/T(!) systems was proposed with the identification of oil from the Paleocene(?)–middle Eocene (46), and Los Cuervos and Carbonera formations have been proposed as excellent potential source rocks (9). However, the low maturity of coals from Barco, Los Cuervos and Carbonera formations indicates low potential to generate and expel oil (5,8,47) because in coals, the beginning of generation is related to  $T_{max}$  of 435 °C (45), and the reported values of  $T_{max}$  for these formations are in the range of 451-458 °C (3 samples from Barco Fm.) 441-448 °C (6 samples from Los Cuervos Fm.) and 436-452 °C (3 samples from the Carbonera Fm.) (5).

Therefore, the results suggest more shale or coally shales as the source rock of terrigenous oils from Los Manueles field, rather than coals from the Paleocene Orocué Formation. Alternatively, according to our geochemical results, a secondary source rock type clastic from marine environment, with terrigenous organic matter input during sedimentation. We suggest another alternative source rock, the Capacho Formation, characterized by carbonates and shales underlying the La Luna. The Capacho Formation presents kerogen Type II and III, and is characterized by a very close thermal maturity in La Luna Formation.

## CONCLUSIONS

Crude oils from Los Manueles field are divided in two groups based on bulk properties and biomarkers distribution. According to various biomarker parameters, we confirm that the crude oil samples were generated by two source rocks with different types of organic matter (marine and terrigenous). The contribution of crude oils from marine environments derives from La Luna Formation, the main source rock of the Maracaibo Basin. For crude oils of terrestrial origin, the source rock is suggested to be the Capacho Formation, marine shale with a higher input of terrestrial organic matter during sedimentation.

## ACKNOWLEDGEMENTS

*This work was funded with research grants from Consejo de Desarrollo Científico y Humanístico de la Universidad Central de Venezuela (CDCH-UCV), under research grants: PG-03-8204-2011/2 and the Fondo Nacional de Ciencia, Tecnología e Innovación (FONACIT), under research grant: G-2012002299. The authors are grateful for the critical comments of three anonymous reviewers who contributed to enhance the original manuscript.*

**Table 4.** Maturity parameters in saturates and aromatic hydrocarbons from oils of Los Manueles field.

Oil Group	Well	C <sub>32</sub> -22S <sup>1</sup>	Ts/(Ts+Tm) <sup>2</sup>	Mor/Hop <sup>3</sup>	%C <sub>29</sub> -20S <sup>4</sup>	%C <sub>29</sub> -ββ <sup>4</sup>	TAS <sup>5</sup>
Group I	CM-1	0.58	0.33	0.15	47	40	0.41
	CM-2	0.59	0.33	0.13	48	44	0.43
	CM-3	0.59	0.33	0.15	48	40	0.44
Group II	CM-4	0.61	0.35	0.10	46	53	0.31
	CM-5	0.61	0.36	0.09	45	53	0.30
	CM-6	0.61	0.36	0.09	47	53	0.35
	CM-7	0.60	0.36	0.09	47	52	0.42

<sup>1</sup> C<sub>32</sub>-22S/C<sub>32</sub>(22S + 22R) = homohopane isomerization (28)<sup>2</sup>Ts/(Ts + Tm) = C<sub>27</sub>18α-trisnorhopane/(C<sub>27</sub>18α-trisnorhopane + C<sub>27</sub>17α(H)-trisnorhopane) (30).<sup>3</sup>Moretanes/Hopanes = C<sub>30</sub>17α(H)-21α(H)-morethane/(C<sub>30</sub>17β(H),21α(H)-morethane + C<sub>30</sub>17α(H)-21β(H)-hopane)(28).<sup>4</sup>%C<sub>29</sub>-20S: C<sub>29</sub>20S/(C<sub>29</sub>20S + C<sub>29</sub>20R) steranes %C<sub>29</sub>αβ: C<sub>29</sub>ββ/(C<sub>29</sub>ββ + C<sub>29</sub>αα) steranes (29,30).<sup>5</sup>TAS = ΣC<sub>20</sub>-C<sub>21</sub>)/ΣC<sub>26</sub>-C<sub>28</sub>) (22).

Oil Group	Well	MPI-1 <sup>6</sup>	MPI-1 <sup>(modified)<sup>7</sup></sup>	MDR <sup>8</sup>	%Rc <sup>9</sup>	TeMeN-1 <sup>10</sup>	TeMeN-2 <sup>11</sup>	TeMeN-3 <sup>12</sup>	TeMeN-4 <sup>13</sup>
Group I	CM-1	0.85	0.95	4.7	0.63	0.60	0.71	0.68	0.25
	CM-2	0.87	0.97	4.4	0.65	0.59	0.70	0.68	0.25
	CM-3	0.86	0.96	4.7	0.63	0.59	0.70	0.71	0.25
Group II	CM-4	0.64	0.71	2.3	0.66	0.60	0.69	0.58	0.24
	CM-5	0.64	0.71	2.4	0.66	0.60	0.69	0.57	0.23
	CM-6	0.64	0.71	2.3	0.64	0.60	0.69	0.59	0.24
	CM-7	0.66	0.73	2.4	0.65	0.59	0.68	0.62	0.23

<sup>6</sup>MPI-1 = 1.5(2MPhe+3MPhe)/(Phe+1MPhe+9MPhe) (32).<sup>7</sup>MPI-1<sub>(modified)</sub> = 1.89(2MPhe+3MPhe)/(Phe+1.26(1MPhe+9MPhe)) (35).<sup>8</sup>Methyldibenzothiophene ratio: MDR = 4-MethylDBT/1-MethylDBT (36).<sup>9</sup>Calculated vitrinite reflectance = Rc = 0.60MPI-1 + 0.40 (33,36).<sup>10</sup> TeMeN-1 = 1,3,6,7-TeMeN/(1,3,6,7-TeMeN + 1,2,5,6-TeMeN + 1,2,3,5-TeMeN) (37,38).<sup>11</sup> TeMeN-2 = 1,3,6,7-TeMeN/(1,3,6,7-TeMeN + 1,2,5,7-TeMeN) (38).<sup>12</sup> TeMeN-3 = 2,3,6,7-TeMeN/(2,3,6,7-TeMeN + 1,2,3,7-TeMeN) (38).<sup>13</sup> TeMeN-4 = 1,3,6,7-TeMeN/Σ TeMeN (38).

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