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Is there a pre-Cretaceous source rock in the Colombia Putumayo Basin? Clues from a study of crude oils by conventional and high resolution geochemical methods

M. MARTÍNEZ[1,*] R. MÁRQUEZ[2] G. GUTIÉRREZ[1] L. MAYA[1] C. MORA[3] W. GUZMÁN[3] J.M. MOLDOWAN[4]

[1]**Ecopetrol, Exploration Vice-Presidency**
Bogotá, Colombia. Martinez E-mail: maria.martinezvi@ecopetrol.com.co

[2]**Ecopetrol, ICP,**
Bucaramanga, Colombia

[3]**Gems S.A.**
Bogotá, Colombia

[4]**Stanford University and Biomarker Technology, Inc.**
Rohnert Park, California 94928, USA

*Corresponding author.

ABSTRACT

A geochemical characterization of sixteen crude oil samples from the Putumayo Basin, southern Colombia, was carried out. This basin is located to the north of Ecuador's Oriente Basin, one of the most prolific hydrocarbon basins in South America. Regardless of the fact that these two basins seem to share the same geological evolution, the volume of hydrocarbon reserves found in the Oriente Basin is five times greater than in the Putumayo Basin. This represents an exploratory opportunity to the extent that a better understanding of the petroleum system processes in the Putumayo Basin can be achieved. Newly available geochemical technology shows evidence that these crude oils originated from Late Cretaceous source rocks. The novel application of an age-related biomarker, the C25-highly branched isoprenoid, has constrained the age of the principal source of all these oils as Late Cretaceous or younger. Advanced geochemical technologies, such as compound specific isotope analyses of biomarkers (CSIA-B) and diamondoids (CSIA-D), and quantitative extended diamondoid analysis (QEDA), have confirmed, repeatedly, that the oil samples are all related to the same source with minor facies variations. The integration of these results with geological data suggests the presence of a very efficient petroleum system, characterized by an alternating sequence of soçurce and reservoir rocks. Thermal maturity of the oils from biomarker and diamondoid parameters ranges from well before the peak of hydrocarbon expulsion to the beginning of the late hydrocarbon generation phase. The aerial distribution of these maturity parameters suggests the existence of two, or possibly three, pods of active source rocks, located to the southwest and to the east of the basin, and possibly to the north. This would modify the classic hydrocarbon migration model for the Putumayo Basin, increasing the hydrocarbon potential of the basin. Given the low level of thermal maturity documented in the Cretaceous sequence that has been drilled, the possibility to evaluate the presence of a very reactive kerogen with hydrocarbon expulsion thresholds at lower temperatures is proposed.

KEYWORDS **Crude Oils. Geochemical Characterization. Petroleum System. Source Rock. Oil Kitchen.**

INTRODUCTION

This study is based on the geochemical characterization of sixteen crude oil samples from Cretaceous reservoirs in the Putumayo Basin, which is located south of Colombia, comprising an area of approximately 110,304km^2 (Fig. I.1, 1997). It is bounded by the fault system of the eastern part of the Eastern Cordillera to the west, the Serranía de la Macarena to the north, the Guyana Shield to the east, and Ecuador's Oriente Basin to the south.

Three main elements are involved in the development of the basin: the craton or stable area; the peri-cratonic area (covered by Cretaceous and Cenozoic sediments); and the Andean area. The Andean area is located at the westernmost part of the basin, adjacent to the foothills, and is characterized by having oil potential in the lower Cretaceous sediments. It has high relief structural traps generated by compressive stress due to the Eastern Cordillera uplift (Kairuz *et al.*, 2000). The basin was deposited in a stable tectonic framework and its depocenter is located immediately east of the fold belt (Fig. I.2).

The tectonic history of the Andean area of the Putumayo basin is represented by three periods of major deformation: i) Jurassic–Cretaceous extensional event with normal faults forming grabens and fault systems that only affect the Caballos Formation and, in some cases, the base of the Villeta Formation; ii) Upper Cretaceous to Lower Paleogene compressional event during the deposition of the Rumiyaco and Pepino formations, which is responsible for the development of the existing structures; and iii) Miocene–Pliocene event, when the entire sedimentary sequence was tilted due to the Andes Cordillera uplift, presenting at this time a slight dip towards the NW (Cooper *et al.*, 1995).

The sedimentary sequence of the basin ranges from Triassic to Recent (Fig. 1). The Triassic-Jurassic sequence is composed of volcanic deposits, siltstones and sandstones, and it is considered as the economic basement (Córdoba *et al.*, 1997). Coastal to shallow marine sandstones and shales of the Caballos Formation, marine limestones, marls, shales and sandstones of the Villeta Formation, and shallow marine to continental siliciclastic sediments of the Rumiyaco Formation comprises the Cretaceous-Paleocene sequence. The Eocene-Miocene sequence comprises the fluvial/alluvial conglomerates of the Pepino Formation, the lacustrine/fluvial shales, siltstones and sandstones of the Orteguaza Formation, and the continental to transitional shales, conglomerates and sandstones with minor gypsum and coal layers of the Orito-Belen Group. This sequence is overlaid by the Pliocene to Quaternary coarse siliciclastic deposits of the Guamues and Caiman formations (Gonçalves *et al.*, 2002).

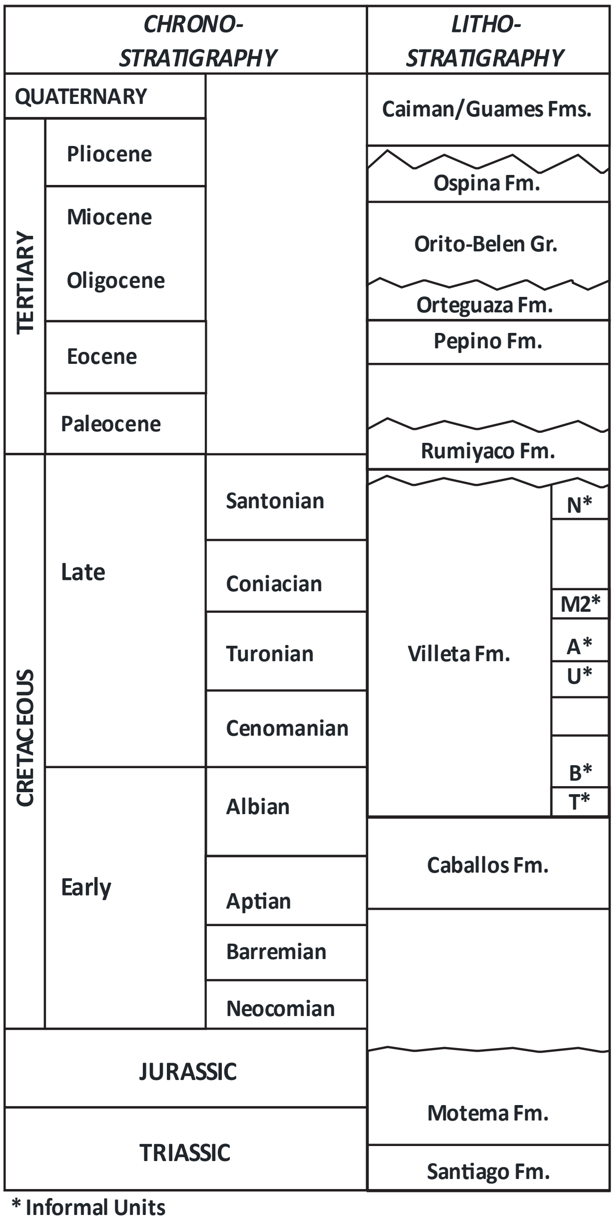

FIGURE 1. Generalized chronostratigraphic and lithostratigraphic chart of the Putumayo Basin (Córdoba *et al.*, 1997).

The organic-rich, marine calcareous shales and marls of the Upper Cretaceous Villeta Formation have been identified as the main petroleum source rocks of the Putumayo Basin (Córdoba *et al.*, 1997; Kairuz *et al.*, 2000; Gonçalves *et al.*, 2002; GEMS S.A., 2010). The marine shales of the Caballos Formation are also considered potential source rocks of the Putumayo Basin (Gonçalves *et al.*, 2002). The possibility of pre-Cretaceous source rocks for the sixteen analyzed crude oil samples has been evaluated.

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METHODOLOGY

All samples were collected from the Lower Cretaceous Caballos Formation and Upper Cretaceous Villeta Formation (Table I.1). They were immediately sent to the laboratory to be analyzed for: bulk parameters, Sulfur, Vanadium and Nickel content, whole oil gas Chromatography (GC), liquid chromatography, and gas chromatography-mass spectrometry (GC-MS). Isotope analyses of the saturated and aromatic fractions were also performed. Then, the integration and evaluation of conventional geochemical and isotopic analysis was accomplished in order to select samples for high-resolution geochemical analysis. These included: i) quantitative diamondoids analyses (QDA), compound specific isotopes analyses in diamondoids (CSIAD), compound specific isotopes analyses in biomarkers (CSIAB) that were performed to all samples; ii) gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS) to six samples, iii) highly branched isoprenoids (HBI) to thirteen samples, and iv) quantitative extended diamondoid analysis (QEDA) to eleven samples. Finally, all results were interpreted and integrated in terms of oil-oil correlations, oil families, biodegradation processes, and thermal maturity. Their implications for the petroleum systems in the basin were examined.

RESULTS

A total of sixteen crude oil samples were submitted for conventional and high-resolution geochemical analysis.

Conventional geochemical analysis

Overall, the crude oils analyzed have well preserved normal alkanes. This fact, and the pristane/n-C17 and phytane/n-C18 relationships, confirm the absence of significant biodegradation effects on those oils. The differences in API gravity values are more likely the product of different source rock facies, or thermal maturity influences.

The classification of oil families and the definition of source rock facies by depositional environments were established from the oil-oil correlation cross plots of source related biomarkers. A cluster-type statistical analysis was performed with selected source rock related parameters (Fig. I.3). In general terms, it is possible to separate the samples analyzed in three main groups: one group consisting of crude oils from Nancy-1 and Cohembí-1 wells (Family 1), which represents one of the end members; the oil from Toroyaco-1 well, that represents another end member; and a third group comprising the rest of the analyzed crude oils (Family 2).

The Pristane/Phytane vs. C35/C34-Hopane, pristane/phytane vs. diasteranes/steranes, Ts/Tm vs. H31/H30, and hopane/steranes vs. tricyclic terpane cross plots clearly show the separation of Family 1 oils (sourced from rock facies deposited in anoxic marine carbonate environments), from Family 2 oils (sourced from rocks with more siliciclastic facies. Toroyaco-1 crude oil would be associated with most proximal source rock facies. Figure 2 shows the pristane/phytane vs. diasteranes/steranes cross plot.

The relationship between thermal maturity of the crude oils as a function of vitrinite reflectance equivalent values obtained from aromatic biomarkers, and API gravity, suggests that the quality of the crude oils depends on their thermal maturity. Generally, the crude oils analyzed are related to a source rocks that reached a thermal maturity level equivalent to the peak of hydrocarbon expulsion phase.

API gravity and thermal maturity parameter maps were prepared in order to assess the regional distribution of some of the variables analyzed, and their impact on the petroleum systems of the basin. The distribution of trends in these variables allowed the identification of two zones of high API gravity and thermal maturity in the Putumayo Basin, located: one in the west and the other in the east (Fig. I.4). Given the absence of significant biodegradation processes in the crude oils analyzed, these two zones may arise due to their proximity to potential oil kitchens or pods of active source rocks.

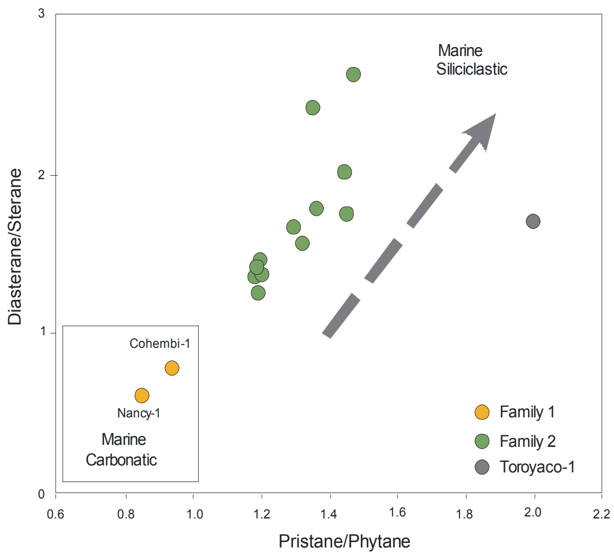

FIGURE 2. Pristane/phytane vs. diasterane/sterane cross plot, shows the separation of the source rock facies for Family 1 and Family 2 crude oils. The Toroyaco-1 crude oil sample would be associated to the most proximal facies.

High resolution geochemical analysis

A summary of the results of the high-resolution geochemical analyses is presented as follows:

Biomarkers in gas chromatography-mass spectrometry-mass spectrometry

From the geochemical interpretation of conventional analysis six crude oil samples were selected for GC-MS-MS. ppm concentrations of the compounds analyzed in steranes and hopanes through GC-MS-MS showed the presence of C30 steranes, suggesting the marine character of the source rock (Peters and Moldowan, 1993). Increased gammacerane concentrations in crude oils of Family 1 suggest a marine carbonic character for the source rocks of this family (Hughes, 1984; Peters and Moldowan, 1993). The cross plot of gammacerane vs. C30-dinosteranes obtained from GC-MS-MS is also consistent with the separation of crude oils into families conducted through biomarkers in GC-MS (Fig. 3).

Quantitative Diamondoids Analysis (QDA)

The 3- + 4-methyldiamantanes vs. C29-sterane cross plot shows that the crude oils of Family 1 have the lowest levels of thermal maturity, and low diamondoid concentrations indicate no oil cracking (Dahl *et al.*, 1999). The crude oils of Family 2 show slightly higher maturity, but still without evidence of cracking, based on the low diamondoid concentrations (Fig. 4). This low biomarker-low diamondoid composition of the crude oils of Family 2 is commensurate with source rocks in the peak expulsion phase of thermal maturity, whereas the higher sterane biomarker concentrations on the oils of Family 1 potentiate a maturity before peak generation.

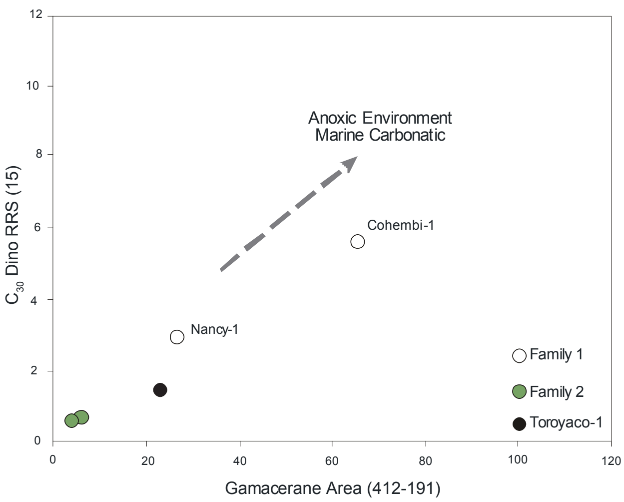

FIGURE 3. Gammacerane vs. C30 dinosterane cross plot from GC-MS-MS. Concentration values are in ppm.

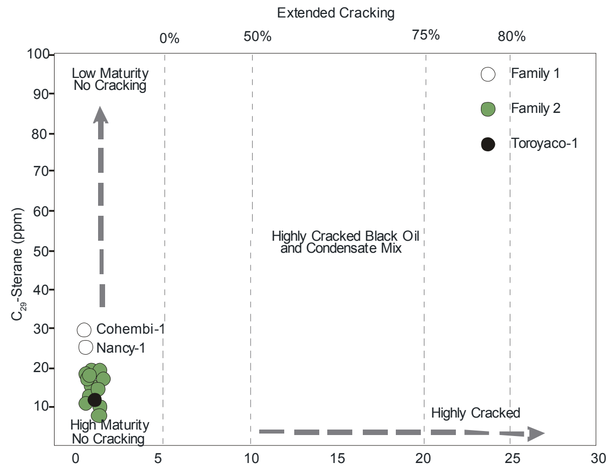

FIGURE 4. The 3- +4-methyl-diamantanes vs c29-sterane cross plot.

The QDA interpretation suggests that the thermal maturity of the crude oils ranges from the peak of hydrocarbon expulsion to the beginning of the late hydrocarbon generation phase.

Compound specific isotopes analyses of diamondoids (CSIA-D), compound specific isotopes analyses of biomarkers (CSIA-B)

The isotopic compositions of the adamantanes and diamantanes isolated from the crude oils show a very similar trend within a narrow range for most of the compounds (Fig. 5). This isotopic correlation between the diamondoids suggests a common source, which age was estimated by age-related biomarkers as Upper Cretaceous.

CSIA-B results for C27, C28 and C29-steranes and for C29 and C30-hopanes, range by <2 per mil for each biomarker for the entire oil-sample set. This rather narrow isotopic range over the entire basin again supports a common source with a consistent depositional environment. The algally-derived C27-steranes are in the range of -28 to -30‰, significantly lighter than the C30-hopanes, which range from -25 to -27‰. With the steranes isotopically lighter than hopanes, one envisions an open marine depositional system without a stratified water column. In a stratified euxinic water column, the bacterially-derived hopanes would show an isotopically lighter aspect due to the utilization of CO_2 respired by heterotrophs (Hayes *et al.*, 1987; Schoell *et al.*, 1994).

Quantitative extended diamandoid analysis (QEDA)

The QEDA analysis of seven crude oil samples allows the identification of some important differences in the crude oil from Toroyaco-1 well. This pattern is observed consistently in the different analyses performed,

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which, added to the fact that this well is located in the northernmost part of the basin, suggests that this crude oil belongs to a different petroleum system.

Highly-branched C25 isoprenoid (HBI) analysis

The presence of the C25 highly-branched isoprenoid at concentrations greater than 100ppm is a reliable indicator associated with source rocks of Late Cretaceous-Tertiary (Damsté *et al.*, 2004). HBI analyses show that all of the sixteen crude oil samples have concentrations of HBI between 53 and 176ppm in the ion m/z 238. These results suggest that all the crude oil samples analyzed are derived from source rocks of Late Cretaceous age.

DISCUSSION

The maturity distribution and API gravity trends allow the identification of two zones with high values for these variables, located west and east of the Putumayo Basin. Considering the absence of significant biodegradation processes, these areas could be associated with oil kitchens, or pods, of active source rocks. The existence of a hydrocarbon kitchen located east of the basin has never been proposed, since in this area of the basin the Cretaceous sedimentary sequence is thinner, has less generative potential, and is much more immature. Our hypothesis would modify the classic model for the migration system in the Putumayo Basin: from west to east (Gonçalves *et al.*, 2002). A detailed review of the geological model of the Putumayo Basin is needed to explain the existence of a potential hydrocarbon kitchen located in the east of the basin.

On the other hand, the integration of the geochemical results of the sixteen crude oil samples with geological data suggests the presence of a very efficient petroleum system, characterized by an alternating sequence of source and reservoir rocks. This fact of the source rocks being in contact directly with the reservoir rocks would increase the hydrocarbon potential of the basin, as the efficiency of oil entrapment is increased. In order to confirm that the source rocks of the Putumayo Basin oils correspond to the Villeta and/or Caballos formations, detailed oil–source rock correlations are needed.

Kinetic analysis of the organic matter in samples of immature rocks from Villeta and/or Caballos formations should be performed in order to identify the presence of a kerogen type with lower activation energies, which would reach the hydrocarbon generation and expulsion phase at lower temperatures. This hypothesis could be an alternative explanation for the potential hydrocarbon kitchen in the east of the basin, given that a low level of thermal maturity has typically been identified in the Cretaceous sedimentary sequence drilled in the Putumayo Basin.

Although the Putumayo and the Oriente Basin in Ecuador apparently share a common geological evolution and there is no clear geological feature that separates them, the volume of hydrocarbon reserves discovered in both basins is contrasting. While in the Putumayo basin have been found about 700 MBP, in the Oriente basin have been found over 3500 MBP. This huge difference between the reserves discovered in both basins represents an exploratory opportunity, to the extent that a better understanding of the mechanism of generation, migration and hydrocarbon charge in the Putumayo Basin can be achieved.

CONCLUSIONS

The interpretation of geochemical analysis of sixteen samples of crude in the Putumayo Basin suggests that these hydrocarbons were generated by organic facies deposited in different marine environments: a carbonate platform and a proximal area of an inner shelf with influence of continental organic matter. Hypothetically, these environments can be correlated with the calcareous and siliciclastic facies alternating in the stratigraphic section of the Cretaceous Villeta Formation present in the basin.

This interpretation based on the present data supports the hypothesis that crude oils related to pre-Cretaceous source rocks are absent in the Putumayo Basin. On

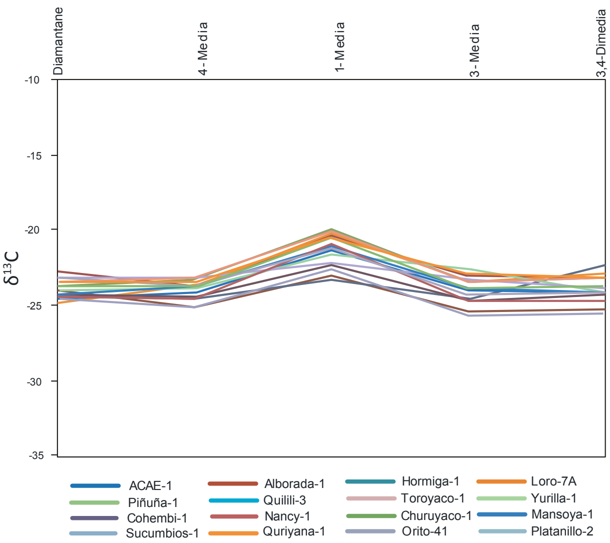

FIGURE 5. A) Isotopic composition distribution of the diamantanes in the analyzed crude oil samples.

the contrary, all evidence points consistently to three facies-differentiated Late Cretaceous sourced petroleum systems: Family 1 oils (sourced from rock facies deposited in anoxic marine carbonate environments), Family 2 oils (sourced from rocks with more siliciclastic facies), and oils sourced from most proximal source rock facies, as the Toroyaco-1 crude sample.

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ELECTRONIC APPENDIX

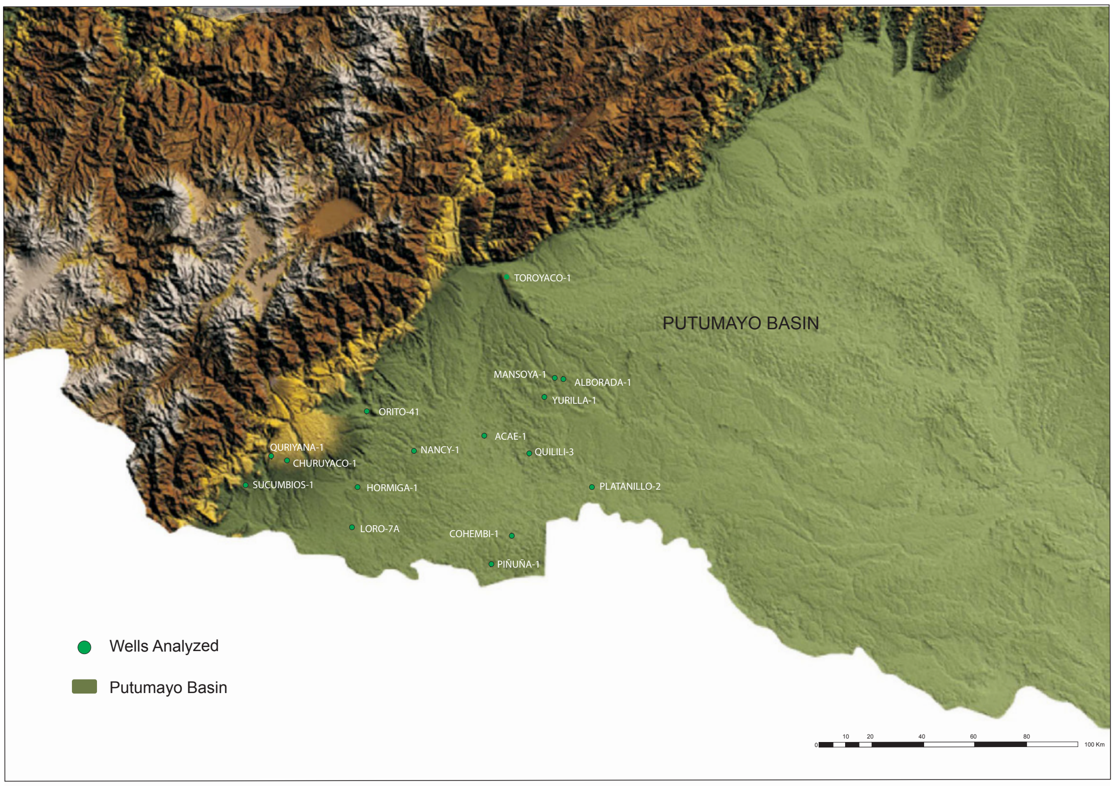

FIGURE I.1. Location of the study area and oil samples analyzed.

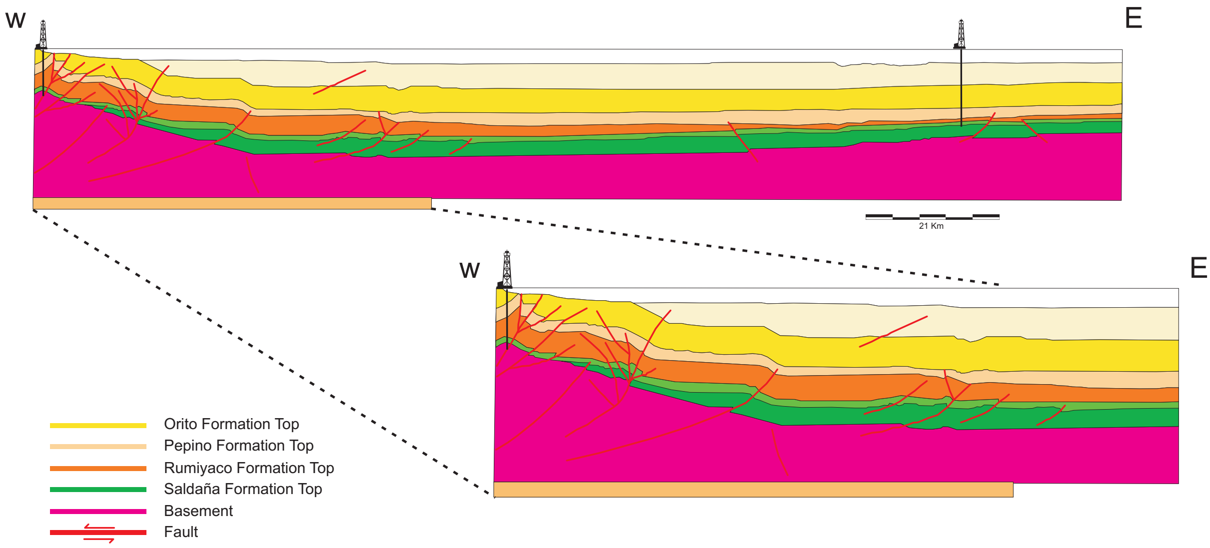

FIGURE I.2. Structural cross section of the Putumayo Basin, EW oriented, located towards the southern part of the basin (GEMS, S.A., 2010).

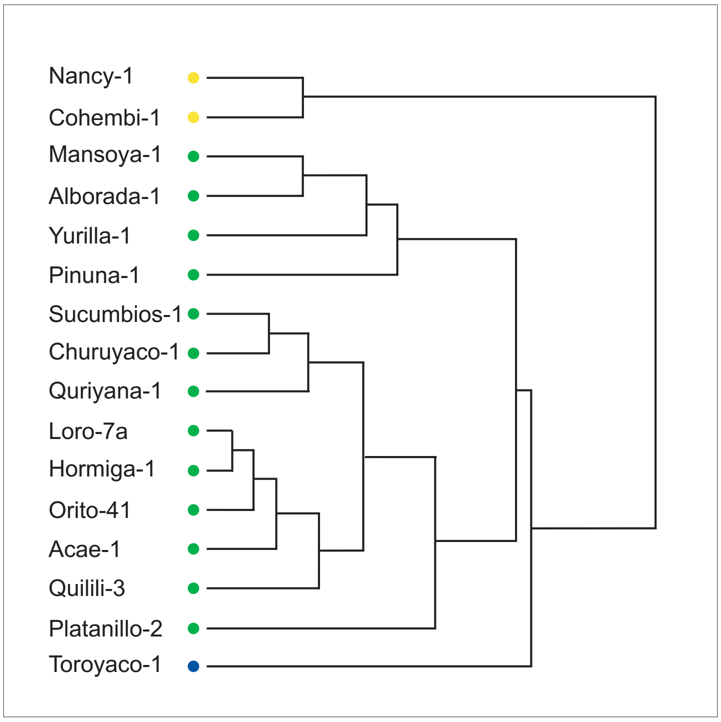

FIGURE I.3. Cluster type statistical analysis of selected source rock related paramaters shows the division of the oil samples in three main groups: Family 1 consisting of crude oils from Nancy-1 and Cohembí-1 wells, representing one of the end members; the oil sample from Toroyaco-1 well, representing another end member, and a third group comprising the rest of the analyzed crude oils (Family 2).

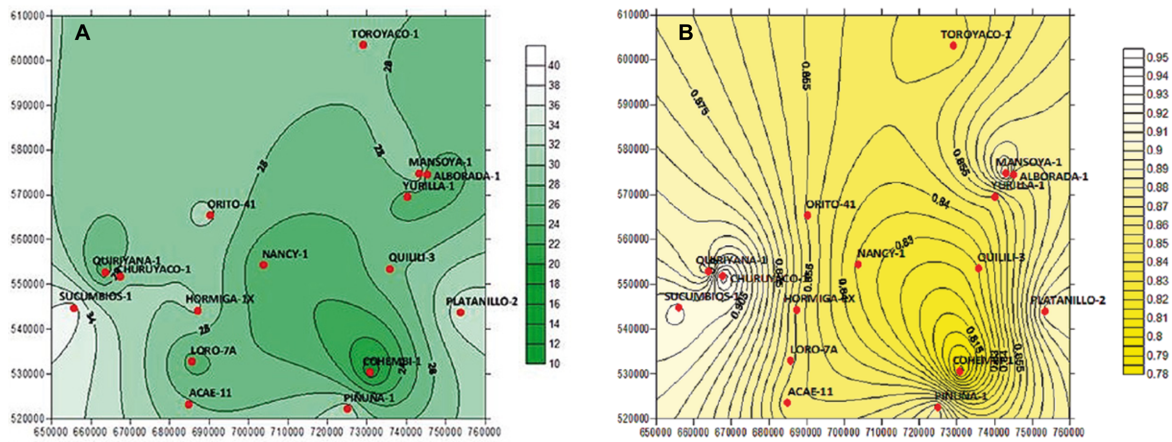

FIGURE I.5. A) API gravity values ditribution, and B) source rock %Ro equivaalent values from aromatic biomarker parameters in the Putumayo Basin.

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TABLE I.1. Stratigraphic location and age of the oil samples analyzed

Sample Well Name	Reservoir	Reservoir Age
NANCY- 1	VILLETA N	UPPER CRETACEOUS
COHEMBI-1	VILLETA N	UPPER CRETACEOUS
MANSOYA-1	VILLETA	UPPER CRETACEOUS
ALBORADA-1	VILLETA U	UPPER CRETACEOUS
YURILLA-1	VILLETA U	UPPER CRETACEOUS
PIÑUÑA-1	VILLETA T	UPPER CRETACEOUS
SUCUMBIOS-1	VILLETA	UPPER CRETACEOUS
CHURUYACO-1	CABALLOS	LOWER CRETACOEUS
QUIRIYANA-1	CABALLOS	LOWER CRETACOEUS
LORO-7A	CABALLOS	LOWER CRETACOEUS
HOTMIGA-1X	CABALLOS	LOWER CRETACOEUS
ORITO-41	VILLETA	UPPER CRETACEOUS
ACAE-11	CABALLOS	LOWER CRETACOEUS
QUILILI-3	VILLETA	UPPER CRETACEOUS
PLATANILLO-2	VILLETA	UPPER CRETACEOUS
TOROYACO-1	VILLETA N	UPPER CRETACEOUS