OIL GEOCHEMISTRY OF THE PUTUMAYO BASIN

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Biomarker fingerprinting of 20 crude oils from Putumayo Basin, Colombia, shows a vertical segregation of oil families. The Lower Cretaceous reservoirs (Caballos and "U" Villeta sands) contain oils that come from a mixture of marine and terrestrial organic matter, deposited in a marginal, "oxic" marine setting. The Upper Cretaceous ("T" and "N" sands) and Tertiary reservoirs contain oils with marine algal input deposited in a reducing, carbonate-rich environment. Lithology, environmental conditions and organic matter type of source rocks as predicted from oil biomarker differences correspond to organic composition of two Cretaceous source rocks. Vertical heterogeneity in the oils, even those from single wells, suggests the presence of two isolated petroleum systems. Hydrocarbons from Lower Cretaceous source rocks charged Lower Cretaceous reservoirs whereas oils from Upper Cretaceous source rocks charged Upper Cretaceous and Tertiary reservoirs. Oil migration from mature source rocks into multiple reservoirs has been stratigraphically updip along the "regional" sandstone units and vertical migration through faults has been limited. Biomarker maturity parameters indicate that all oils were generated from early thermal maturity oil window.

La caracterización detallada de la composición de crudos en la cuenca del Putumayo, Colombia, evidencia una fuerte segregación vertical en las familias de aceites. Los crudos en yacimientos del Cretáceo Inferior (Fm. Caballos y arena "U" de la Fm. Villeta) provienen de una materia orgánica mixta (terrestre y marina) depositada en el ambiente "óxico" de plataforma somera. Los hidrocarburos en yacimientos del Cretáceo Superior (arenas "T" y "N" de la Fm. Villeta) y del Terciario Inferior provienen de materia orgánica algal depositada en un ambiente marino reductor, rico en carbonatos. La litología, condiciones ambientales y tipo de materia orgánicas de las rocas fuente del Cretáceo. Las marcadas diferencias en composición entre crudos en diversos yacimientos, aún en un mismo pozo, evidencian la presencia de al menos dos sistemas petrolíferos independientes. Las rocas fuertes basales cargaron los yacimientos del Cretáceo Superior y del Terciario Inferior y del Terciario Inferior. La migración de crudos desde las áreas con roca fuerte maduras ha sido esencialmente a lo largo de las unidades arenosas adyacentes y la migración vertical ha sido muy limitada. Los parámetros indicadores de madurez de los crudos indican que éstos fueron generados en la zona de madurez temprana de la ventana de generación.

Keywords : Putumayo, oil chemistry, biomarker.



Figure 1. Map showing the sedimentary basins of Colombia (light gray) the location of the study area (detail) with sample location

INTRODUCTION

Commercial oil production in the Putumayo basin started in the mid 1960s, yet little have been published about the origin of oil. Lithology, environmental conditions and organic matter type of source rocks were interpreted from bulk properties, trace elements, carbon isotopic (saturated and aromatic fractions) and biomarker composition of 20 reservoir oil samples.

Understanding the origin of crude families improves prediction of oil type in undrilled prospects. Understanding oil generation, migration and accumulation processes contributes to rank exploratory areas and improve the success ratio of exploration drilling.

The objectives of this study are: (1) to identify the number of probable sources of oils (2) evaluate type of organic matter input, lithology and environment of source rocks, (3) assess the thermal maturity of oils and (4) to describe processes that may have affected oils after they were expelled from their source rock(s).

General Geology.

The Putumayo basin of southwest Colombia (Figure 1) is one of a series of sub-Andean basins east of the Andean Mountain chain from Venezuela to Argentina. The basin is a structural monocline dipping toward the west, and shallows toward the Guyana shield to the east. Its sedimentary section is over 3.000 m. thick and ranges in age from Jurassic to Holocene (Cáceres and Teatin, 1985). Its extension in Ecuador is called Oriente basin.

The Cretaceous strata are divided into two formations. The basal Aptian Caballos Formation unconformably overlies the Jurassic or older basement and consists of continental (braided to deltaic) strata. The overlying Villeta Formation ranges in age from Albian to Campanian and is composed of shales, marls, limestones and sandstones deposited in shallow marine to outer shelf. "U", "T" and "N" sandstone units within the Villeta Formation and Caballos sandstone are the main oil reservoirs (Figure 2). Some production is obtained from younger Eocene sandstone reservoirs.

Source rock stratigraphy and paleoenvironments.

Prolific source rocks are recognized in Cretaceous strata throughout northern South America. In Putumayo and Oriente basins, the Villeta (or Napo) Formation is the main source rock (Dashwood and Abbotts, 1990; Mello *et al.*, 1995; Cáceres and Teatin, 1985). Coeval organic-rich layers are also found in

Age		Formation		Lithology	Description	Thickness	
Pleisto- pilocene		Caiman Guamues			Alluvial fans Sadstones - Conglomerates	250′	
ТЕRТІАRУ		Ospina			Claystones and sandtones Shallow lake		
	Miocene	Jrito Group	Orita - Belen		Shales Interbedded muddy sandstones	5.400´ 450´	
	Oligocene	0.	Orteguaza		Green laminar shales - fissile interbedded muddy sanstone Continental environment		
	Eocene	Pepino			Mainly mudstones Conglomerates at the base and top Continental environment	350′	
	Paleoc.	Rumiyaco			Gray and red mudstones interbedded with siltstones and fine sandstones. Transtional (Marine to continental)	1.800′	
CRETACEOUS	Albian-Campanian	Villeta			"N" Dark shales and silty limestone "T" Fine sandstones "U" Marine with continental cycles	1.060 ′	
	Apitan -Albian	Caballos			Dark fine to medium grain sanstones black shales Transtional environment	220'	$[\circ']$
		Motema				?	
			\sim			?	
Basement Igneous and metamorphic rocks							
	~	~~~	. Unconf	ormity	Limestone Conglom	ierate ock	

Figure 2. Generalized Stratigraphic Column - Putumayo Basin

Cretaceous strata of other sub-Andean basins of South America, such as in La Luna (Venezuela and Colombia), Gachetá (Colombia) and Chonta (Perú) Formations (Zumberge, 1984; Rivadeneira, 1986; Talukdar *et al.* 1986 and Ramón and Bachu, 1994).

The source rock characteristics of Cretaceous strata in Putumayo-Oriente basin vary geographically and stratigraphically (Dashwood and Abbotts, 1990 and Cáceres and Teatin, 1985). The Cretaceous Villeta Formation comprises a series of shales, calcareous shales, and limestones. Locally these fine-grained strata are interrupted by "U", "T" and "N" progradational shoreface and transitional sandstones. Overall, this section deepens up from the basal Albian sandstone into Turonian marls and limestones. This trend corresponds to a sea-level rise recorded in the latest Cenomanian-earliest Turonian and to the worldwide. Oceanic Anoxic Event 2 (OAE-2) reported by Jenkyns (1980).

Richer organic facies were deposited westward in the structurally deeper part of the basin and organic content decreases toward the Guyana Shield (Dashwood and Abbotts, 1990 and Cáceres and Teatin, 1985). RockEval pyrolysis data show average potentialyield values around 10 kg HC/t of rock in Oriente basin and hydrogen indices of approximately 600 mg HC/g of organic carbon in Putumayo basin (Mello *et al.*, 1995 and Tegelaar *et al.*, 1995).

Mello *et al.* (1995), Dashwood and Abbotts (1990), Rivadeneira (1986) and Cáceres and Teatin (1985) reported low thermal maturity for source rocks and suggested that reservoired oils in Putumayo and Oriente basins came from an exhumed source in the presentday position of the Eastern Cordillera. Tegelaar *et al.* (1995) reported that expulsion started 8 Ma and has stopped in the zones of Andean uplift.

In a detailed biostratigraphic and geochemical study of source rocks in the Oriente basin, Mello *et al.* (1995) reported different organic facies at two stratigraphic positions: Upper Albian and Cenomanian-Turonian.

The first end-member, recorded in Upper Albian strata of the Napo Formation have organic carbon content ranging from 0,4 to 4 % wt., show medium hydrocarbon potential (up to 10 kg HC/t of rock), mainly type II/III kerogen (HI up to 350 mg HC/g of organic carbon). Additionally petrographic analysis shows

predominantly liptinitic and humic macerals and lesser amorphous organic debris (Mello et al., 1995). These dark shales show planktonic microfossil composed of rare foraminiferids (Hedbergella trocoidea, Heterohelix globulosa, and H. moremani), sparse and low-diversity assemblages of dinoflagellates and calcareous nannofossils. This impoverished biota suggests shallower and nearshore depositional environments in comparison to those present during the Cenomanian-Turonian. Benthonic microfauna is also poor, although slightly more diversified than that recovered from Cenomanian-Turonian strata (see above), and represented by rare calcareous (Gavelinella berthelini-reussi plexus) and agglutinated foraminiferids and ostracods indicating dysaerobic bottom water conditions (Mello et al., 1995). The bitumen extracted from these strata show predominance of high-molecular weight n-alkanes $(C_{25}-C_{29})$ with odd/ even preference, pristane/phytane ratio greater than one, high dia/regular sterane ratio, lesser C27 sterane with respect to their C₂₈ and C₂₉ counterparts, and presence of tetracyclic terpanes (Mello et al., 1995).

The second organic facies member, in Cenomanian-Turonian rocks show medium to very high organic carbon content (up to 13 wt.%) and have medium to excellent hydrocarbon source potential (up to 78 kg HC/t of rock), of mainly type II kerogen (hydrogen indices up to 740 mg HC/g of organic carbon). Petrographic analysis show dominance of amorphous, sapropelic kerogen, with minor contribution of liptinitic and woody materials (Mello et al., 1995). The planktonic microfossil assemblage of these rocks is composed of abundant foraminiferids typical of shallow shelves (Heterohelix globulosa, H. moremani, and H. reussi) and rare species typical of deeper oceans (Praeglobotruncana cf. P. praehelvetica). Lowdiversity assemblages of dinoflagellates and calcareous nannofossils, in addition to these foram assemblages indicate well-oxygenated epipelagic surface waters (e.g., Koutsoukos et al. 1991). On the other hand, benthonic microfauna is highly impoverished, represented by rare agglutinated foraminiferids (Ammomarginulina cf. A. colombianus) and ostracods indicating dysaerobic-to-anaerobic bottom water conditions (Koutsoukos et al. 1991). Occasionally, there are stratigraphic intervals with no benthonic microfauna, which represent times of anoxia.



Figure 3. Oil bulk properties and oil families in the Putumayo Basin

Geochemically, these second source member is characterized by predominance of low-molecular weight n-alkanes, pristane/phytane ratio lower than one, low proportion of diasteranes, low hopane/sterane ratio (<4), high proportion of low-weight steranes, dominance of C₂₇ sterane over the C₂₈ and C₂₉ counterparts, Ts/Tm less than 1, abundance of tricyclic terpanes components ranging from C₁₉ to C₃₉, some gammacerane and β -carotene, and 35/34 hopane greater than 1 (Mello *et al.*, 1995).

RESULTS AND DISCUSION

Oil Geochemistry and Oil/Source Correlation.

Based on bulk oil properties, oil samples analyzed in this study are classified in three genetic oil families, trace elements, isotopic and biomarker composition. Slight biomarker composition differences subdivide some families into subfamilies, resulting in five oil subfamilies (Figures 3, 4, 5):



Figure 4. Source rock lithology as predicted from oil biomarkers.

Family	Sub-family	Geographic/Stratigraphic position
А		North / Upper Cretaceous
В	$\rm B1$ and $\rm B2$	South / Upper Cretaceous
С	C1 and C2.	North / Lower Cretaceous

Additionally, families A and C are located toward the north and include oil fields such as Toroyaco, Linda, Mary and Miraflor (Figure 1). The former includes oils from "N" sandstone of the Villeta and the latter consists of oils from Caballos, and "T" and "U" sandstones. The southern family B includes oils from Orito, and Nancy fields (Figure 1). Oils from this family come from "U", "T", "N" Cretaceous and from Eocene reservoirs.

Family A is characterized by a relatively high sulfur content (1,5%), lower API (27°-28°), predominance of low-molecular-weight alkanes, relatively high concentration of vanadium and nickel (ppm), and high



Figure 5. Organic matter type and depositional environment of the source rock as interopreted from oil biomarkers.

C₂₇/C₂₈+C₂₉ sterane ratio (Figures 3, 5, 6). These composition indicate an algal material deposited in a reducing, marly/carbonate environment (Lewan, 1984; Moldowan *et al.*, 1985 and Volkman, 1986). Stable carbon isotopic compositions of the aliphatic and aromatic fractions are plotted in Figure 3. The isotopic composition suggests that Family A oils were derived from marine organic matter (Sofer, 1984). Low Ts/Tm, C₂₇ rearranged/regular steranes ratios, and

 C_{29}/C_{30} hopane ratios indicate that the source rock for these oils was deposited in a marly/carbonate-rich environment (Figure 4). Family A also exhibits low pristane/phytane and high vanadium/nickel, 35/34 hopane and gammacerane/hopane ratios which indicate that its source rock was deposited under reducing conditions (Figure 3).

In general, family B oils have intermediate



Figura 6. Comparison of the GC and terpane distribution between the two end member families.

biomarker composition between those of families A and C (Figure 4). Family B oils have moderate API gravity (27°-31°) and exhibit wide sulfur content (0,5%-1,2%, Figure 3). Similar to family A, they have high concentration of vanadium and nickel, and they plot in the "marine" side (Sofer, 1984) of the isotopic composition plot (Figure 3). Relative abundance of C₂₇steranes over their C₂₈ and C₂₉ counterparts (Figure 3), predominance of low molecular-weight n-alkanes, and very low 19 - 20 tricyclic terpanes as compared to C₂₃-tricyclic terpane (Figure 5) indicate a dominant algal input to the source rock (Moldowan *et al.*, 1985 and Volkman, 1986). Low 27 rearranged/regular steranes and pristane/phytane ratios, and high C₃₅/C₃₄ hopane ratios indicate its source rock was deposited in a reducing, carbonate-rich environment (Figure 4).

Family C has a different biomarker composition from the other families. This family has a lower sulfur content (0,3% - 0,7%), and a higher API gravity $(29^{\circ} - 34^{\circ})$. Isotopic composition of saturates and aromatic compounds and lower proportion of C₂₇-steranes (Figure 3) indicate more terrestrial, oxic, higher plant influence (Sofer, 1984; Moldowan *et al.*, 1985 and Volkman, 1986). Relative abundance of rearranged steranes with respect to their regular counterparts, higher Ts/Tm and saturate/aromatic ratios, and low C₃₅ hopane abundance (Figure 4) suggest a siliciclastic source rock composition (McKirdy *et al.*, 1983; Riolo *et al.*, 1986 and Hughes, 1984). Finally, lower tricyclic terpanes concentration, high pristane/phytane and 19+20/23 tricyclic terpane ratios and relative abundance of high molecular weight n-alkanes (Figures 5, 6) indicate a significant contribution of higher plants in a rather oxic environment (Tissot and Welte, 1984 and Peters and Moldowan, 1993).

Migration History

Lithology, environmental conditions and organic matter type of the source rocks as predicted from oil biomarker differences correspond to organic composition differences between the two Cretaceous source rocks. In general, oils in Lower Cretaceous reservoirs (Caballos and "U" sandstones) belong to family C. Their biomarker composition suggest oils generated from a mixture of marine and terrestrial organic matter deposited in a suboxic marine, probably deltaic, environment (Figures 5, 6). These features closely match characteristics of the Albian source rock described by Mello et al. (1995). On the other side, family-A and -B oils from Upper Cretaceous reservoirs show biomarker composition typical of oils generated from marine algal organic matter deposited in a reducing, marly/carbonate environment (Figures 5, 6). This interpretation corresponds to the composition described by Mello et al. (1995) for Cenomanian-Turonian source rocks.

Vertical heterogeneity in the oils, even those from single wells, suggests the presence of two isolated petroleum systems. Hydrocarbons from Lower Cretaceous source rocks charged lower reservoirs whereas hydrocarbons from Upper Cretaceous source rocks charged Upper Cretaceous and Tertiary reservoirs (Figure 6). Oil migration from mature source rocks into multiple reservoirs has been stratigraphically updip along the "regional" sandstone units and vertical migration through faults has been limited. Expelled oils from the Albian source did not migrate toward Upper Cretaceous and Tertiary reservoirs, which indicates that migration is laterally updip along "regional" sandstone units and vertical migration through faults is restricted.

CONCLUSIONS

• The parallel trend between the lower and upper source rocks and reservoired oils can be used to

establish a genetic relationship among oils and source rocks. Aptian/Albian marginal marine source rock charged lower Caballos and "U" sandstone of the Villeta Formation. Source rocks of this petroleum system have a stronger terrestrial input deposited in a rather oxic environment, probably with deltaic influence. The Cenomanian-Turonian source charged "T" and "N" Upper Cretaceous and Eocene reservoirs. The more reducing, algal marine character of the source matches oil biomarker composition.

• The fact that most oils from different stratigraphic positions, even those from the same wells, have a strong difference in biomarker composition indicates two separate petroleum systems in this basin. Petroleum systems in the Putumayo basin can be classified as laterally drained but vertically isolated.

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