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By Eng. Jhoan Jose Urdaneta

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Keywords: fingerprint, biomarkers, pristane, phytane, star diagram.

I. Introduction

The Maracaibo Lake Basin has the most economically important oil fields for the Western Venezuelan Region, which are composed of several wells that produce oil from deposits located at different stratigraphic levels of Cretaceous and tertiary age. The data and samples that were analyzed and studied were sampled at the wellhead, using the methodology learned from the Zuliano Institute of Technological Research (INZIT).

The results obtained from these analyzes allowed to show the presence of crude oils with different geochemical characteristics indicating the origin of organic matter, depositional environment, degree of maturity, API gravity and the possibility of several alteration processes within the reservoir. Among the main processes of degradation of an oil can be mentioned: biodegradation, water washing, thermal alteration, among others. Also, the differences detected would point to a lack of communication between several compartments that have been isolated between them and, consequently, have followed different lines of structural and compositional evolution.

Finally, the molecular parameters of the crude oils of interest were determined, through analysis of biomarkers extracted from crude oil by gas chromatography coupled to mass spectrometry, this in order to mitigate the molecular uncertainty between the deposits.

a) Geographic Location

The study area is located northwest of the Bolivarian Republic of Venezuela, within the Maracaibo Oil Basin, which has an estimated extension of 47,705 km2. To the west-northwest, the basin is bounded by the foothills of the Sierra de Perijá; to the east-northeast by the western foothills of the Serranía de Trujillo; to the southeast by the Andean foothills towards the Motatán River; to the north and imaginary delimited by a line on the border between the states Zulia and Falcón and by the geological line of the Falla de Oca-Ancón. The lines mentioned above are quite arbitrary in the physiographic and geological sense, but they actually correspond to the geo-economic nature of the oil basin as such. At the local level, the study was prepared in Block I belonging to the Lagomar Production Unit of the Maracaibo District, which is located in the north-central part of Lake Maracaibo, occupying an area of 242,324 km2 and being divided into flank East and west flank. Specifically, the study area, called VLA0016 / VLA0033, whose size is approximately 11,888 km2, corresponds to Lagunillas Field and is located in the north-central area of El Pilar in Block I of Lake Maracaibo. Area VLA0016 / VLA0033 structurally limits the west due to a normal type fault with the Urdaneta Lago Production Unit, to the east with the Lama-Icotea Fault, to its north part with an arbitrary limit of the Medium Pink Production Unit and to the south with two faults that are intercepted at the level of the same member Santa Barbara. Table 2 shows the UTM coordinates that delimit the study area and Figure 1 shows the geographical location of Area VLA0016 / VLA0033.

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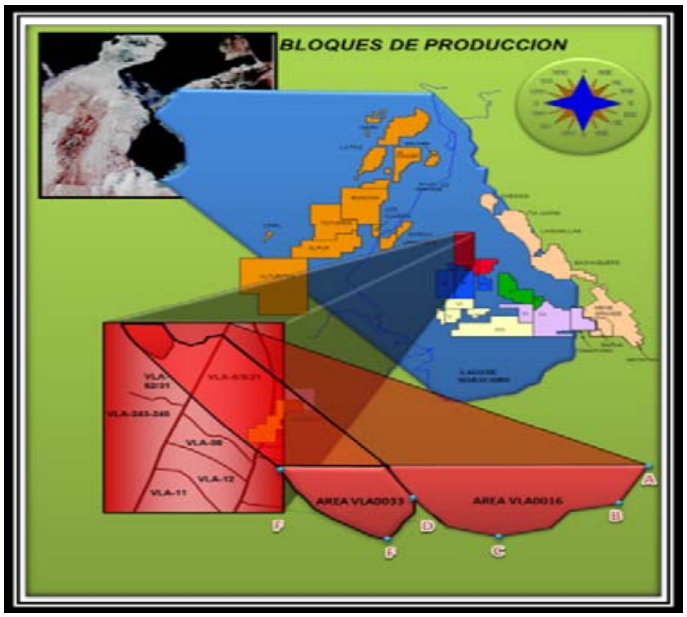


Illustration 1: Geographic Location of the Study Area. Area VLA0033 / VLA0016 in Block I of Lake Maracaibo, Venezuela.

b) Methodological Framework

The investigation of this work is descriptive and interpretive. The universe of samples analyzed was 9 wells distributed in areas VLA0016 and VLA0033 of Block I Lagunillas field of the Maracaibo Lake Basin, with emphasis on medium and light crudes from the area (9 Wells), thanks to the fact that they were achieved Perform a greater number of analyzes. It involved the sampling of these wells of the Lagomar Production Unit (U.P. Lagomar).

In the first place, we proceeded to search and compile all the information available regarding previous studies and bibliography. The samples were subjected to SARA analysis (separation of the saturated, aromatic, resin and asphalt fractions), to subsequently analyze the aromatic and saturated fractions through gas chromatography coupled to mass spectrometry in order to quantify relative the biomarkers present in the oil, in order to characterize and simulate the deposits.

c) Results and Discussion

The results obtained in this investigation, through the processing, analysis and interpretation of the data thrown by the population of crude oils studied, were carried out through a geological study of the area, and its subsequent sampling at the wellhead, which were subsequently analyzed in the laboratory, in order to determine the geochemical characterization of the crudes in the area.

d) General Characteristics of Crude

The marine crudes of the Maracaibo Lake Basin, coming from wells completed in different deposits of the geological column of this basin, have been generated mostly by the La Luna Formation.

According to the general composition of the crude oils (saturated hydrocarbons, aromatic hydrocarbons and resins+asphaltenes), the percentage of saturated hydrocarbons in relation to API gravity can also provide maturity trends, the higher the saturated content, the lower the aromatic and more asphaltene resins; hence the crudes become lighter crudes like those in this study.

Geochemical analyzes carried out on the samples of crude oil from Tertiary deposits included SARA analysis, gas chromatography coupled to mass spectrometry of the Saturated and Aromatic fractions to review the concentration and distribution of biomarkers of these hydrocarbons.

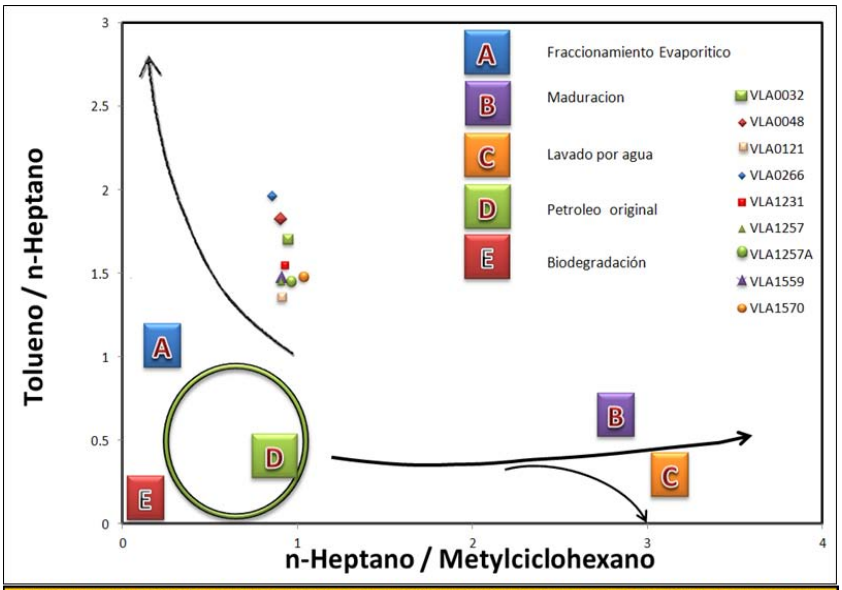
II. Relationship of Paraffinity vs. Aromaticity of Thompson (1988)

The characterization, correlation and classification of hydrocarbons is established based on their origin, degree of maturity alteration within the reservoir such as biodegradation, evaporative fractionation water washing, and hydrocarbon mixtures, for this reason the methodology proposed by KF Thompson is proposed (1988), which is based on the evidence that the light fraction of some crude oils that contain very high concentrations of aromatic compounds and naphthenes, while the proportion of n-alkane compounds is low.

Thus, the terms aromaticity are defined (Toluene / n-C7), which is related to evaporative fractionation, and paraffinicity (n-C7- / Methylcyclohexane), a value that increases with the maturity of the crude. The graph proposed by Thompson allows classification of light and condensed

crudes according to the type of alteration: evaporative fractionation, maturity, water washing and biodegradation.

In this graph, the direction of the arrows indicates a tendency of increase in the process or that the process is more advanced, for example, in the study area crudes, they are being affected, by an alteration of evaporative fractionation, located in zone A, on the other hand it also shows a good maturity, but as the evaporative fractionation process occurs, residual crudes tend to increase aromaticity, in zone A, while if the light fraction migrated is analyzed, an increase in The paraffinity.



CARACTERIZACIÓN GEOQUÍMICA DE LAS ARENAS B DEL VLA0016/VLA0033 Y BASAL LA ROSA DEL VLA0006, DEL BLOQUE I DE LA UNIDAD DE EXPLOTACIÓN LAGOMAR DE LA CUENCA DEL LAGO DE MARACAIBO.

RELACION DE COMPUESTOS	POZOS DEL AREA DE ESTUDIO							
Tolueno / n-Heptano	VLA0032	VLA0048	VLA0121	VLA0266	VLA1231	VLA1257	VLA1559	VLA1570
	1;70580402	1;83285652	1;36039403	1;96891433	1;55451925	1;45635028	1;7696649	1;48189273
n-Heptano / Metilciclohexano	VLA0032	VLA0048	VLA0121	VLA0266	VLA1231	VLA1257	VLA1559	VLA1570
	0;56947824	0;89784546	0;90791122	0;55640589	0;58184432	0;53963417	0;56331998	1;03343242

Illustration 2: Relationship of Paraffinity vs. Aromaticity

III. Paraffin ratio to Aromaticity Determination of Correlation and Transformation of Crude oil According to Halpern (1995)

Looking for the differences in the data of the C7-compounds of unaltered oils compared to biodegraded crude oils of the same family, interaction relationships were constructed in order to emphasize the differences.

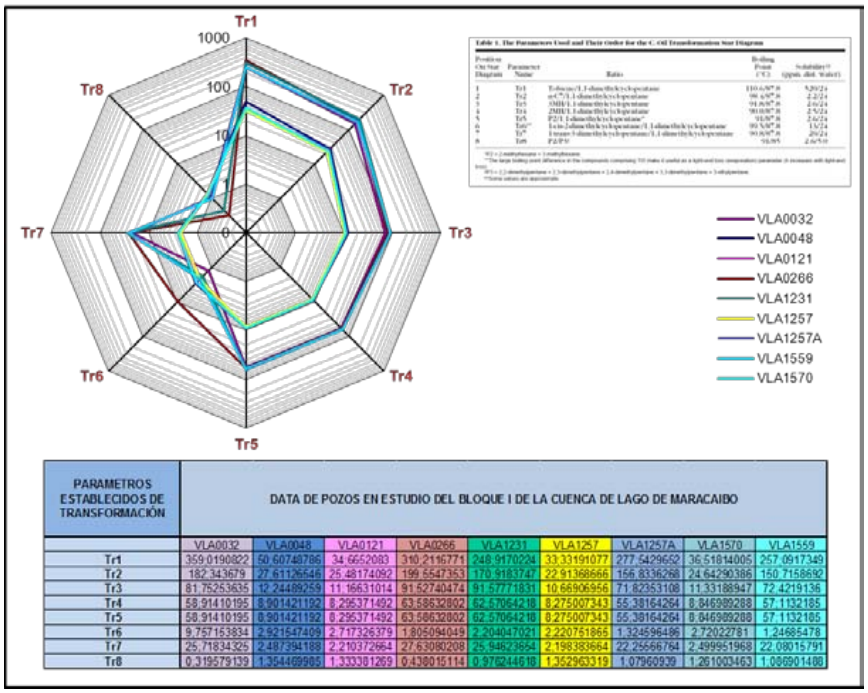
Parameter Tr1 measures the decrease in toluene which is compound C7; more soluble in water, and therefore it is useful to determine the alteration (water wash). The remaining relationships measure biodegradation and the susceptibility of the compounds involved decreases counterclockwise towards the Tr8 relationship, that is, the more resistant and stable relationship with biodegradation. The Tr6 parameter is composed of compounds that differ significantly in boiling points, so it turns out to be a parameter more resistant (less susceptible) to transformation than the smaller Tr parameters. Consequently, parameter Tr6 is very useful for measuring evaporation caused by inappropriate handling of samples and probably by fractionation-migration effect, in both cases the parameter will increase its value. On the other hand, the star diagram to determine correlations between oils is formed by relationships that are resistant or stable to the transformation processes and that are related to the origin of the crude oils. This means that relationships are virtually invariant within the same family, but that they show significant changes between the crude oils of different families.

The C1 to C5 ratios can be used to monitor evaporation or fractionation-migration between samples of the same family. The C1 ratio has a difference in boiling temperatures of -6 between the numerator and the denominator and should decrease with evaporation, while the C5 ratio has a difference of +8 and therefore must increase.

The star diagram for the transformation of crudes based on the high percentage of toluene for compound C7, indicates that the crudes under study do not show water wash disturbance, of the nine (9) samples, only VLA1257 wells were differentiated, VLA0121, VLA1570 and VLA0048 for presenting a lower value of toluene in the Tr1 peak, not being affected by this type of alteration. However, it can be inferred that the total of the samples analyzed (8) show alterations

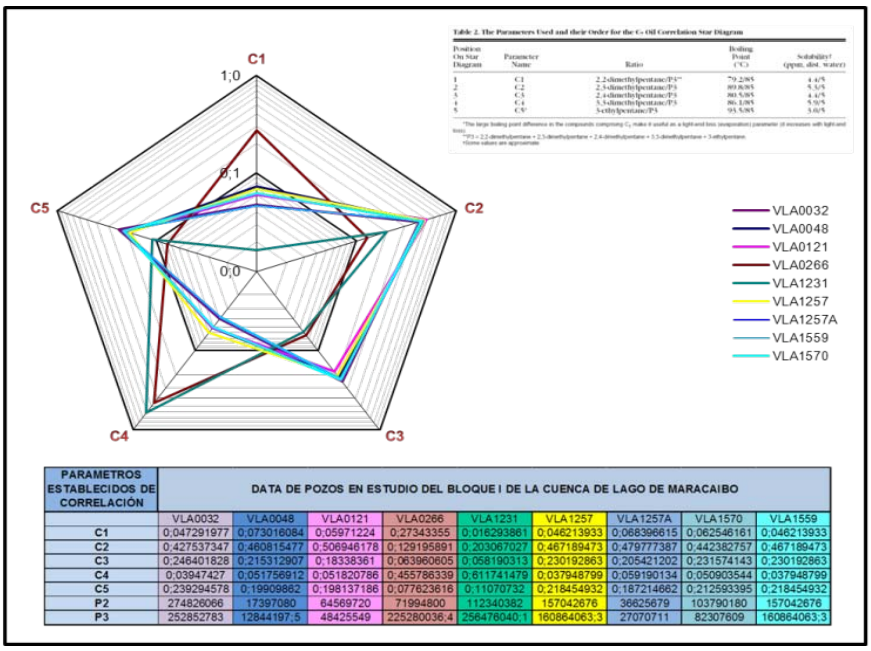
due to evaporative fractionation. Parameter Tr6 affects all crudes of the analyzed wells, except for well VLA0266, which presents a different alteration process associated more with a fractionation-migration alteration, due to the resistance it opposes with respect to the rest of the crudes.

The star diagram to determine correlations of crude oil as stated by Halpern (1988), shows that the samples in studies exhibit a similar profile, coupled with this, it is necessary for parameter C1 in all crude oils except for wells VLA0266 and VLA1570, differ from the others, this being an indication of a possible fractionation - migration, where other authors associate it with a poor handling of the sample during its preparation, additionally the hydrocarbons under study have a high degree of maturation and biodegradation.



PARAMETROS ESTABLECIDOS DE TRANSFORMACIÓN	DATA DE POZOS EN ESTUDIO DEL BLOQUE I DE LA CUENCA DE LAGO DE MARACAIBO								
	VLA0032	VLA0048	VLA0121	VLA0266	VLA1231	VLA1257	VLA1257A	VLA1570	VLA1559
Tr1	359.0190822	50.60748786	34.6652083	310.2116771	248.9170224	33.33191077	277.5429652	36.51614005	257.0917349
Tr2	182.343679	27.61126546	25.48174092	199.5547353	170.9183747	22.91368666	156.8336266	24.64290386	150.7158692
Tr3	81.75253635	12.24489259	11.16631014	91.52740474	91.57771831	10.66906956	71.82353108	11.33188947	72.4219136
Tr4	58.91410195	8.901421192	8.295371492	63.58632802	62.57064218	8.275007343	55.38164264	8.846989288	57.1132185
Tr5	58.91410195	8.901421192	8.295371492	63.58632802	62.57064218	8.275007343	55.38164264	8.846989288	57.1132185
Tr6	9.757153834	2.921547409	2.717326379	1.805094049	2.204047021	2.220751865	1.324596486	2.72022781	1.24685478
Tr7	25.71834325	2.487394188	2.210372664	27.63080208	25.94623864	2.198383664	22.25666764	2.499951968	22.08015791
Tr8	0.319579139	1.354469965	1.333081269	0.436015114	0.976244618	1.352963319	1.07960939	1.261003463	1.086901488

Illustration 3: Halpern star diagram (1988) to determine crude oil transformation

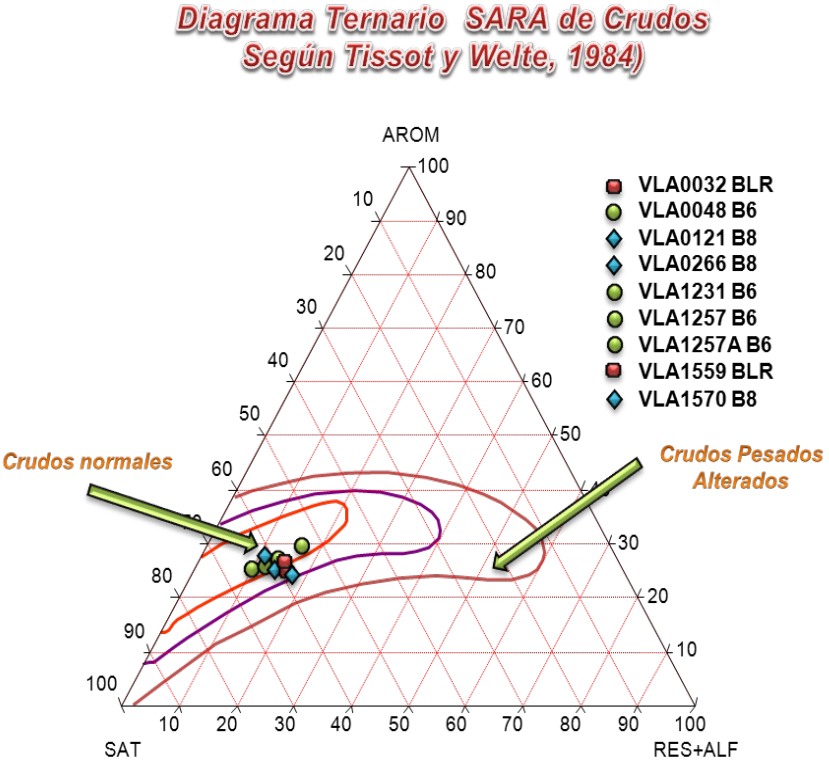


PARAMETROS ESTABLECIDOS DE CORRELACIÓN	DATA DE POZOS EN ESTUDIO DEL BLOQUE I DE LA CUENCA DE LAGO DE MARACAIBO								
	VLA0032	VLA0048	VLA0121	VLA0266	VLA1231	VLA1257	VLA1257A	VLA1570	VLA1559
C1	0;047291977	0;073016084	0;05971224	0;27343355	0;016293861	0;046213933	0;068396615	0;062546161	0;046213933
C2	0;427537347	0;460815477	0;506946178	0;129195891	0;203067027	0;467189473	0;479777387	0;442382757	0;467189473
C3	0;246401828	0;215312907	0;18338361	0;063960605	0;058190313	0;230192863	0;205421202	0;231574143	0;230192863
C4	0;03947427	0;051756912	0;051820786	0;455786339	0;611741479	0;037948799	0;059190134	0;050903544	0;037948799
C5	0;239294578	0;19909862	0;198137186	0;077623616	0;11070732	0;218454932	0;187214662	0;212593395	0;218454932
P2	274826066	17397080	64569720	71994800	112340382	157042676	36625679	103790180	157042676
P3	252852783	12844197.5	48425549	225280036.4	256476040.1	160864063.3	27070711	82307609	160864063.3

Illustration 4: Halpern star diagram (1988) to determine crude correlation

IV. Ternary Diagrams to Recognize Geochemical Crude Classes

The results obtained in the analyzes of the composition of the crudes based on their solubility (SARA) and the ternary diagram derived from them, are shown in Figure 5, it is observed that the grouping of data corresponding to all the crudes of the wells studied, they mostly enter the classification of normal crudes, as referenced, The SARA composition for the sands under study, are mainly of paraffinic origin (saturated), and it could be indicated that these crudes because they are at greater depth have a greater maturity level than the raw ones in the shallowest arenas of adjacent areas.



POZOS	% SATURADOS	% AROMÁTICOS	% RESINAS	% ASFALTENOS	% RES+ASF
VLA 0032	59;55	24;17	15;69	0;59	16;28
VLA 0266	59;18	24;62	15;90	0;30	16;20
VLA 1231	59;70	26;69	13;23	0;38	13;61
VLA 1257	54;36	28;68	16;35	0;61	16;96
VLA 1559	59;60	25;13	14;81	0;47	15;28
VLA0048	62;52	25;05	12;2	0;23	12;43
VLA0121	61;55	27;06	11;12	0;27	11;39
VLA1257A	65;29	24;55	10;06	0;1	10;16
VLA1570	61;33	24;35	13;79	0;53	14;32

Illustration 5: Ternary diagram of the SARA fractions (saturated, aromatic, resins and asphaltenes) with information on the raw materials of the study area

V. Relationship Between Pr / n-C17 and F / n-C18

In general terms, the relations between isoprenoids are parameters that define the type of contribution of organic matter since a ratio of Pr / Ph less than 1 indicates environments of anoxic deposits and conversely, relations of Pr / Ph greater than 1 indicate environments oxides or disóxicos. If these relationships exceed the value of 3 it is already considered a clear land contribution. When analyzing the data, it is observed that all the samples have a Pr / Ph ratio of less than 1. According to this relationship, an origin of the marine organic matter can be inferred with some contribution of terrestrial organic matter.

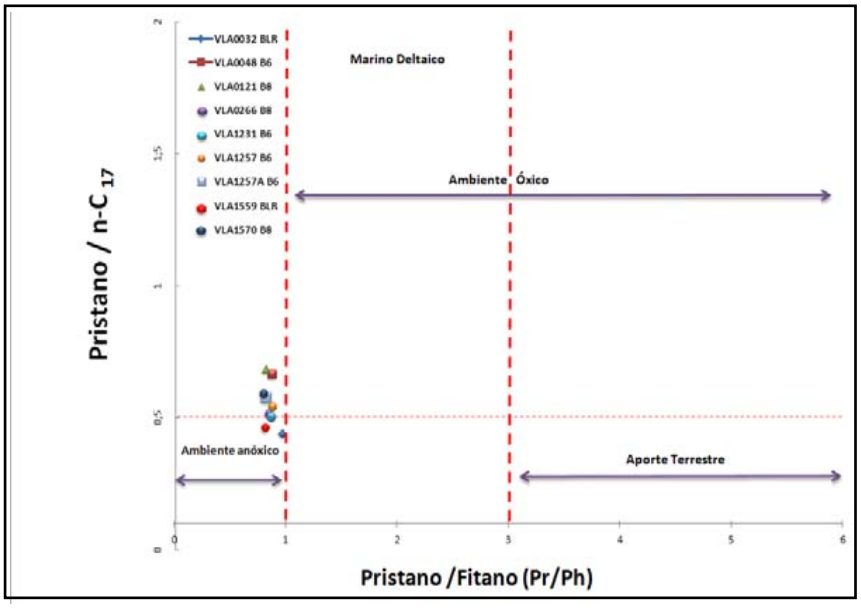


Illustration 6: Pr / Ph vs. Relationships Pr / nC17 of the crudes of the study area

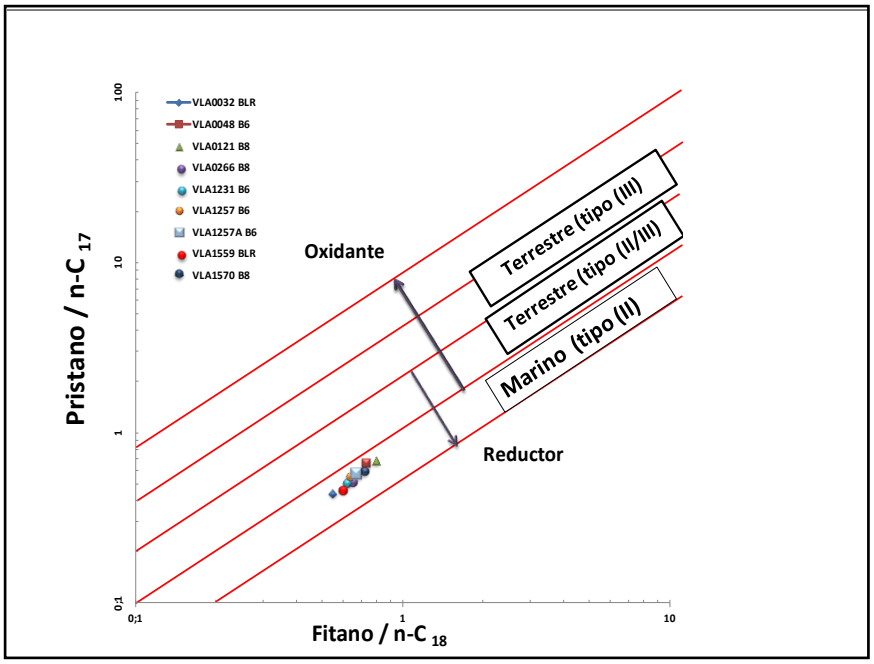


Illustration 7: Pr / Ph vs. Relationships Pr / nC17 of the crudes of the study area

On the other hand, the relation Pr / nC17 vs. Ph / nC18 according to Hunt, (1996), also shows values lower than one, which is particular to an organic matter of marine type in conditions of reduction which is attributed to a state of maturity developed, characteristic of the crudes of the area.

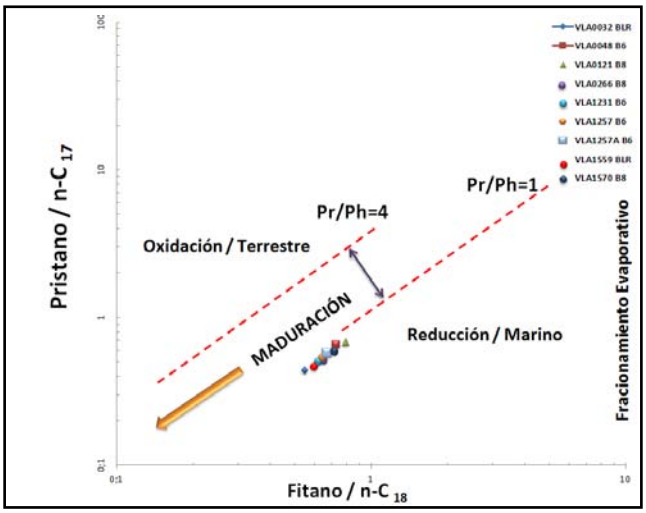


Illustration 8: Pr / nC17 vs. relationships. Ph / nC18 of the crudes of the study area

The bimodal distribution of n-alkanes reveals contribution of marine organic matter, and the Pristano / Fitano ratio indicates conditions of reduction. This is attributed to the advanced state of thermal maturity of the samples. The CPI (Preferential Carbon Index) markers confirm that it is in the presence of a mature oil with possible mixtures, according to Escobar (2007).

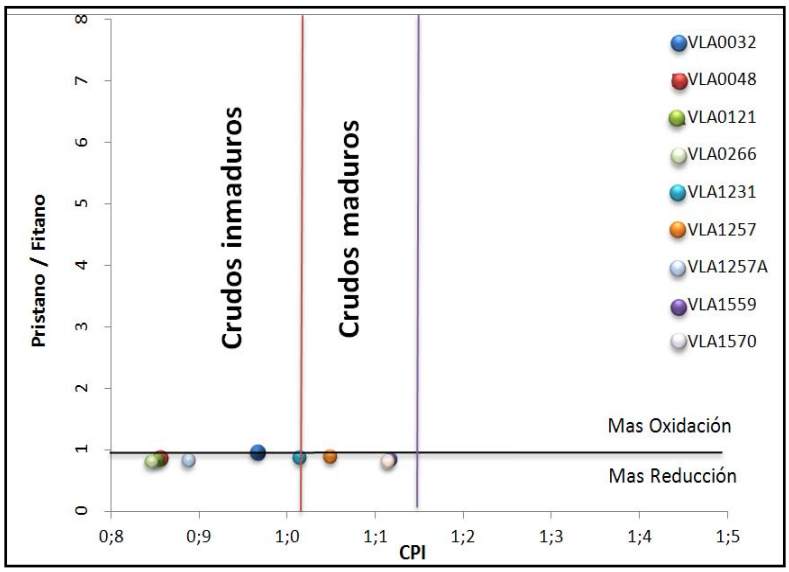


Illustration 9: Pr / Ph vs. Relationships CPI of the crudes of the study area

VI. Thermal Maturity

The Ts / Tm ratios are frequently used to determine the degree of maturity. As the degree of maturity increases, Tm increases while Ts remains constant. An increase in the Ts / Tm ratio would indicate an increase in the degree of evolution (Philp, 1985).

If we look at the values of Ts / Tm, they present values of 0.47 and 0.55 respectively. Characterizing the samples as relatively mature. However, Ts and Tm also depend on the type of organic matter, Ts and Tm are biomarkers that are characterized by their resistance to biodegradation.

That is why the application of the Ts / Tm ratio as an indicator of maturity should be used wisely, since the oil that has the highest ratios may have suffered some type of biodegradation, while abnormally low relationships may show a provenance. of a carbonaceous mother rock.

Crudes from the area of interest under study have a wide range of maturity where the Ts parameters (Ts + Tm) vary between the values of 0.41 to 0.55. In graph 34, it is observed that the relation Ts (Ts + Tm) presents a definite tendency to increase the API gravity of the crudes, the anomalous relationship of maturity Vs API Gravity that the study crudes present, probably the result of some cause of fractionation-migration type alteration as observed in previous results, and these also a good thermal maturity of hydrocarbons as the values grow.

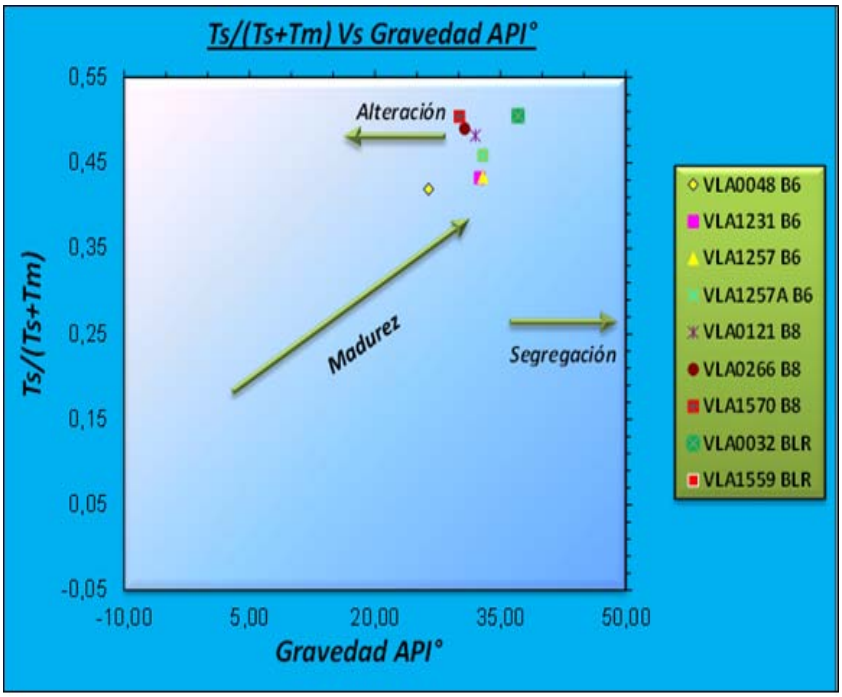


Illustration 10: Relationship of the Hópanos with the diagenesis of the crudos in the area of study

Integrating the information of the related crudes, it can be observed that the crudes have good maturity induced by the gradual burial of the generating rocks of the Formation La Luna, Gómez and Urdaneta (2013).

In this way, a significant amount of light crudes in the Maracaibo Basin have been generated at a relatively late stage of generation. However, it can be seen that biodegradation has also affected some light crudes specifically those of Sands B in the study area.

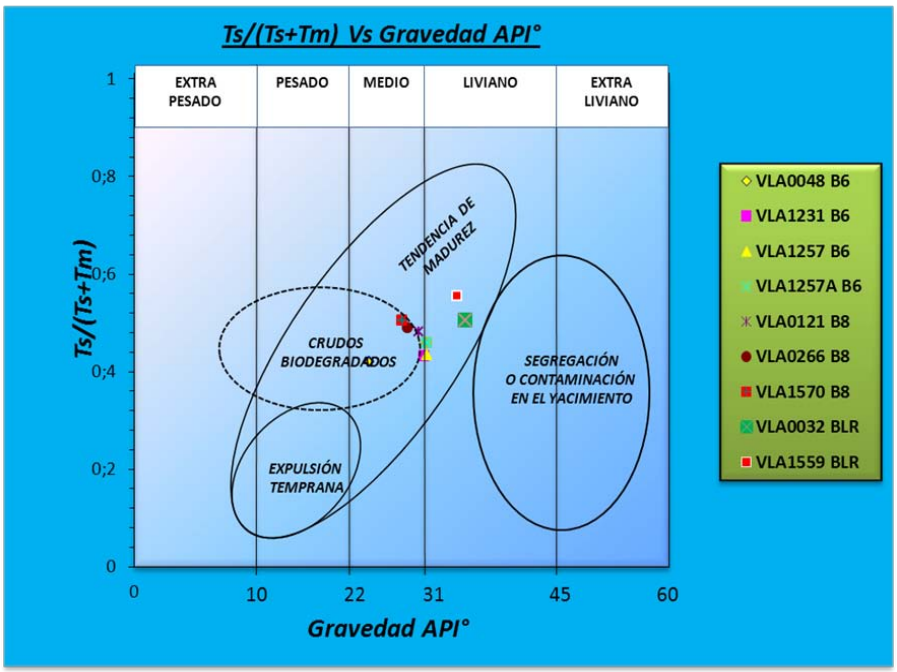


Illustration 11: Generalized relationship between API Gravity and the maturity of the crudes of the study area, using the parameter Ts / (Ts + Tm)

Another parameter used to determine the level of maturity is the methylphenanthrene index (MPI-1). This index is based on the distribution of methylphenanthrene and its methylated counterparts. These can be derived from steroids and triterpenoids originally present in the biological starting material; or they may originate from phenanthrene methylation reactions. The isomers that are more stable from the thermodynamic point of view are, 2, 3 methylphenanthrene, versus 1, 9 methylphenanthrene, according to Peters et al., (2005). They also serve to estimate the percentage of vitrinite reflectance calculated, since it has been observed that they have a linear relationship, according to Peters et al., (2005). As the following illustration shows, all the samples studied have a vitrinite value of approximately equal 1, which are mature samples and that all of them are within the oil generation window.

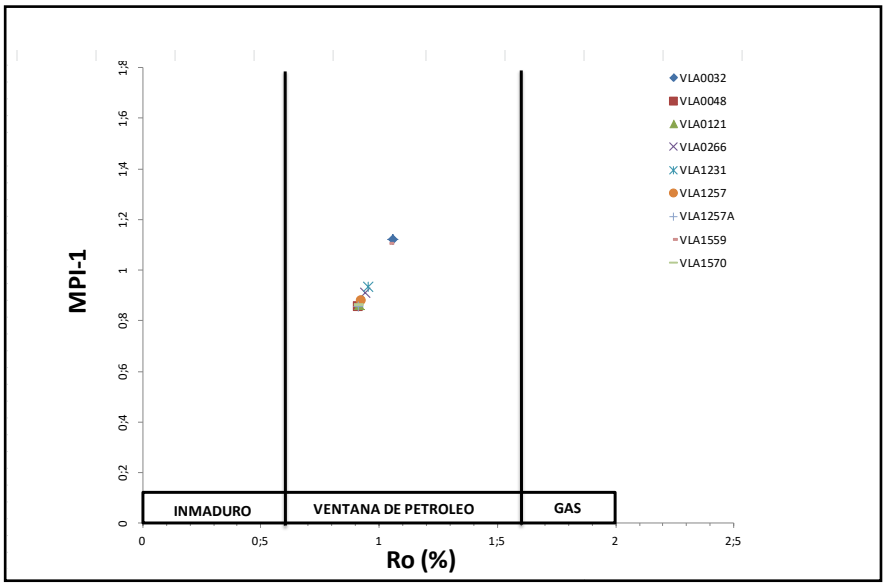


Illustration 12: Relationship between the methyl-phenanthrene index and the value of vitrinite

VII. Conclusions and Recommendations

- Through the C7OCSD, the fingerprint of the crude oil was differentiated in each of the samples from the area of interest, with molecular differences between them.
- Through C7OTSD, a high percentage of toluene is shown, indicating that the crudes have not been altered by water washing, indicating a progressive biodegradation.
- Crudes of interest show a good maturation, also indicating that they have a contribution of terrestrial organic matter.
- The MDBT compound shows a stepped shape to the right, indicating origin of siliciclastic crude.
- Serosity value vs. Pristano / Fitano is> 1 which indicates marine origin.
- The analysis of hopanoids indicates precursor abundance of marine origin.
- The Toluene / n-Heptane ratio shows that our crudes were affected by evaporative fractionation.
- The application of organic geochemistry as an alternative tool to the traditional PLT and SPT, allows an effective and low-cost approach in the monitoring of joint production of wells in the area, eliminating the mechanical intervention of the well.
- The geological study should be reviewed to validate if there are failures that prevent the mixing of crude in the Deposits.
- The geochemical study should be extended to other areas with the purpose of further development of the field.
- Take pure samples of the Deposits to characterize and determine possible areas of coalescence.
- It is recommended to calibrate with the results obtained in the study and confirm the geological model of the area.
- It is advisable to carry out an isotopic study of gases to complement and have a greater characterization of the Deposits.
- Chemostratigraphic studies are recommended to make this study more robust.

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