GEOCHEMICAL EVALUATION OF THE MIDDLE MAGDALENA BASIN, COLOMBIA

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The chemical composition of 25 crude oils from Tertiary reservoirs and 12 rock extracts from five organic-rich Cretaceous formations in the Middle Magdalena Basin, Colombia were studied in detail by geochemical methods in order to understand their genetic relationships. The oils have been geochemically classified into four main groups based on the sulfur content, pristane/phytane, dibenzothiophene /phenanthrene, concentrations of oleanane and terpane distributions. Each group occur in different geographic locations. Oils were mainly derived from calcareous, siliciclastic and mixture of these two facies of the Upper Cretaceous La Luna Formation. Source-oil correlation is supported by sterane and terpane distributions of and carbon isotope ratios. Some oils in the eastern margin contain relatively higher concentrations of higher plant indicators than the remaining oil samples. The molecular compositions of the oils observed in this study appear to be consistent with the inferred depositional sequence of anoxic marine/pelagic carbonate facies in the north/western sector of the Middle Magdalena, while the eastern sector received a higher proportion of clastic input. This documentation supports the interpretation that the Middle Magdalena oils have been generated “locally”, as opposed to have migrated from the region of the Eastern Cordillera. Biomarker maturity parameters indicate that the majority of oils were generated in the early thermal maturity oil window except the Colorado-38 oil which was generated in the middle thermal maturity oil window. Oil maturity data also supports the short migration distances of oils from the early-mature source rocks to the reservoir rocks. The composition of some oils (e.g., La Cira, Infantas, Conde and Bonanza) is unusual in that gas chromatographic data contains an n-alkane and isoprenoid distribution normally associated with moderately degraded oils, but they also contain a relatively high abundance of gasoline hydrocarbons. This particular gas chromatographic pattern may be explained by the addition of migrant gas/condensate to the “in situ” biodegraded oils. Secondary condensates may also have charged the less biodegraded oils (e.g., Cantagallo-23 and Casabe-471), which could explain the “V” pattern of the n-alkane distribution. This phenomena is observed in productive basins in other parts of the world. The range of oil gravities measured in the Middle Magdalena Basin is attributed to organic facies variations, different levels of biodegradation and late charge of condensate rather than to thermal maturity and migration-related effects.

Keywords: *biomarker, cretaceous, source, Colombia, oil, maturity*

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Este estudio presenta los resultados de la caracterización geoquímica de 25 muestras de aceites en yacimientos del Terciario y de 12 muestras de roca fuente del Cretáceo, en el Valle Medio del Magdalena. Relaciones genéticas crudo-crudo y crudo-roca fuente, se establecen con base en análisis de biomarcadores (GC/MS y MS/MS) y composición isotópica. Los contenidos de azufre, relaciones pristano/fitano, dibenzotiofeno/fenantreno, concentración de oleanano y distribución de terpanos y esteranos indican la presencia de cuatro grupos principales de aceites encontrados en diferentes localidades. Los aceites de esta cuenca fueron generados a partir de facies calcáreas, y siliciclásticas de la Formación La Luna del Cretáceo Superior. Correlación con la roca fuente está soportada en distribución de terpanos y esteranos y en composición isotópica. Algunos de los aceites producidos en la margen oriental contienen mayores concentraciones de biomarcadores que indican contribución de plantas superiores. Los cambios regionales en la composición de los aceites es consistente con los cambios de facies de la Formación La Luna, de marina, pelágica y rica en carbonatos hacia la parte norte y occidental de la cuenca a más siliciclástica y con influencia terrestre en la porción oriental de la cuenca. Estas tendencias indican que la generación de aceites es de caracter local y contradice la migración desde la Cordillera Oriental propuesta en estudios anteriores. Los indicadores de madurez sugieren que la mayoría de los aceites fueron generados en la zona de madurez temprana, excepto la muestra del campo Colorado, generada en la zona media de madurez termal. Los resultados de madurez soportan la teoría de migración local. La composición de algunas muestras de aceite presentan composiciones anómalas, debido a que los perfiles cromatográficos indican estados intermedios de biodegradación (ausencia de n-alcanos de medio y alto peso molecular) pero presentan concentraciones anómalamente altas de gasolinas. Estos patrones indicarían la migración secundaria de condensados sobre los aceites biodegradados. Este fenómeno se observa en otras cuencas sedimentarias del mundo. La variación de gravedades API en los aceites del Valle Medio del Magdalena es causada por cambios de facies en la roca fuente, por diversos grados de biodegradación y por la carga secundaria de condensados y no por variaciones en madurez termal o distancias de migración.

INTRODUCTION

Oils produced from Tertiary reservoirs in this basin possess a wide range of bulk compositional properties (API gravity, sulfur content, gasoline hydrocarbons, etc.) that has been interpreted by several authors as a result of either long distance migration or different degrees of biodegradation (Govea and Aguilera, 1985; Illich, 1983). This paper shows that the compositional changes resulted from facies changes in the La Luna source horizons and possibly a secondary contribution from the Umir Fm. in the eastern margin. Parallel trends in oil composition and facies distribution in the La Luna Formation support the idea of local sources instead of long distance migration from the Eastern Cordillera.

Because biomarkers are derived from biological precursor molecules present in specific organisms that live only under certain conditions, it is logical to attempt to use biomarkers as indicators of those life conditions. Biomarkers provide information about the type of organic matter and its environment of deposition which together constitute“organic facies”. In the present study, a wide variety of quantitative analytical data were utilized to distinguish the oils. These data included whole-oil GC patterns, carbon isotopes (whole oil, saturated and aromatic hydrocarbons), and gas chromatography-mass spectrometric data. This data set was used to identify the type of organic matter, the lithology and the depositional conditions of all probable source rocks, and to describe the processes that may have affected the oils after they were expelled from their source(s). Figure 1 shows the locations of those fields from which samples were obtained.

GEOLOGIC SETTING

A brief review of the Cretaceous stratigraphy is provided to better understand the environments in which the source rocks were deposited. More detailed descriptions of the basin geology can be found on Olsen (1954), Morales *et al*. (1958), Schamel (1991) and Montgomery (1992). Producing oils come mainly from Tertiary reservoirs. Some production from Cretaceous limestones is reported in the northernmost oil fields. Recent discoveries indicate a new play from fluvial clastic and marine limestone reservoirs of the Upper

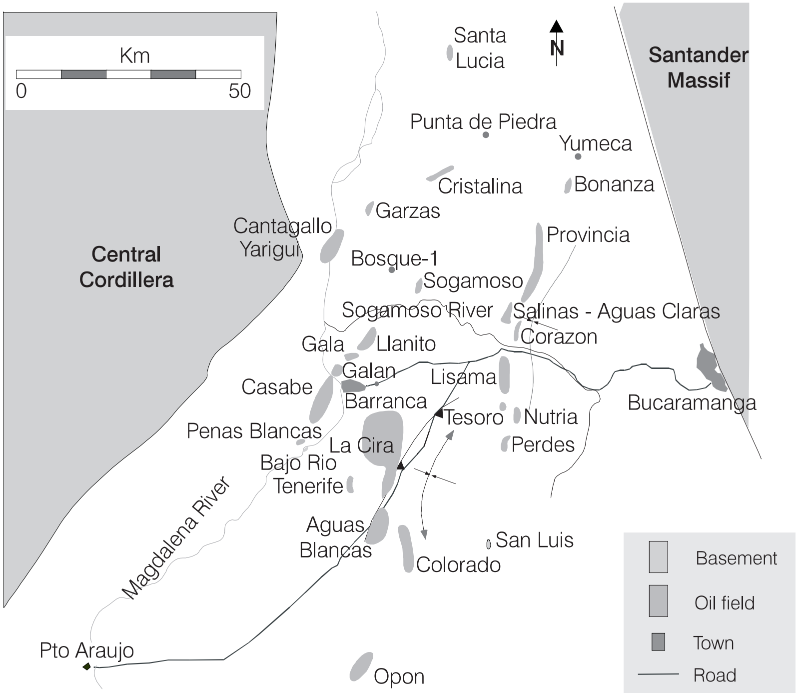


Figure 1. Map of the middle Magdalena basin showing the location of oil samples analysed in this study. Source rock samples from previous studies are also shown.

Cretaceous Cimarrona Formation (Cunningham and Namson, 1997).

The sedimentary section in the basin ranges in age from Jurassic to Recent (Figure 2). The Jurassic sediments consist of red siltstones and sandstones deposited in alluvial environments and restricted to grabens. Cretaceous strata comprise mainly a series of marine shales, marls, and limestones. Overall, paleo-depositional depths increase up from the basal continental/ deltaic sandstones into marine-shelf shales, marls and limestones in the Turonian-Coniacian and decreases back to shallow marine and transitional environments in the Upper Cretaceous. This trend has been associated with sea-level changes with a maximum rise recorded in the latest Cenomanian-earliest Turonian.

Basal, Valanginian-Hauterivian, alluvial sandstones and conglomerates of the Tambor Formation lie unconformably over Jurassic sediments. Jurassic-rock clasts evidence an erosional event at the base of the Cretaceous sequence (Morales *et al.*, 1958). These red sediments are covered by dark gray siltstones and fine sandstones of the Hauterivian Cumbre Formation and by Hauterivian (South) to Barremian (North) Rosablanca Formation. This Formation consists of grainstones and evaporites that grade upward into shaly limestones, micrites and biomicrites (Morales *et al*, 1958). Abundant pelecypods, cephalopods, gastropods, annelids, and echinoids are found in these rocks. Morales et al. (1958) interpreted this formation as upper neritic to nearshore and Ortiz *et al.* (1997) interpreted it as estuarine. Ortiz *et al.* (1997) reported a non-calcareous sandstone toward the top of the formation that might have reservoir potential.

The overlying Barremian-Aptian (South-North) La Paja Formation consists of black, thinly laminated, locally calcareous shales deposited in a marine platform. The lower part is rich in calcareous concretions, calcite veins, cephalopods and worms (Morales *et al,* 1958). The upper part consists of marls and is transitional with the overlying Tablazo Formation. The Late Aptian to Early Albian Tablazo Formation is composed of very fossiliferous (pelecypods), clayey limestones that grade upward into fossiliferous limestones. According to Morales *et al.* (1958) this formation is upper neritic in the Sogamoso area (central part of the basin, Figure. 1) to middle neritic in the northern part of the basin. These limestones are overlaid by soft, platy, carbonaceous, gray to black, locally calcareous and concretionary shales of Albian age called the Simiti Shale (Morales *et al.*, 1958). Morales *et al.* (1958) reported light green oil in vugs and ammonite chambers. In some places, toward the very top, thin conglomeratic streaks composed of small pebbles, phosphate nodules, fish teeth, and sand. Morales *et al.* (1958) reported a shallowing up trend, but these sediments might correspond to a transgressive lag indicating a deepening event toward the top of the formation. The overlying Late Albian to Cenomanian marine, argillaceous, dark gray limestones and calcareous shales of the Salto Formation supports this last interpretation.

La Luna Formation in the Middle Magdalena basin is similar to the one described in Venezuela (Zumberge, 1985). In the Middle Magdalena basin, however, it is generally divided into three members: Salada, Pujamana and Galembo.The Early Turonian Salada Member consists of hard, black, thinly bedded, finely laminated, limy shales with some thin beds of black fine-grained limestones (Morales *et al.*, 1958). This member contains abundant planktonic foraminifera and radiolaria but lacks benthonic foraminifera. The occurrence of streaks and concretions of pyrite are characteristic of this member. The Late Turonian to possibly Early Coniacian Pujamana Member is composed of gray to black, calcareous, thin bedded shale. The Late Turonian to Coniacian and possibly Santonian Galembo Member consists of thinly bedded, black, calcareous shale with interbeds of thin argillaceous limestones. Frequent thin beds of blue-black cherts occur. Numerous ammonite-bearing concretions are found in this member. The three members of the La Luna Formation contain variable carbonate contents: The Galembo Member generally contains minor-to-trace amounts of carbonate (avg. = 2,4%), in contrast, the Pujamana and Salada members are carbonate-rich (43,2% and 40,4%), respectively (Zumberge, 1984). Low oxic conditions in the water-sediment interface are interpreted based on abundance of pyrite and lack of benthonic foraminifera. The presence of planktonic foraminifera and other pelagic fossils in these members suggests that they were deposited in moderately deep water with restricted circulation (Dickey, 1992).

The uppermost Cretaceous (Santonian to Maastrichtian) sediments are represented by dark gray to black, thin-bedded shales. The lower half of the formation has thin ferruginous layers, lenses and small

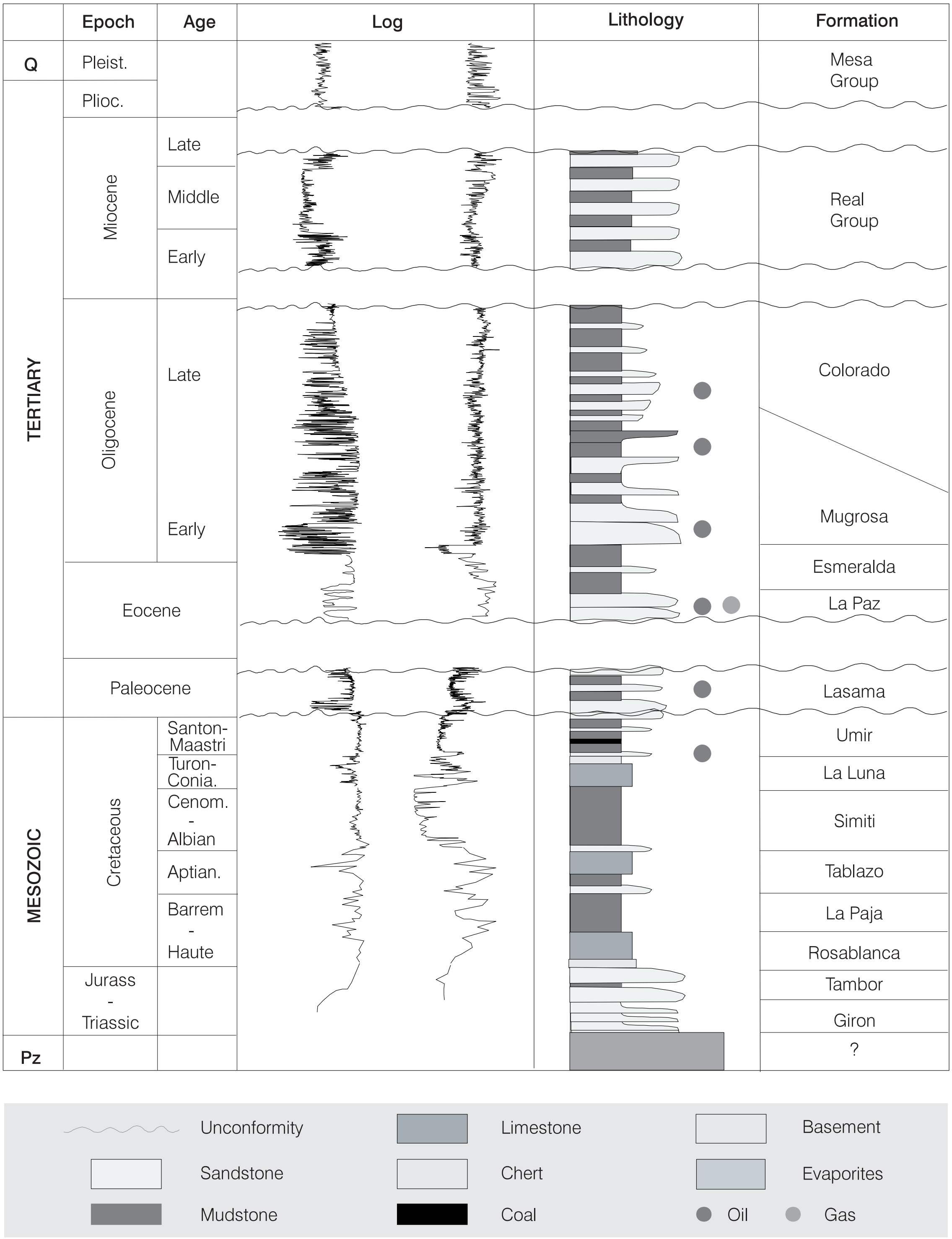


Figure 2. Stratigraphic column and nomenclature in the Middle Magdalena Basin.

concretions and carbonaceous laminae. The upper part contains numerous coal seamlets, thin layers of ironstone and thin intercalations of fine sandstones and siltstones (Morales *et al.*, 1958). Current ripples are by far the dominant sedimentary structure. This formation records the transition from shallow marine to continental conditions in the late Cretaceous.

SOURCE ROCKS

The La Luna Formation has been assumed to be the main source rock in the Middle Magdalena basin (Perez-Tellez, 1994; Dickey, 1992; Govea and Aguilera, 1985; Zumberge, 1984). Although other Cretaceous formations have good source rock properties, they have been generally underestimated. Recently, detailed research by Ecopetrol has evaluated the generation potential of several Cretaceous horizons (Mora *et al.*, 1996; Rangel *et al.*, 1996). A summary of their main results is presented in the following section.

Dark gray shales of the Cumbre Formation have good total organic content - TOC - (1% - 7,8%) of type II kerogen in the late oil window (Ro ≈1,1% - 1,2%). Solid bitumen contents range between 15% - 25%.

Analysis of the limestones and micrites of the Rosablanca Formation in Casabe-199, Norean-1, Bosques-1, Llanito-1 and Yumeca-1 show fair to good values (TOC ≈ 0,5% - 3,6%) of types III and II (?) kerogen (Figure 3). Solid bitumen contents are high, generally ranging between 5% - 20% and reaching values up to 50% of the organic matter. Thermal maturity range between 1% Ro in Yumeca-1 and Norean-1 wells to 1,2% - 1,4% in Bosques-1 and Casabe-199 wells. Yumeca-1 well show 0,5% - 3,6% TOC with low amounts of solid bitumen.

Dark to light gray shales of the La Paja Formation show fair potential, with TOC values around 1,2% of type II kerogen. Vitrinite values (1,1% - 1,38% Ro) indicate this formation is in the gas zone. Solid bitumen contents (1% - 5%) evidence past generation potential. Published reports suggest good source potential in this formation (Dickey, 1992).

Biomicrites and calcareous shales of the Tablazo Formation show good TOC values, although part of this comes from solid bitumen (20% - 25%). As in the case of the La Paja Formation, this sequence is in the gas zone (Ro ≈1,1% - 1,35%). Ecopetrol reports 75% - 80% of the organic matter are lipids.

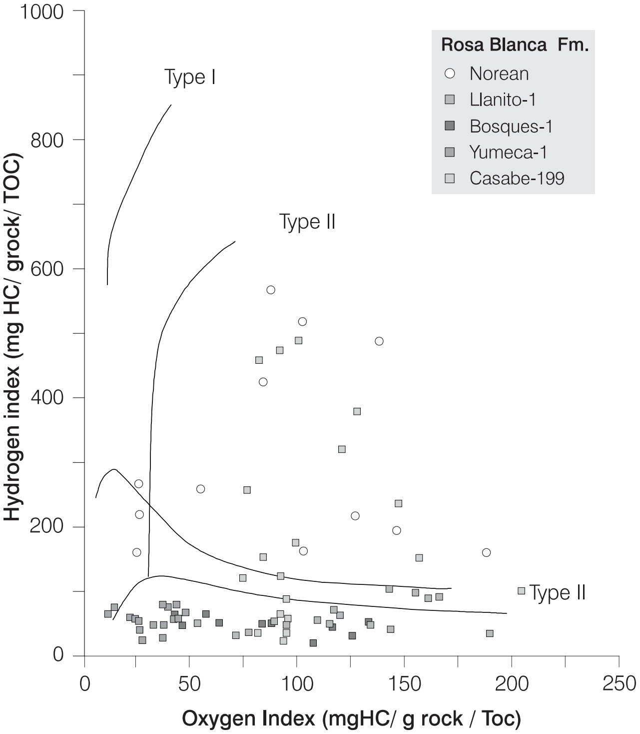


Figure 3. Type of kerogen in the Rosablanca Fm. as interpreted from Rock-Eval Pyrolysis from cuttings Vitrinite reflectance = 1% - 1,4%

Simiti Formation dark gray shales have TOC values from 1,5% - 3,6% and vitrinite values between 0,71% - 0,95%. It is mainly composed of lipids (85% - 100%) in the Casabe, Yumeca, Norean and Punta de Piedra wells. Llanito and Bosques show higher terrestrial input (15% - 25%). Solid bitumen ranges up to 10% of the organic matter.

The La Luna Formation analyzed in Norean, Casabe and Llanito wells shows good to fair TOC values (0,5% - > 3%) and type II kerogen (Figure 4). Maturity levels range between 0,9 and 1% vitrinite reflectance. Zumberge (1984) reported average TOC values of 3,51% in the Pujamana Member and 4,51% in the Salada Member. The difference might be explained by the fact that Ecopetrol did extensive continuous sampling in several wells while Zumberge's results are from isolated outcrop samples. Zumberge (1984) reported that the kerogen from the La Luna Formation is predominantly fine-grained, amorphous material with few well-defined vitrinite particles and pollen suggesting little terrestrial input. GC-FID traces for saturated

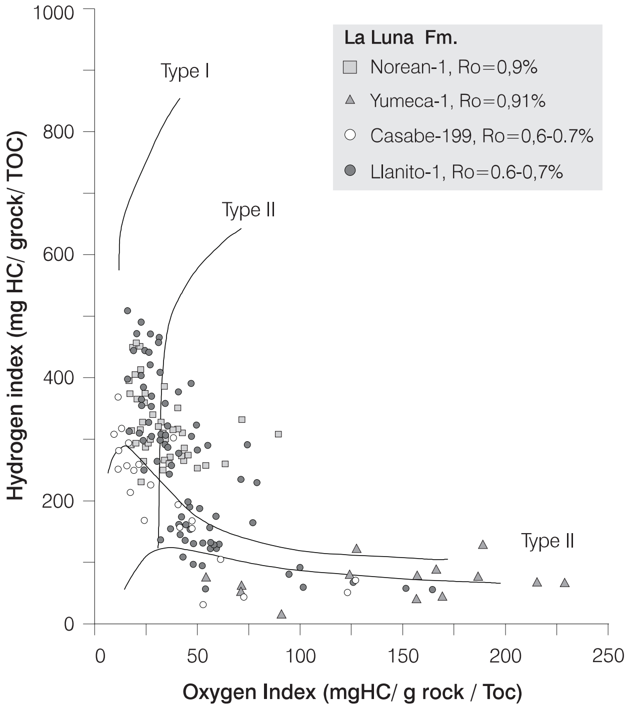


Figure 4. Type of Kerogen in the La Luna Fm. as interpreted from Rock-Eval pyrolysis from cuttings vitrinite reflectance phown by well.

hydrocarbon fractions (Figure 5) from the La Luna Formation in the Middle Magdalena Basin generally are dominated by acyclic isoprenoids and n-alkanes in the carbon number range of C_{15} to C_{33} (Zumberge, 1985).

The uppermost Umir Formation shows variable source potential. In the Lisama area (eastern margin), organic content is very lean and of poor quality. About 60 km NNE, in the Yumeca well, Ecopetrol reports two 500 to 800 ft. sections of fair-to-good source potential (TOC > 3%, type III-II kerogen, hydrogen index ≈ 200 - 350 mg HC/g rock/TOC, Figure 6) but immature (Ro ≈ 0,6%). Ecopetrol reports kerogen is 50% vitrinitic and 50% lipidic. A basal 300 ft. horizon has an average TOC of 1,8% - 2% and is composed mainly of type II kerogen. Good source potential (hydrogen index ≈ 340 - 420 mg HC/ g rock/ TOC) is reported from the coals and organic rich shales from the time-equivalent, Guaduas Formation in the Eastern Cordillera (García-González, 1997).

Biomarker analysis of several Createaceous organic-rich horizons indicate that these rocks are composed of marine organic matter deposited in a marine shelf with little terrestrial input. Most samples are characterized by abundant tricyclic terpanes dominated by C_{23} tricyclic (Figure 5), No oleanane or other higher plant biomarker indicator were found in the source rock samples. Rosablanca and La Luna samples have high

(a) La luna, 7160'

(b) Simiti, 7360'

(c) Rosablanca, 10470'

(d) La Luna Outcrop, Salada Mambre

Figure 5. Terpane biomarker distribution for several Cretaceous sour ce horizons in the middle Magdalena basin (a), (b) and (c) are cutting samples from casabe-199 welle and (d) is an outcrop samples east of the basin (from Zumberge, 1985).

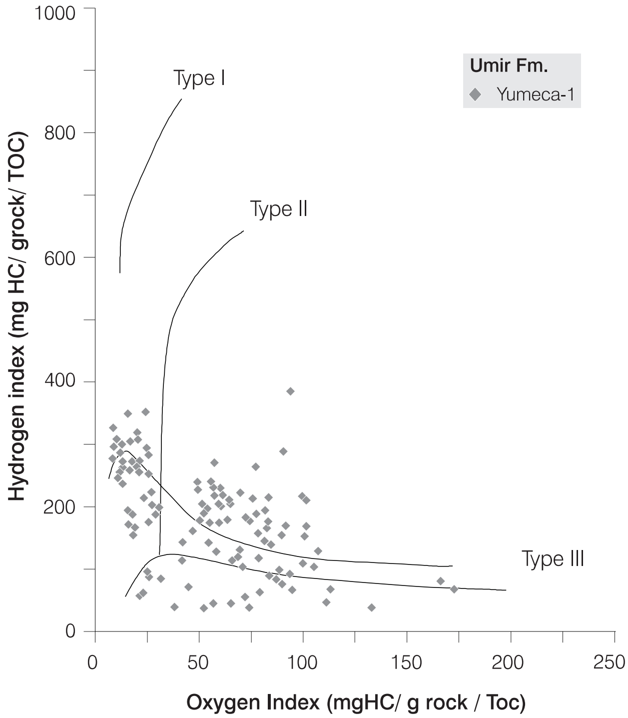


Figure 6. Type of kerogen in the Umir Fm. as interpreted from Rock-Eval pyrolysis from cuttings of Yumeca-1 well. Vitrinite reflectance = 0,6%

C_{35}/C_{34} homohopane ratio indica-ting carbonate-prone, reducing enviroments (Figure 5).

As evidenced by Ecopetrol's analysis, several organic-rich horizons are present in the Cretaceous sections besides the La Luna Formation. However, the abundance of solid bitumen in some samples makes the source rock characterization by Rock-Eval pyrolysis unreliable.

MATURITY OF THE CRETACEOUS SECTION

The few scattered vitrinite data show that the Lower Cretaceous section is late mature (Ro ≈ 1,0% - 1,4%) across the basin. Maturity level of the La Luna Formation ranges from early mature on the western side of the basin (Ro ≈ 0,7% in Casabe and Llanito fields) to middle mature (main oil window) in the east margin (Ro ≈ 0,9% - 1% in Yumeca well) near La Salina thrust. Higher maturity values (Ro ≈ 1% - 1,1%) are observed for samples on the eastern side of the main thrust fault (Zumberge, 1984), indicating that this area experienced greater burial depths prior to uplift.

Figure 7 shows the vertical distribution of vitrinite reflectance values of several wells in the Middle Magdalena Basin. High vitrinite reflectance values at shallow depths (e.g. Norean and Casabe) indicate that these wells are not at maximum burial depths. Differences in heat flow are difficult to support because of the close distance between sampled wells (maximum 60 km). It is possible that vitrinite reflectance in the hydrogen-rich La Luna Formation might be suppressed.

SAMPLES AND METHODS

Whole oils were analyzed by gas chromatography (GC) on an HP 5890 instrument equipped with a 60 m * 0,25 mm i.d. capillary column coated with a film 0,25-microns-thick of dimethylpolysiloxane. Crude oils were separated, using medium pressure liquid chromatography, into saturate, and aromatic hydrocarbons, NSO compounds, and asphaltenes. Gas chromatography-mass spectrometry (GC/MS) was performed on the saturate and aromatic hydrocarbons using a 60 m *

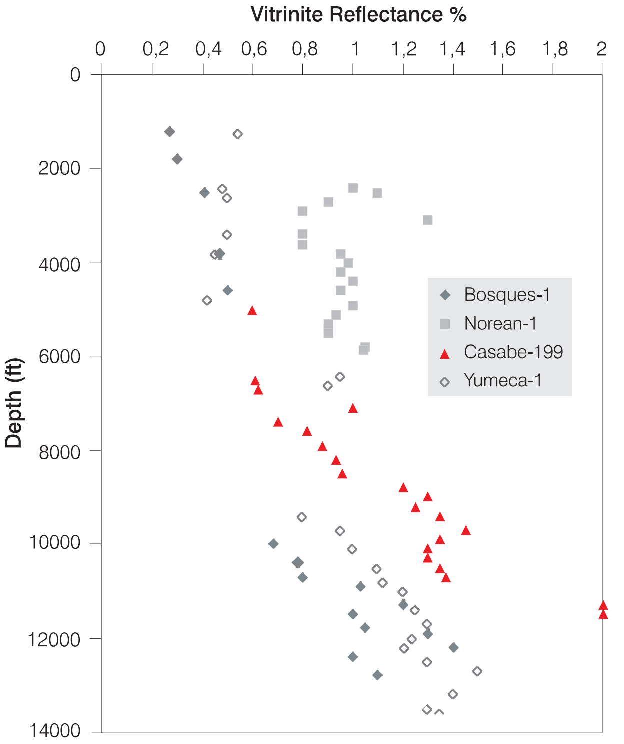


Figure 7. Vertical profile of vitrinite reflectance in the middle Magdalena Basin. Data from Ecopetrol. Note the higher Ro gradient in samples below 7.000' indicating higher heat flow in the Lower Cretaceous.

0,25 mm i.d. capillary column coated with a film 0,1-microns-thick of DB-5 phenyl methylpolysiloxane. Gas chromatography-mass spectrometry-mass spectrometry (GC/MS/MS) analysis of the saturate fraction was performed on a Fisons AutoSpec Q coupled to a HP 5890 gas chromatography equipped with a 60 m ∗ 0,25 mm i.d. fused silica column coated with a film 0,25-microns-thick of DB-1. Stable carbon isotope ratios are reported in parts per thousand (per mil) relative to the PDB standard. Further details on analytical methods are described in Hughes and Dzou (1995).

The concentrations of selected biomarkers were determined by adding standards, 5β-cholane for saturates and d_{10}-anthracene for aromatics. Response factors for the components of interest relative to the internal standards were assumed to be 1,0. While this is not strictly true, it is sufficient for the purpose of comparing samples with one another.

RESULTS AND DISCUSSION

Bulk Properties

API gravities for oils in the Middle Magdalena Basin range from 15° to more than 35° and generally decrease from ESE to WNW (Figure 8). In the east, API gravities generally range between 25° and 37°, although some shallow biodegraded oils have low API gravities (< 20°). The regional variation in API gravities is approximately mirrored by that of the sulfur content of the oils (Figure 9). Oils in the northern/western part of the basin have relatively high sulfur contents (1,0% to 1,9%) compared to those found in the eastern part (0,1% to 0,9%). Figure 10 shows direct correlation between sulfur contents and API gravities and pristane/phytane ratios.

Carbon isotopic composition of the Middle Magdalena Basin saturate and aromatic fractions generally fall in the range of -26 to -28 (Figure 10). The oils plot below the best separation line for marine and terrestrial derived oils, consistent with a marine origin for these oils (Sofer, 1984). Similar carbon isotopic compositions suggest Middle Magdalena oils have similar composition of organic matter input.

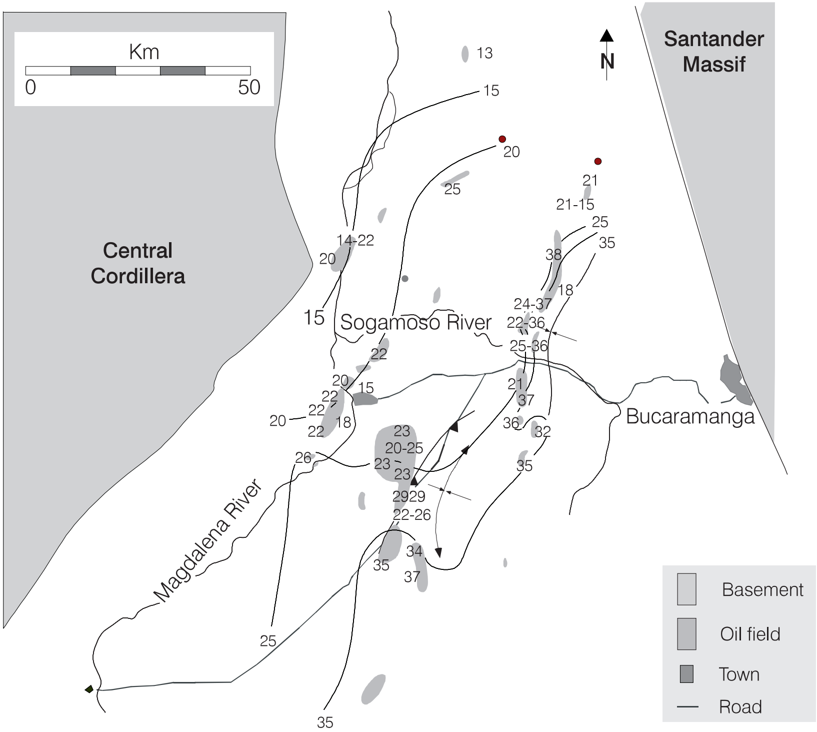


Figure 8. Distribution of API gravities in the analyzed olis. Note regional increase toward the west-northwest, parallet to sulfur contents (Figure 9) and pristane/phytaneratios (Figure 15) indicating source rock lithology control on API gravity.

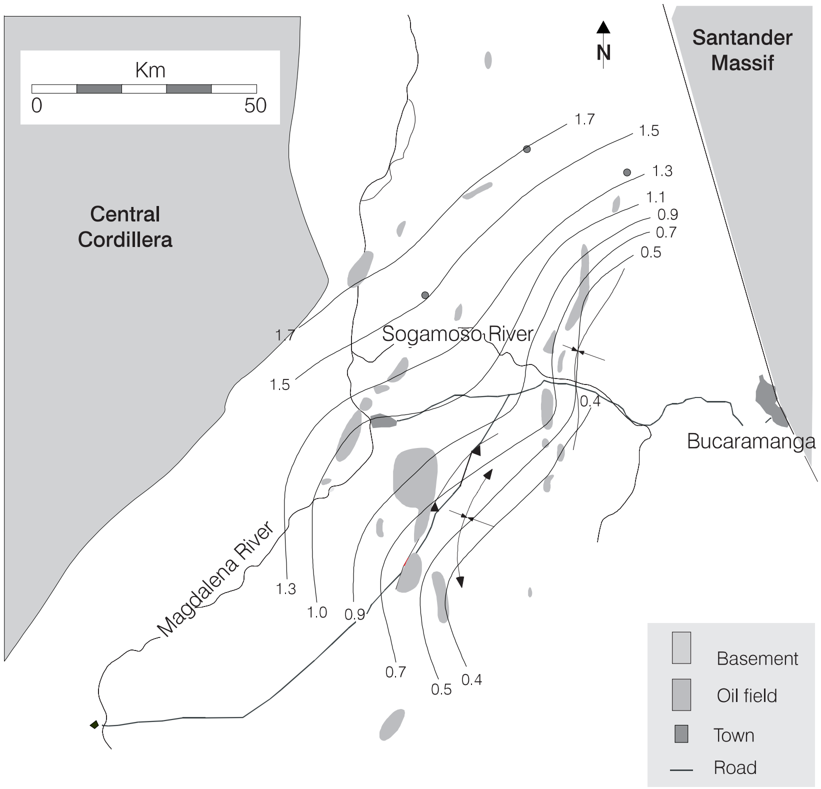


Figure 9. Distribution of sulfur contents in the analyzed olis. Note regional increase in the percentage content toward the west-northwest Indicating more carbonate source rock influence

Oil Families and Source Rock Properties as Indicated by Oil Biomarkers

Similar sterane carbon number distribution (m/z 218, ββ steranes) in oils suggests that the sterane-producing biota which contributed to the source rocks were very similar (Figure 11). Caipal-10, Bonanza-5, Teca-164 and Conde-7 sterane carbon number contents have been altered due to heavy biodegradation. Lisama-13 is relatively richer in C_{29} steranes, which indicate higher plant input. Most oils from the Middle Magdalena basin have similar terpane mass spectrograms (Figure 12). A closer look of biomarker composition, however, reveal differences among the oils (Figures 13, 14)

Middle Magdalena oils have been geochemically classified into four main groups based on the sulfur contents, pristane/phytane ratios, dibenzothiophene/phenanthrene ratios, concentration of oleanane, and terpane distributions (Figures 10 and 13). Each group occupies a different geographic area (Figure 15). Mass fragmentograms (m/z 191) shown in Figure 12 illustrate some of the differences among these groups. Group N oils have the highest amounts of low molecular-weight and extended tricyclic terpanes. Also, the Sum(C_{31} - C_{35}) homohopane/C_{30} hopane ratio is the highest (Figure 12a). Group C3 oils have lower proportions of low molecular-weight tricyclic terpanes and Sum(C_{31} - C_{35}) homohopane/C_{30} hopane ratio (Figure 12b). Groups C1, C2 and E2 have similar terpane distributions as group C3. Group E1 oils have the lowest amounts of all of tricyclic terpanes (Figure 12c). Also, C_{24} tetracyclic/C_{26} tricyclics ratios changes among these groups. The variations in proportion of tricyclic terpanes to hopanes are due to subtle source input changes. Cross plots of biomarker parameters indicate that the four major groups can be further divided into 7 subgroups (Figures 13, 14, 15):

Group N oils :	Cantagallo-23, Cristalina-4, Yarigui-57

Group C1 oils : Casabe-471, Conde-7, Galan-31, Infantas-1559, La Cira-1792, Llanito-97, San Luis-4, San Silvestre-39, Bonanza-5, Gala-8
Group C2 oils : Bajo Rio-1, Peñas Blancas-3
Group C3 oils : Aguas Blancas-2, Colorado-38
Group E1 oils : Lisama-13 and Peroles-2
Group E2 oils : Nutria-28, Tesoro-29
Group S oils : Caipal-10, Palagua-7, Teca-164, Toqui Toqui Este-2

Northern/western oils (group N) have low pristane/phytane, C_{19}/C_{21} tricyclic, $C_{19}+C_{20}/C_{23}$ tricyclic and rearranged sterane (diasterane) to regular sterane ratios, and have the highest C_{35}/C_{34} homohopane ratio and dibenzothiophene/phenanthrene ratios (Figure 13, 14). All these parameters indicate that their source rock was deposited in a carbonate-rich, reducing environment. The Group E1 oils, located in the eastern margin, are distinguished by the relatively higher concentrations of oleanane and pristane/phytane and rearranged/regular sterane ratios. Also they have lower C_{23} tricyclic/C_{30} hopane and C_{29} tricyclic/Ts + Tm ratios and lower homohopane concentrations (Figures 12, 13, 14). All these features indicate relatively more higher plant input in a less-reducing, siliciclastic environment. The remaining groups (C and S) show intermediate compositions and they might be derived from mix of the first two organic facies.

Sulfur content is an indicator of source lithology: high sulfur contents indicative of oils from carbonate rocks or calcareous marls. The regional variation in the sulfur contents suggests that oils in the west were sourced by marine carbonate/marl, whereas oils in the east were generated from marine shales.Unfortunately, sulfur content is also a maturity/biodegradation-influenced parameter. The ratio of dibenzothiophene to phenanthrene and the ratio of pristane to phytane, when coupled together, provide a novel, convenient and powerful way to infer crude oil source rock depositional environments and lithologies (Hughes *et al.*, 1995). The cross plot in Figure 14b indicate that oils in the eastern margin (e.g., Lisama, Peroles) were generated from source rocks deposited in a shale-dominated environment. The abundance of reactive sulfur was quite low due to scavenging by iron to form pyrite. Western/northern oils (e.g., Cantagallo) were generated from source rocks deposited in a marine carbonate or calcareous marl environments. Sufficient sulfate ion concentration and low concentrations of reactive iron resulted in significant amounts of reactive sulfur available for incorporation into the organic matter of these source rocks. This explains why intervals with high carbonate contents contain only minor amounts of pyrite whereas dominantly siliciclastic intervals contain abundant pyrite. Most oil samples, in the central part of the basin, were derived from a mixture of carbonate/calcareous and siliciclastic source rocks. Geographic distribution of pristane/phytane ratios indicates that the western/northern oils were deposited in more reducing conditions, while the oils in the eastern margin were derived from source rocks deposited in more oxic conditions (Figure 16).

The molecular composition of the oils observed in this study appear to be consistent with the inferred depositional sequence of anoxic marine/pelagic carbonate facies in the northern/western sector of the Middle Magdalena basin, whereas the eastern sector received an increased proportion of clastic input. The documentation presented above provides circumstantial evidence for the interpretation that the Middle Magdalena oils have been generated “locally”, as opposed to long-distance migration from the region of the Eastern Cordillera.

The stronger compositional difference and the relatively high pristane/phytane (> 2,0) ratios of some oils in the eastern margin (e.g.Lisama, Peroles, Aguas Claras) indicate the contribution of marine facies, relatively richer in higher plants, and closer to the shoreline. It is possible that the organic-rich layers of the Umir Formation, that have experienced a similar thermal history to La Luna Formation, have contributed to some of the oils in the eastern margin. No source sample was available to support this hypothesis.

Oil Alteration and Mixing

Oils from Middle Magdalena basin show a wide range of GC profiles, from heavily biodegraded residues to unaltered oils (Figure 17). In general, biodegradation is more common in the central and western portions of the basin, where the reservoirs are shallower and cooler. Examination of the GC data indicates that the oils can be divided into sub-groups related to the extent

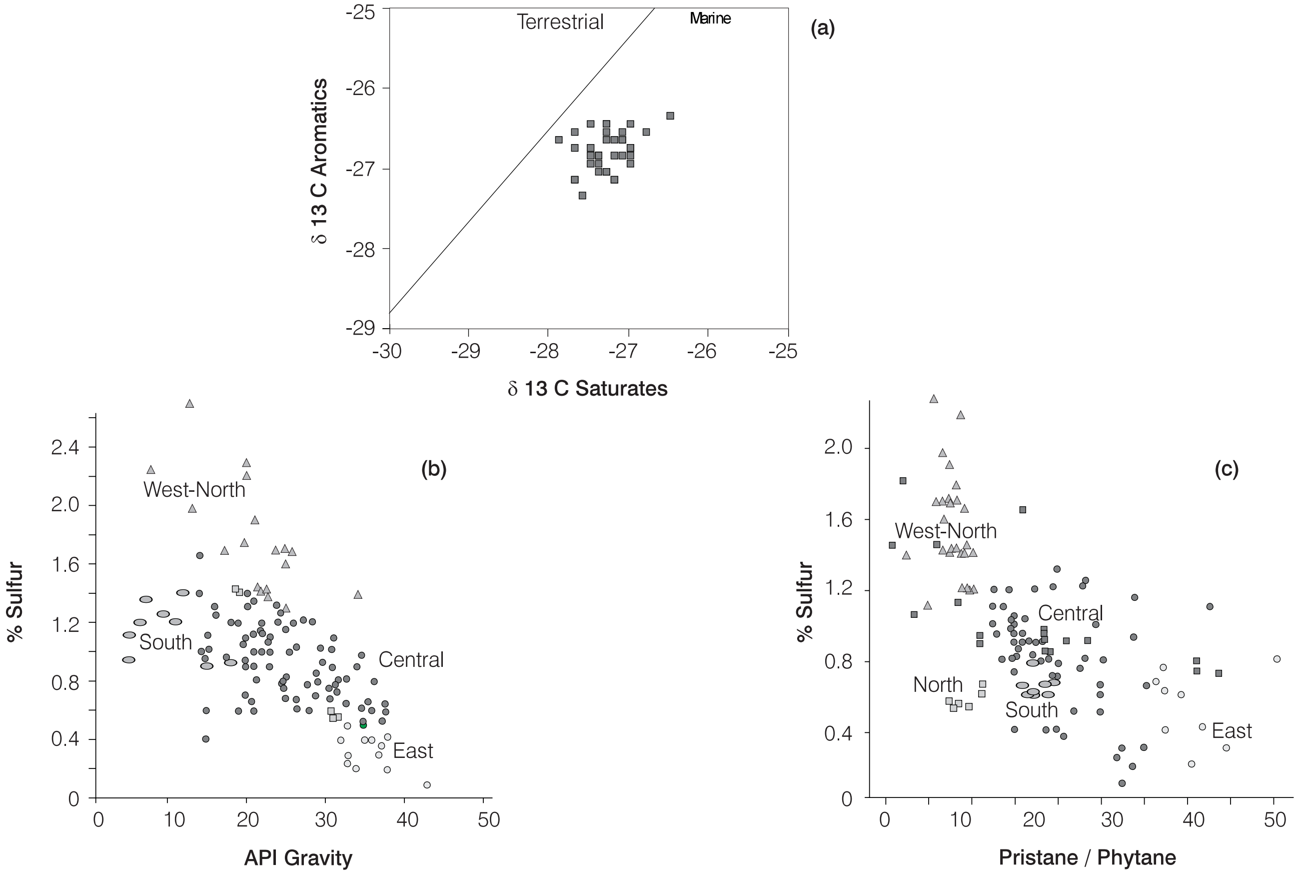


Figure 10. Bulk properties of Middle Magdalena oils.
(a) isotope composition, (b) sulfur versus API gravity and (c) sulfur versus pristane/phytane ratio.
data from previous work compled by Ecopetrol (Rangel et al., 1996) and from this study

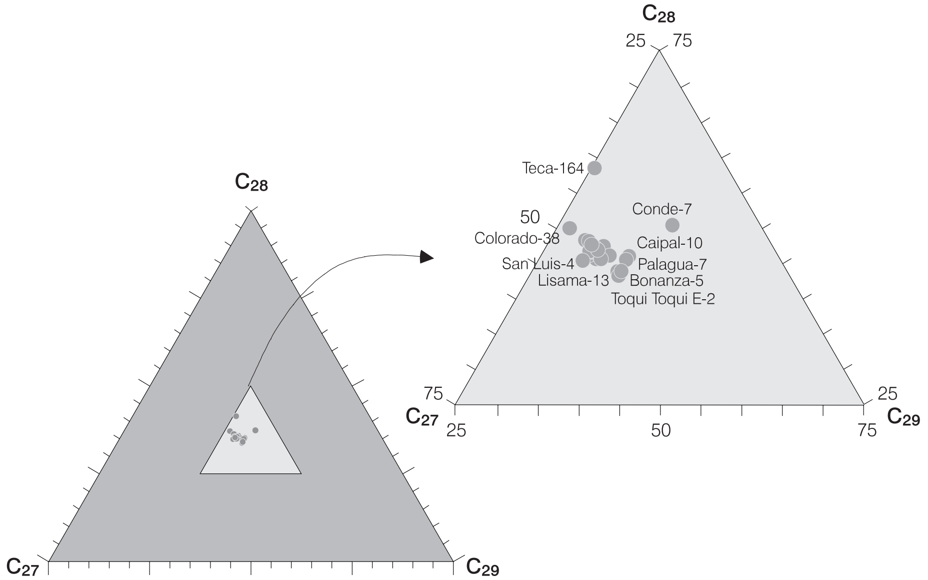
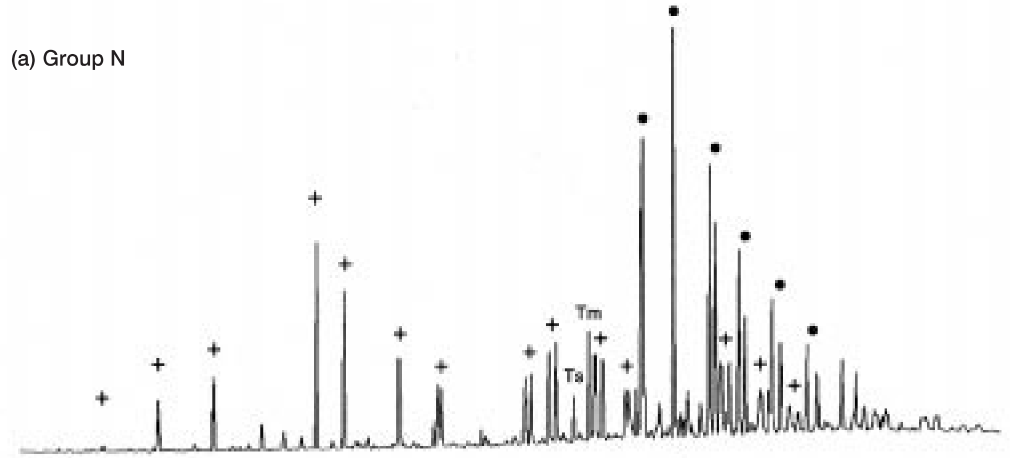
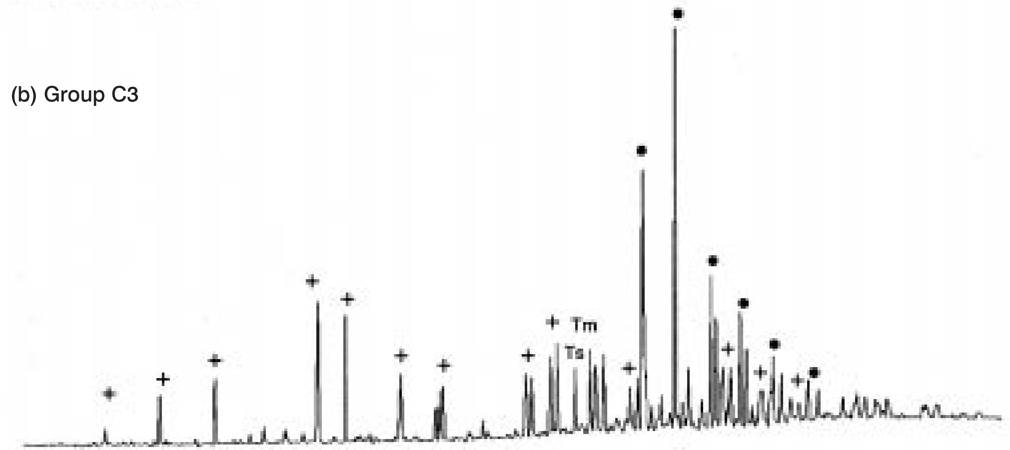


Figure 11. Ternary diagram showing the relative abundances of C_{27}, C_{28} and C_{29} $\beta\beta$ Steranes
in the saturate fractions of oils determined by GC/MS(m/z 218) composition for most oils.
Teca-164 and Conde-7 are heavily biodegraded oils.


(a) Group N


(b) Group C3

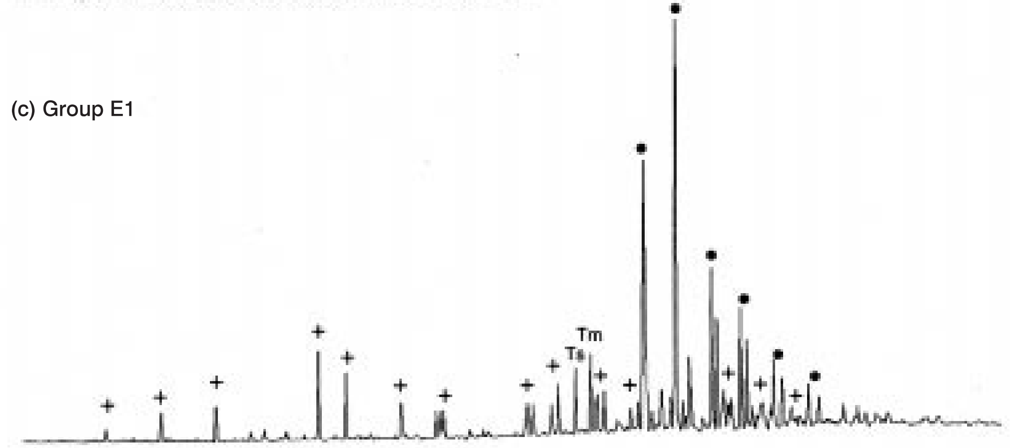

(c) Group E1

Figure 12. Mass fragmentosgrams (m/z 191) of select Middle Magdalena oils. Crosses indicate tricyclies terpanes and circles indicate hopanes

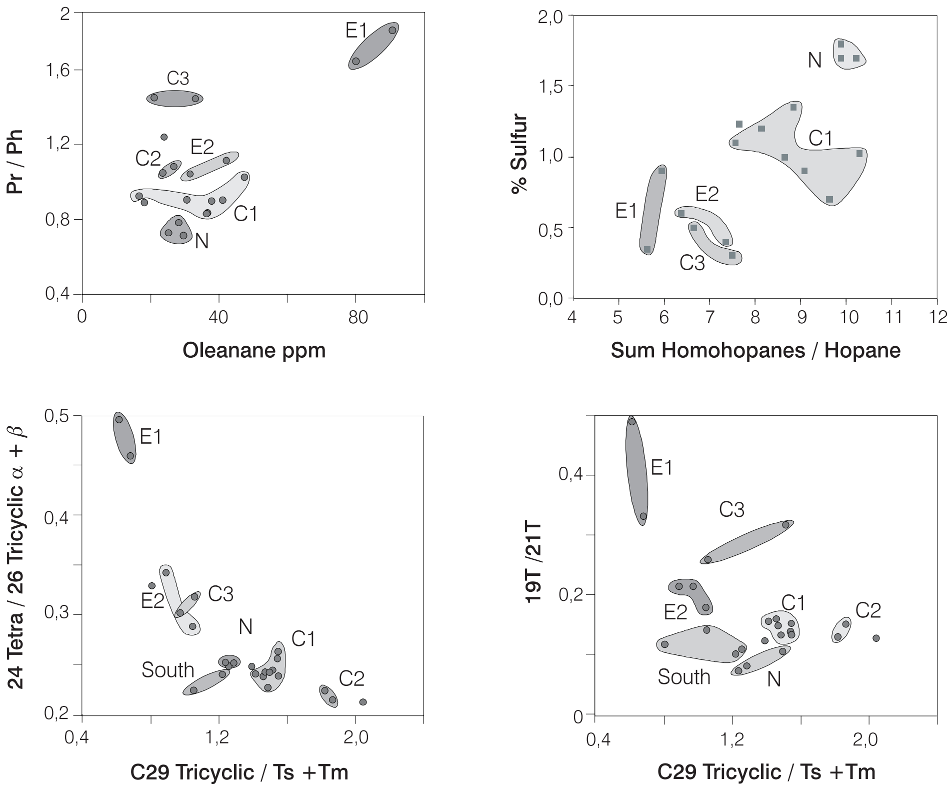


Figure 13. Oil families in the Middle Magdalena Basin, Colombia

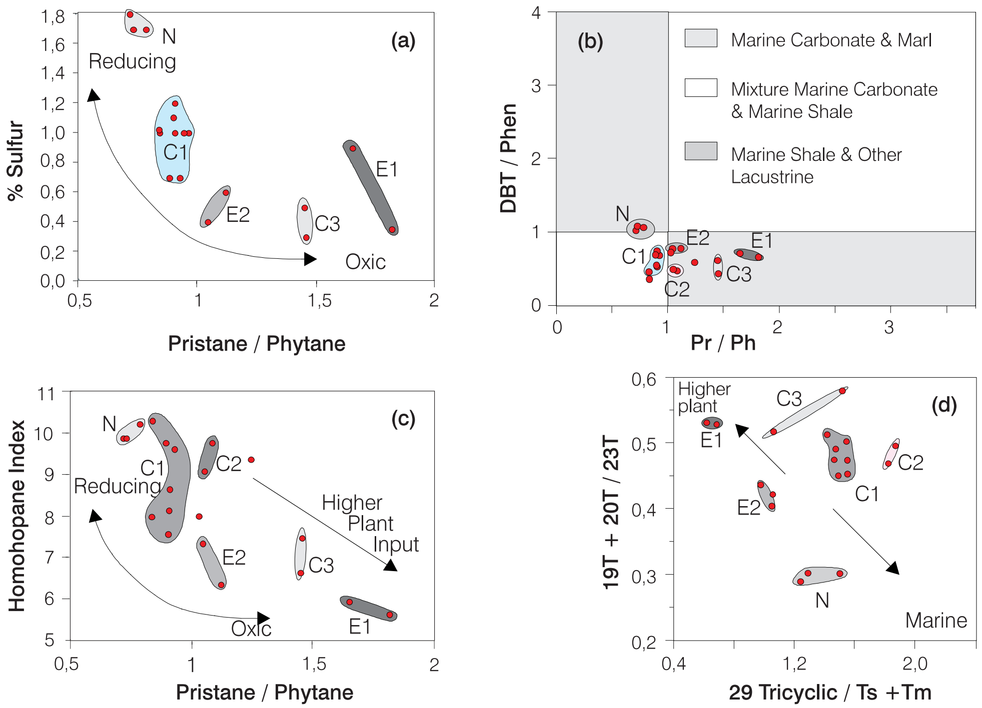


Figure 14. Biomarker parameters that indicate source rock properties

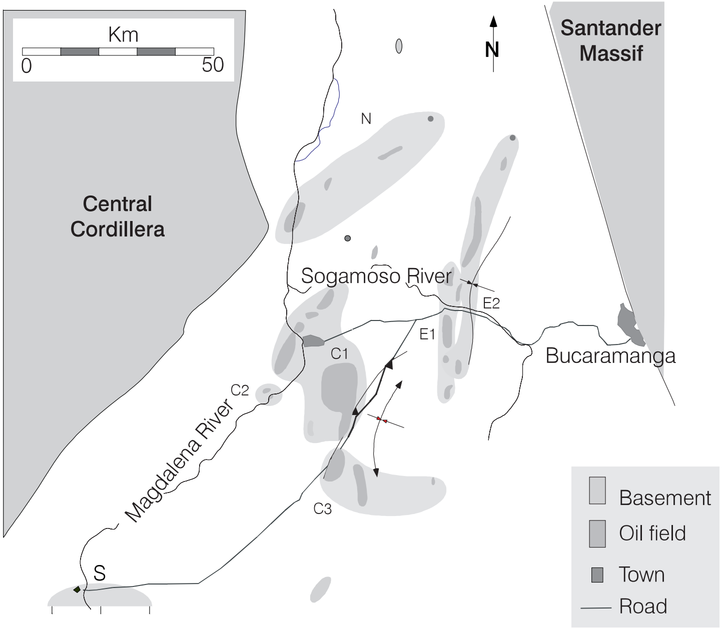


Figure 15. Geographic distribution of families in the Middle Magdalena basin. Letters correspond to geographic location (N = North, C = Central, E =East, S = South).

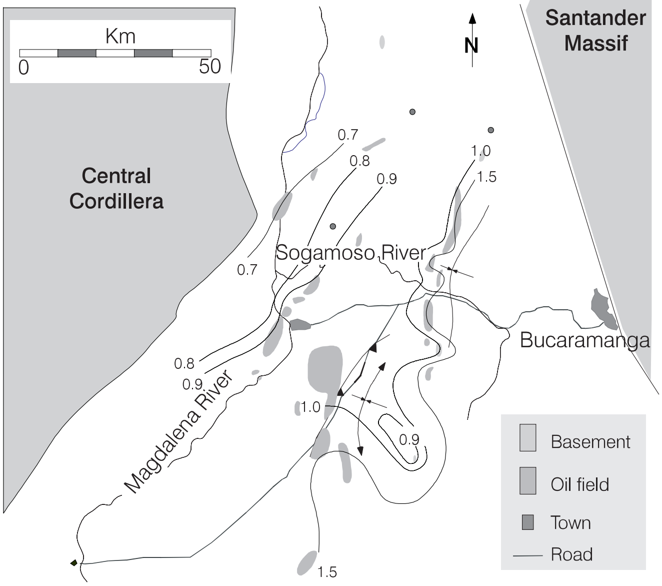


Figure 16. Distribution of pristane / phytane ratio in the analyzed olis. Note regional decrease in the ratio toward the west-northwest indicating more reducing conditions during deposition of the source rocks.

to which the oils have been altered (Table 1)

Middle Magdalena oil compositions suggest a complex migration history. The composition of some oils (e.g., La Cira, Infantas, Conde and Bonanza) is unusual in that gas chromatographic data contains an n-alkane and isoprenoid distribution normally associated with moderately degraded oils, but they also contain a relatively high abundance of gasoline hydrocarbons

Table 1.

SUB-GROUP	Oil Type	Oils	Characteristic features	Biodegradation Ranking*
I	Unaltered	Aguas Blancas-2, Bajo Río-1, Colorado-38 Cristalina-4, Nitria-28, Peñas Blancas-3, Peroles-2, San Luis-4, Tesoro-29	Abundant n-alkanes	Unaltered
II	Partly altered	Casabe-471, Cantagallo-23, Gala-8, Infantas-1559, Llanito-97, Palagua-7, Toqui Toqui Este-1, Yarigues-57	Isoprenoids and n-alkanes present in equal amounts	2
III	Moderately altered	Galan -31, Lisama-13, San Silvestre-39	Isoprenoids predominant	4
IV	Heavyly altered	Bonanza-5, Caipal-10, Conde-7, L Cira-1792, Teca-164	Isoprenoids absent	6

* After Peters and Moldowan (1993)

(Figure 17). There is still some debate on the exact order in which different compounds are removed, but most studies propose more or less the same biodegradation sequence (Peters and Moldowan, 1993). Short chain n-alkanes are removed faster than longer chain n-alkanes which in turn are removed faster than branched and isoprenoid hydrocarbons. The high proportion of short-chain alkanes in oil samples other-wise poor in n-alkanes is unusual, as these hydrocarbons are more rapidly degraded by bacteria than longer-chain alkanes. This particular gas chromatographic pattern may be explained by the addition of a secondary input of migrated gas/conden-sate to the "in situ" biodegraded oils. The proposed sequence of processes is: oil migration into reservoir, biodegradation, and emplacement of migrant gas/condensate in the reservoir. Secondary condensate may have also charged the less biodegraded oils (e.g., Cantagallo-23 and Casabe-471), which could explain the "V" pattern of n-alkane distributions in these oils (Figure 17). The addition of gas condensated may have enhanced the oil API gravity of some Middle Magdalena biodegraded oils. This phenomena was interpreted by Dickey (1992) as late thermal cracking of the biodegraded oils. The low thermal gradients present in the basin and the shallow reservoir depths make this process unlikely. The presence of condensate in La Cira field might be explained by leaking of the underlying oil (with solution gas) reservoirs. The origin of the condensate in the other fields is unknown at present. One possible origin for the secondary condensate is migration from deep source rocks in the late oil window. In any case, the possibility of a deeper reservoir might be a future exploration target.

Thermal Maturity of Oils

Estimates of the relative thermal maturity of the oils are based on thermal maturation-dependent biomarker parameters like C_{29} sterane ratios and concentrations, Ts/Ts + Tm and triaromatic sterane ratios (Figure 18). This information can provide a clue to the quantity and quality of the oil that may have been generated and coupled with quantitative petroleum conversion measurements (e.g., basin modeling), can help evaluate the timing of petroleum migration. The majority of Middle Magdalena oils were generated from early mature (0,6% - 0,8% Ro) oil window except the Colorado-38 oil which was generated in the middle mature (0,8% - 1,0% Ro) oil window.

Vitrinite reflectance data indicate the La Luna Formation ranges from early to middle maturity in the oil window in the basin (Figure 7). Similarities in thermal maturity between source rock and oils, suggest most migration occurred from local kitchens into nearby reservoirs. The close relationships between faulted/fractured zones and oil saturated sandstones/oil seeps observed by the author in the field, supports the idea of migration along fractures/faults and not along the pre-Eocene unconformity as previous workers suggested (Mora *et al*., 1996; Rangel *et al*., 1996). The absence of regional sandstones above or below the unconformity and the wide distribution of shales on top of it

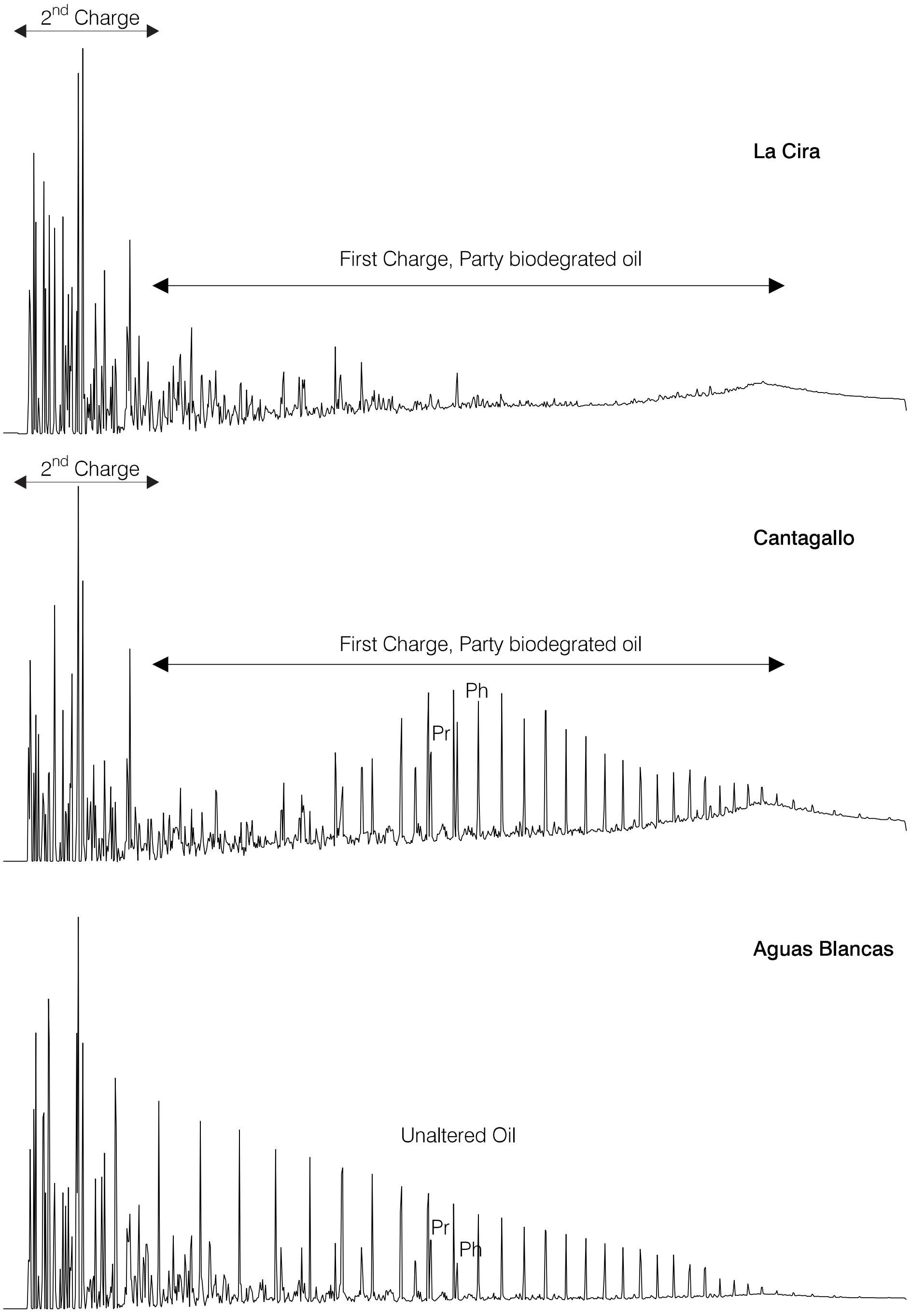


Figure 17. Gas chromatograms (whole oil) of of select Middle Magdalena Basin oils. Pristane (pr) and phytane (Ph) are shown

also denies the possibility of this surface to be the plumbing pathway. Simple lateral updip migration within the Tertiary strata can occur in the southern part of the basin (e.g. Cocorná, Palagua fields).

Slight compositional differences in the southernmost oils (e.g. Bajo Rio, Aguas Blancas, Colorado) of the central part of the basin evidencing slightly higher thermal maturity can be explained by mixing with recently generated oils. It is hypothesized that this second migration could come from the foredeep located southeast of these fields. Additional work need to be done to evaluate this possibility.

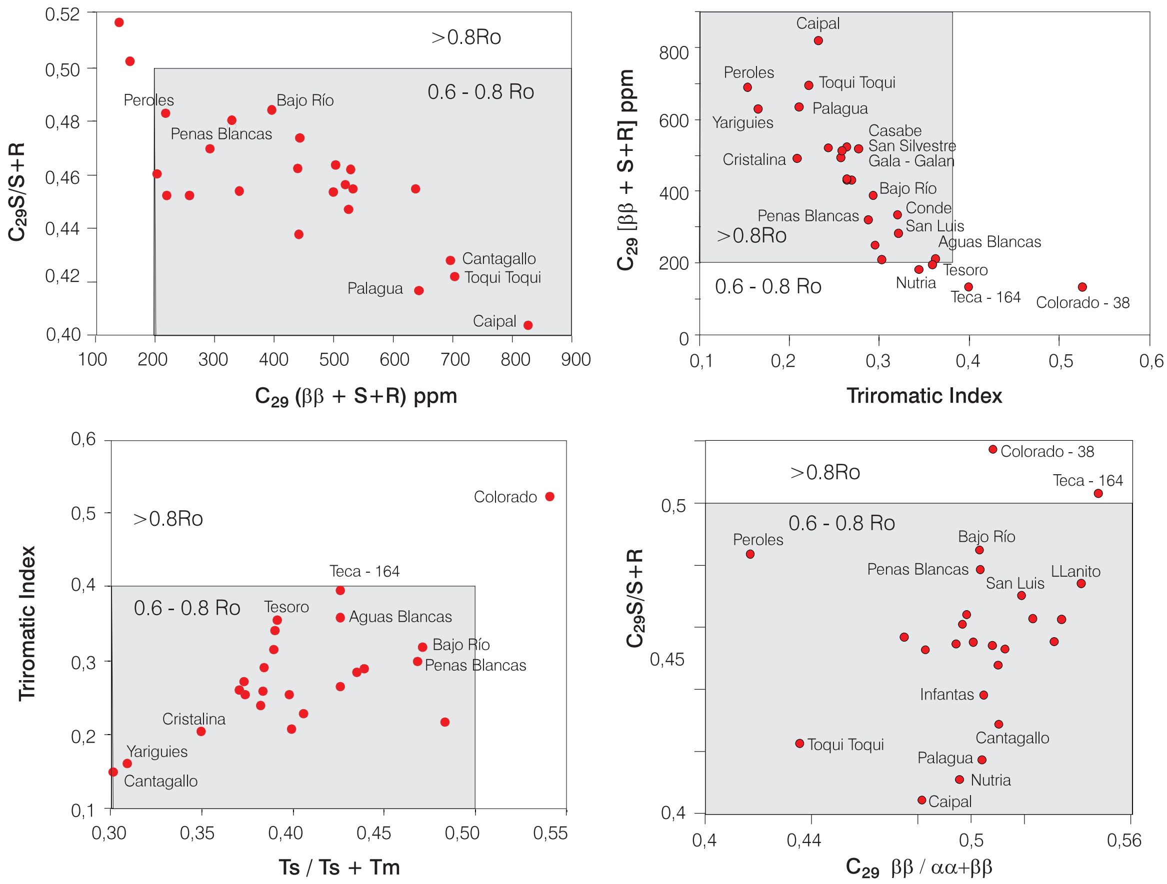


Figure 18. Thermal maturity assessment of the Midddle Magdalena oils.

Timing of Oil Generation and Migration History

Previous understanding is that the La Luna Formation started to generate oil in the most deeply buried areas during the Early-Middle Miocene and continued until a phase of regional uplift during the Pliocene (Govea and Aguilera, 1985). Pratsch and Lawrence (1982) suggested that oil migration came from the deep eastern basin flank.

Mora (1997) proposed 3 main generation and expulsion events. Basal, Lower Cretaceous limestones started oil generation during the Late Paleocene (55 ma.). During a second event in the Late Eocene-Middle Miocene interval these rocks were depleted and Upper Cretaceous sources started contributing hy-drocarbons. A last generation event from Upper Cretaceous source rocks started in the Late Miocene and is still going on in some places.

The author agrees with the number of generation events of Mora (1997) but propose different timing. One dimensional modeling and measured vitrinite reflectances of the Lower Cretaceous organic-rich horizons indicate that they reached the oil window in the Paleocene. Vertical vitrinite reflectance distribution (Figure 7) show strong vitrinite gradients for Lower Cretaceous (Simiti and older) samples in Casabe, Yumeca and Bosques wells. This might indicate a higher heat flow regime during the Cretaceous. Most of the generated oil was lost during the Eocene erosional event. In the La Cira area, thousands of feet of Cretaceous sediments were eroded (Dickey, 1992). Rangel *et al.* (1996) and Mora *et al.* (1996) suggested that some of the oils in the northernmost fields (e.g. Buturama) correlate to Lower Cretaceous Rosablanca and Tablazo Formations, respectively. Early-Late Miocene deposition of the Real Formation strata, pushed Upper Cretaceous source horizons into the oil generation window. During the Middle-Late Miocene several local, deep zones in the basin were generating hydrocarbons from the Upper Cretaceous La Luna members. Uplifting in the central and northern portion of the basin stopped generation. Strong burial in the foredeeps west of the thrust associated with Andean uplift of the Eastern Cordillera pushed the source rocks again into the oil window. Local kitchens west of Opón and in the Nuevo Mundo Syncline (Provincia, Figure 1) areas are today in the oil window. Source rocks of the Umir Formation have experienced subsidence histories that are very similar to those of the La Luna Formation. Thus, its organic-rich horizons could have contributed oil to the fields in the eastern margin. This more recent generation event explains the slight changes in composition and more importantly the presence of gas and condensate mixed with biodegraded oils.

CONCLUSIONS

The range of oil gravities measured in the Middle Magdalena basin is attributed to organic facies variations, levels of biodegradation and late charge of condensate rather than to thermal maturity and migration-related effects based on the following key points:

- The limited range of carbon isotope values and sterane carbon number distribution indicates all the samples were derived from similar organic matter.
- Whole oil gas chromatograms show the Middle Magdalena oils range from unbiodegraded to heavily biodegraded. A number of the oils appear to be mixtures of remigrated condensate and a biodegraded residual oil.
- Biomarker composition suggests that Middle Magdalena oils come from a siliciclastic and a carbonate/marl marine facies of the La Luna Formation. Due to the lack of clastic-derived iron, marine carbonate/calcareous marl-sourced oils are characterized by low API gravity and high sulfur, whereas oils derived from marine shales have high API gravity and lower sulfur content.
- Maturity estimates based on biomarker maturity parameters indicate the oils are at similar level of maturity (early mature) except Colorado-38 which was generated in the middle oil window.

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