Revista Latino Americana de Geoquimica Organica, Vol. 5, pp. 5-24, 1999

PETROLEUM GEOCHEMISTRY OF OILS IN THE FOOTHILLS OF THE LLANOS BASIN, COLOMBIA

Rangel, A.*, Brooks,. P.W. ** & Giraldo, B.*.

*ICP, Ecopetrol, Colombia
** Cenpes, Petrobrás, Brazil

ABSTRACT – Twenty three oils from the Llanos Basin (Colombia), most of them located in the central area, were analyzed for organic geochemical parameters to improve the understanding of the oil phases involved in the accumulated oils of the area, to quantify the mixing of the main generation pulses, and to make inferences concerning the migration processes involved. The analytical program included determination of the S, Ni and V content of the whole oils, gas chromatographic analysis of the saturate fraction, and d^{13}C analysis of the saturate and aromatic fractions. Saturate, aromatic and NSO fractions were analyzed by GC-MS for sterane and triterpane distributions, phenanthrene and dibenzothiophene distributions and alkylated carbazoles respectively. In general, the results obtained for the oils show major variations of several parameters associated with source rock paleoenvironment, type of organic matter, oil preservation and source rock lithology. The pristane/phytane ratios range from a 1.04 to 5.11. The oleanane/hopane ratios range from ca. 0.1 to greater than 0.5. The demethylated hopanes range from low concentration to very high concentration. The ratios Ts/Tm, C_{35}/C_{34} hopanes, C_{30} hopane/C_{27} sterane, C_{24} tetracyclic terpane/C_{26} tricyclic terpane also vary from extremely low values to relatively high values. The geochemical characteristics of the oils from the central area of the Llanos Basin indicate that there have been three different phases of oil generation from different source rocks. The oil families identified in previous work represent mixed pulses of oils in which the extent of mixing depends on the location of the wells within the basin. The first phase of oil was originated from Upper Cretaceous carbonate shale facies. This oil, is widely distributed in the central platform area and exhibits a relatively low oleanane/hopane ratio (less than 0.1), low C_{24} tetracyclic/C_{26} tricyclic terpane ratio, pristane/phytane ratios of less than 2, and high C_{23} tricyclic/hopane. The second oil phase identificated in the central foothills, is distinguished by high oleanane/hopane ratios (from 0.58 to 0.65) and was probably derived from a shale interval of the Mirador Formation (Tertiary). The third phase, with a high hopane/sterane ratio (higher than 10), relatively high oleanane/hopane ratios (from 0.22 to 0.5), relatively high C_{24} tetracyclic/C_{26} tricyclic ratios and high diasteranes/steranes, was probably derived from a different Tertiary source rock or from a more siliciclastic Upper Cretaceous source rock. Most of this pulse is present in reservoirs in the foothills region of the basin with only some reaching the central platform. The contribution of the main Tertiary pulse (the oleanane rich oil), to oils present in the foothills wells is estimated to be as high as 52%. The carbazoles, particularly the shielded and partial shielded isomers were, as expected, relatively enriched in those oils thought to have migrated further from the postulated source rocks.

RESUMEN – Veintitrés crudos de la cuencas de los Llanos Orientales, Colombia fueron caracterizados geoquímicamente con el fin de mejorar nuestro conocimiento acerca de las fases de crudo presentes, cuantificar el grado de mezcla de los principales pulsos de generación y hacer algunas inferencias relacionadas con los procesos de migración. El programa analítico incluyó la determinación del contenido de S, Ni and V en el crudo total, cromatografia de gases de la fracción de saturados, análisis ^{13}C de la fracción de saturados y aromáticos, análisis GCMS en la fracción de Saturados Aromáticos y NSO. Los resultados obtenidos muestran variaciones amplias en muchos parámetros asociados a paleoambiente, tipo de materia orgánica y preservación del crudo. La relación pristano/fitano varía entre 1.04 y 5.11. La relación oleanano/hopano varía entre 0.1 a mayor que 0.5. Los hopanos demetilados varían entre un rango de concentración relativamente bajo a muy alto. Las relaciones Ts/Tm, C_{35}/C_{34} hopanos, C_{30} hopanos/C_{27} esteranos, C_{24} tetracíclicos /C_{26} tricíclicos también varían desde valores extremadamente bajos a valores relativamente altos. Las características de los crudos del área central de la Cuenca Llanos indican al menos tres diferentes fases de generación de crudo desde tres diferentes rocas fuentes. Las familias de crudo identificadas en los trabajos previos representan mezclas de diferentes pulsos de crudos. La extensión de mezcla de dichos pulsos depende de la localización de los pozos en la cuenca. La primera fase se considera originada de una facies de shale calcáreo del Cretáceo Superior. Este crudo está ampliamente distribuido en la plataforma central y exhibe una relación oleanano/hopano relativamente baja (menor que 0.1), relación C_{24} tetracíclicos/C_{26} tricíclicos baja, pristano/fitano menor que 2, y alto C_{23} tricíclico/shopano. La segunda fase de crudos identificada en el área central se caracteriza por una alta relación oleanano/hopano (0.58 a 0.65). Esta fase fue derivada posiblemente del intervalo de shales de la Formación Mirador (Terciario). La terceras fase, con una relación hopano/esteranos alta (mayor que 10), relación oleanano/hopano relativamente alta (0.22 a 0.5), relación relativamente alta de C_{24} tetracíclicos/C_{26} tricíclicos y altos diasterano/esteranos, fue posiblemente derivada de otra roca fuente terciaria o de una roca siliciclástica de Cretáceo Superior. La mayor parte de este pulso está presente en reservarios del piedemonte con solo una pequeña parte alcanzando reservorios de la plataforma. La contribución del mayor pulso terciario (el crudo rico en oleanano), a los crudos presentes en el piedemonte se estima ilegó a ser máximo el 52%. Los carbazoles en particular los isómeros *shielded* y los parcialmente *shielded* se encuentran relativamente enriquecidos en aquellos crudos que se estima han migrado más legos de las rocas madres propuestas.

KEY WORDS - Llanos Basin, gas chromatography, paleoenvironments, type of organic matter, phases of oil generation.

INTRODUCTION

The Llanos Basin, is located to the east of the Eastern Cordillera in Colombia (Figure 1). The main emphasis of this study, is the study of oils in the central foothills of this basin.

Oil exploration in the Llanos Basin was very limited and sporadic before the discovery of the giant Caño Limón Field, with an estimated 1200 MBOP (millions of barrels of oil in place). Subsequently, the area was covered by very active exploration resulting in the discovery of the Cusiana Field (1600 MBOP). Thus, the Llanos Basin became the most prolific petroleum province in Colombia.

Despite the size of the reserves and the petroleum potential of this area, there have been only a few organic geochemical studies to date and many key issues remain unanswered. These include the quantification of the mixing of the recognized oil generation pulses, the characterization of the different organic facies in the Cretaceous and Tertiary sequences, the characterization of the post generation processes and migration.

Palmer and Russel (1988), identified five genetic families of oils in the Llanos Basin and made some speculative oil - source rock correlations, indicating that the Cretaceous Une Formation has a positive correlation to one oil family located in

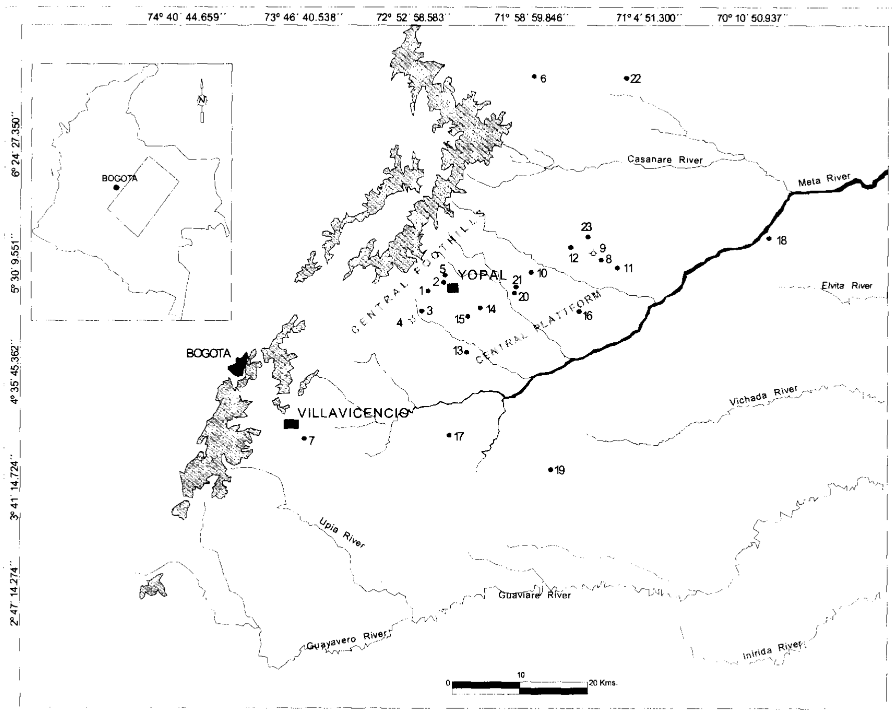

Figure 1. Map showing the study area with sample location.

the central Llanos Basin. Rangel et al. (1991) confirmed the existence of five oil families and established their geographic distribution within the basin and a genetic correlation between two of the families and source rocks within Upper Cretaceous sedimentary rocks. The five oil families in this work are the following: Family A, located in the northern Llanos Basin, derived from clastic-poor source rock deposited in a marine, reducing environment. Family B oils are located in the central platform, and are derived from source rocks deposited in a nonmarine, reducing/oxidizing environment. Family C oils are also located in the central platform have features indicatives of an origin from a marine-terrestrially-influenced, slightly oxidized environment. The Family D oils are located in central and southern Llanos Basin and are broadly similar to the oils of Family C but are affected by varying degrees of biodegradation. Family E oils are located in the southern Llanos Basin originated from marine source rocks slightly influenced by terrestrial organic matter deposited in reducing/oxidizing environment. Their geochemical characteristics have also been affected by biodegradation.

Tegelaar et al. (1995), conducted an integrated geochemical and basin modeling approach to define the petroleum systems in the foothills of the southern Llanos and Putumayo basins and to provide some answers to the timing of expulsion and maturity of the oil kitchen relative to the Andean orogeny. According to the authors, the oils of Cusiana and Cupiagua area are the result of two phases of hydrocarbon generation. The first phase derived from the Cretaceous source rock and the second phase comes from an active kitchen located in the deep foothills involving Tertiary source rocks. Miller (1994), studied the timing of oil migration and proposed that the first migration episodes occurred during the Eocene time from the Late Cretaceous sediments in the Cretaceous depocenter, and a later migration occurred during the Miocene Andean orogeny during the subsequent thrust-fold deformation. Regarding geochemical processes, Droz and Pigott (1995) studied the Cusiana field oils, suggesting a marine clastic source rock for these oils. These reservoirs contains solid bitumen which in their opinion could be related to multiple origins from gas deasphalting or thermal cracking to low grade pyrobitumen.

The objectives of this paper are 1. To improve the understanding of oil phases (pulses of oils generated from different source rocks) involved in the accumulated oils of the area. 2. To quantify the mixing of the main generation pulses. 3 To make some inferences concerning the migration processes. This study was conducted through a focused organic geochemical study of 23 oils, from four major geographic locations within the basin, i.e. foothills, central platform, northern platform and southern platform. These oils are representative of the five oil families identified in previous studies

GEOLOGICAL SETTING

The Llanos Basin is a northeast trending structural depression that developed over the Guyana Shield. It is located to the east of the Eastern Cordillera. Three tectonic areas are recognized in the basin: the folded belt or foothills (the western area), the foreland or subandean block and the platform (the central and eastern area)

The sedimentary rocks, according to Cooper et al. (1995), were deposited in a basin that evolved from a back-arc basin in the Late Cretaceous to a foreland basin in the Early Tertiary. Rocks older than Late Cretaceous includes a succession of Paleozoic metamorphic and sedimentary rocks. Upper Cretaceous strata generally overlie directly on Paleozoic basement. Figure 2 shows the stratigraphic chart of the Llanos Basin.

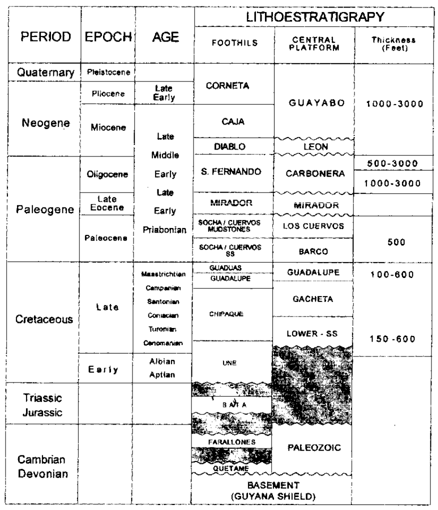

Figure 2. Generalized stratigraphic section of the study area.

The back-arc megasequence began in the Cenomanian time with the deposition of a series of shallow marine and shoreline sandstones denominated as Une Formation. During the Turonian-Early Coniacian global sea level rise (Haq et al., 1987) with anoxic upwelling conditions resulted in deposition of marine mudstones. These sediments formed the Gachetá Formation, the inferred source rock for most of the hydrocarbon of the Llanos Basin, Miller (1979). Their time-equivalent lithostratigraphic units, in the rest of Colombian basins i.e. La Luna Formation in the Middle Magdalena Basin and Villeta Formation in the Upper Magdalena Basin are recognized oil source rocks. A relative sea level falls during the Coniacian to Early Santonian terminated the anoxic marine sedimentation, allowing the deposition of the Guadalupe Formation in a shallow marine environment. This formation constitutes the oldest reservoir unit of the basin. The top of this sequence is a shale unit, the Maastrichtian-Paleocene Guaduas Formation.

In the foreland megasequence, Paleocene sediments were deposited in fluvial, coastal plain and deltaic environments, preserved as the Barco and Los Cuervos Formations toward the west of the Llanos Basin. The Barco Formation, which forms the basal transgressive part of the sequence (Notestein et al., 1994), consists mainly of sandstones and forms the middle reservoir unit of the basin whereas the Los Cuervos Formation is mainly mudstones. During the Early to Middle Eocene, erosion caused significant regional truncation of Paleocene strata.

The third major tectonostratigraphic unit began in the Late Eocene with a retrogradational basal sandstone, the Mirador Formation. This formation in the central foothills area consists primarily of coarse sandstone with interbedded fine-grained sandstone, siltstone and mudstones deposited in estuarine and coastal plain settings (Reyes, 1996; Fajardo, 1995). The largest and most important reservoirs of the central foothills occur in this unit. Also some organic rich layers in this unit may have contributed to the oil generation in the Llanos Basin. The Mirador Formation is overlain by the Carbonera Formation composed of four retrogradational shale units interbedded with coastal plain and deltaic sandstones together with thin coals. The shales are often a good quality source rock unit and may have contributed to some of the accumulation in the Llanos Basin. This formation extended from Early Oligocene to the end of Early Miocene.

The Andean orogeny took place during the late Miocene, which segmented the basin, with the eastern area becoming the Llanos Basin. The final depositional episode was the deposition of coarse continental clastics, The Miocene Leon Formation and the Miocene-Holocene Guayabo Formation, a thick molasse deposited following the withdrawal of the sea from the Llanos Basin.

MATERIALS AND METHODS

Oil samples were examined for sulfur, Ni and V content and API gravity. The saturate and aromatic fractions were examined for carbon isotope composition, the saturate, aromatic and NSO fractions were examined for distribution of biomarkers by GC-MS and the saturates were also analyzed by GC-MS-MS.

Total alkane fractions or branched/cyclic sub-fractions were analyzed in the selected ion recording mode on either a H.P. 5890 GC-MS system or a Micromass Ultima high resolution GC-MS system. The GC column in both analyses was a 30 m HP-5 temperature programmed from 60-320 at 4 deg C/minute and helium carrier gas at 1.5 ml/min. Low resolution selected ion recording was performed on the 5890 MSD monitoring ions m/z 177,191,217,218,259 for the saturate fractions, ions m/z 178,192, 206, 184,198 (phenanthrenes and dibenzothiophenes) and m/z 231 (triaromatic steranes) for the aromatic fractions and ions 195, 209 for the NSO fractions (alkylated carbozoles). Saturate fractions were also analyzed by MRM using the Micromass Ultima and monitoring the transitions 412->369 (bicadinanes) and the C26-C30 sterane molecular ions->217 and the C27-C35 triterpane molecular ions ->191.

GEOCHEMICAL RESULTS

Table 1 shows the data obtained for the bulk analysis and Table 2 shows the molecular level analyses. For ease of interpretation, the oils in the Tables have been grouped into four major categories based on geographic location within the basin, i.e. central foothills, central platform, northern platform and southern platform (see Figure 1 for sample location map).

The oils of the Llanos Basin show a wide range of variation in their bulk parameters as well as in the biomarker parameters. The API varies between 10° (oil 17) and 41° (oil 3) whereas the sulfur content ranges from 0.10% (oils 1 and 6) to 1.35% (oil 19). The pristane/phytane ratios, range from 1.04 (oil 23) to 5.11 (oil 20). All of the oils contain oleanane (oleanane/hopane ratio varies from 0.09 to 0.62), and in some of them bicadinanes were detected. Many of these oils contain minor amounts of bisnorhopane. Most of the oils contain abundant demethylated hopanes (25-norhopane/hopane varies between 0.04 and 2.47). The proportions of: diasteranes to regular steranes, steranes to hopanes, C_{35} hopane/C_{34} hopane, C_{24} tetracyclic/C_{26} tricyclic show wide variations. The isotopic composition of the saturate and aromatic hydrocarbons varies by approximately 4 $^{o}/_{oo}$. The

Table 1. Bulk parameters of the crude oils from the Llanos, Basin, Colombia

Geographic Location	CENTRAL FOOTHILLS					NORTHERN FOOTHILLS	SOUHTERN AREA	CENTRAL PLATFORM			
Well	**1** Guadalupe to Mirador	**2** Barco	**3** Guadalupe to Mirador	**4** Guadalupe to Mirador	**5** Barco to Mirador	**6** Mirador	**7** ---	**8** ---	**9** Carbonera	**10** Guadalupe to Mirador	**11** Carbonera
Gravity	39,6	n.a.	41,6	36,7	n.a.	37	24,1	34,1	33,4	17,8	33
% Sulphur	0,10	n.a.	0,23	0,30	n.a.	0,1	1,18	0,17	0,15	0,18	0,23
Pr/Ph	3,64	n.a.	3,33	3,75	n.a.	2,4	3,89	3,05	2,92	2,53	1,95
V/Ni	1,00	n.a.	1,60	2,00	n.a.	2	7,00	---	---	---	---
$_{13}$C Saturada	-28,20	n.a.	-26,95	-27,30	n.a.	-28,4	-26,27	-28,4	---	-25,76	-27,1
$_{13}$C Aromática	-25,69	n.a.	-25,82	-25,90	n.a.	-27,1	-25,60	-26,4	---	-25,3	-25,6

Geographic Location	CENTRAL PLATFORM										NORTHERN PLATFORM	
Well	**12** Carbonera	**13** Mirador	**14** Gacheta	**15** Mirador	**16** Carbonera	**17** Tertiary	**18** Carbonera	**19** Tertiary	**20** Mirador	**21** Mirador	**22** Mirador	**23** Carbonera
Gravity	28,0	23,4	14,8	---	14,6	10,2	18,5	13,80	39,4	40,7	34	23,8
% Sulphur	0,19	0,66	0,31	---	0,21	0,76	0,32	1,350	0,19	0,18	0,55	0,5
Pr/Ph	2,24	3,29	2,12	2,70	2,34	4,46	---	---	5,11	4,71	1,54	1,04
V/Ni	---	---	---	---	---	7,00	1,00	---	---	---	2,00	---
$_{13}$C Saturada	-26,70	-26,3	-26,4	-26,64	-26,2	-25,79	-27,92	-26,98	-26,1	-28,1	-29	-28,2
$_{13}$C Aromática	-24,9	-25,1	-25,4	-25,72	-24,8	-24,78	-27,19	-26,27	-24,4	-26,1	-28,2	-27,9

n.a.: not analized

Table 2. Biomarker parameters of the crude oils from the Llanos Basin, Colombia

Geographic Location	CENTRAL FOOTHILLS					NORTHERN FOOTHILLS	SOUHTERN FOOTHILLS	CENTRAL FOOTHILLS			
Well	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Distance of Migration	12,91	12,30	15,18	15,99	10,76	18,45	16,92	42,44	41,52	30,76	43,06
Ts/Tm	0,69	0,54	0,40	0,53	0,55	0,53	0,77	0,44	1,02	0,86	1,00
C23 tri/hopane	0,49	0,07	0,54	1,90	0,25	0,51	1,07	0,21	1,35	1,74	2,23
C24 Tet/hopane	0,21	0,19	0,18	0,40	0,15	0,17	0,29	0,11	0,04	0,29	0,21
C24 tet/C26 Tri	1,42	16,00	1,36	1,15	3,85	1,07	1,12	1,70	1,17	0,73	0,76
C29/Hopane	0,61	0,67	0,63	0,76	0,56	0,63	0,70	0,60	0,70	0,78	0,72
C29X/C29 Norhopane	0,53	0,48	0,15	0,22	0,48	0,29	0,11	0,27	0,38	0,28	0,31
Nisnorthopane/Hopane	0,25	0,04	0,37	n.a.	0,03	0,14	n.a.	0,06	n.a.	n.a.	n.a.
Oleanane/Hopane	0,62	0,28	0,58	0,36	0,22	0,28	0,25	0,12	0,08	0,22	0,09
C31 22R/22S	2,12	1,42	1,71	1,06	1,70	2,10	1,67	1,65	0,92	0,85	0,81
C35/C34 Hopane	0,19	0,50	0,33	1,48	1,00	0,27	0,31	0,27	0,73	4,90	0,82
25-norhopane/hopane	0,19	0,05	0,36	0,42	0,04	0,13	1,68	2,05	0,05	0,05	0,04
C30 Hopane/C29 sterane	5,48	12,80	6,98	17,96	14,07	3,64	3,02	8,20	9,02	8,38	7,95
Dia C27/20R C27	1,75	4,18	1,43	2,85	2,88	1,68	1,82	1,31	2,19	1,81	1,47
20S C29/20R C29	1,27	0,81	0,85	0,71	1,50	1,13	0,66	1,03	0,73	0,83	0,53
14B17B C29/20R C29	1,87	1,51	1,20	3,61	2,30	1,34	1,43	1,16	2,21	2,52	2,45
C27/C29	0,79	0,39	1,04	1,45	0,60	1,15	0,90	0,92	1,14	1,47	1,48
C28/C29	0,85	0,39	0,99	1,25	0,53	1,09	0,79	0,87	0,92	1,27	1,24
Bicadinanes/Hopane	n.a.	3,10	1,14	1,00	3,40	n.a.	0,95	n.a.	1,27	1,00	n.a.
phenanthrene/dibenzothiophene	9,90	11,00	8,50	7,60	10,70	2,40	6,20	183,0	13,00	10,80	4,00
26/28 triaromatics	1,37	1,89	0,98	0,41	2,00	0,41	0,80	0,99	1,02	1,32	1,14
27/28 triaromatics	1,11	0,89	1,20	0,69	1,30	0,61	0,19	1,03	1,11	1,30	1,31
phenanthrene/triaromatics	4.900	3.980	163	188	3.015	14,00	3,50	34,0	44,0	15,70	9,70
1,8 / total carbozoles	0,13	0,14	0,15	n.a.	0,17	0,15	0,17	0,09	0,12	0,17	0,17
1,8 / partial shielded	0,18	0,20	0,21	n.a.	0,24	0,23	0,22	0,15	0,16	0,24	0,22
1,8 / non shielded	0,45	0,50	0,49	n.a.	0,62	0,47	0,74	0,21	0,43	0,56	0,74
partial / non shielded	2,50	2,53	2,31	n.a.	2,61	2,07	3,39	1,40	2,74	2,36	3,39
1 methyl / non shielded	0,61	0,67	0,63	n.a.	0,66	0,64	0,92	0,53	0,86	0,57	0,92
Naphalene Comp/1,8 Carba	0,20	0,27	0,13	n.a.	0,45	0,31	0,31	28,50	---	13,10	7,90

n.a.: not analized

Table 2. Biomarker parameters of the crude oils from the Llanos Basin, Colombia

Geographic Location		CENTRAL FOOTHILLS					NORTHERN FOOTHILLS	SOUHTERN FOOTHILLS	CENTRAL FOOTHILLS			
Well	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**
Distance of Migration	35,08	30,76	22,45	19,94	46,14	43,06	72,29	76,9	30,14	30,76	43,06	39,98
Ts/Tm	1,02	0,87	1,15	1,06	1,11	0,85	0,96	0,91	0,48	0,35	1,00	1,14
C23 tri/Hopane	0,40	1,00	1,02	8,53	1,07	2,22	9,40	8,40	0,98	1,20	0,63	0,82
C24 Tet/Hopane	0,10	0,30	0,43	0,02	0,30	0,54	1,10	0,99	0,30	0,10	0,07	0,06
C24 tet/C26 Tri	0,84	1,55	1,38	0,57	1,39	1,89	0,28	0,78	1,70	5,70	0,31	0,20
C29 /Hopane	0,57	0,73	0,72	0,73	0,67	0,75	2,79	1,01	0,75	0,60	0,50	0,48
C29X/C29 Norhopane	0,37	0,41	0,69	0,63	0,54	0,23	0,37	0,28	0,23	0,25	0,16	0,10
Bisnorhopane/Hopane	0,09	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0,05	0,05	0,06
Oleanane/Hopane	0,14	0,10	0,12	0,09	0,11	0,18	0,44	0,24	0,40	0,50	0,15	0,10
C31 22R/22S	2,16	1,35	1,41	1,34	0,97	1,47	0,14	0,73	1,33	1,49	2,45	1,50
C35 /C34 Hopane	0,26	0,87	0,82	5,70	0,74	1,12	0,88	0,78	6,10	1,08	0,14	1,01
25-norhopane/hopane	0,09	0,62	1,78	1,69	0,33	0,97	2,47	1,77	0,09	0,04	0,15	0,24
C30 Hopane/C29 sterane	3,47	8,56	6,38	1,69	8,81	6,21	0,92	5,53	20,98	11,30	1,91	1,81
Dia C27/20R C27	2,00	6,07	9,96	11,20	4,51	4,70	1,15	2,90	1,96	2,45	0,64	0,57
20S C29/20R C29	0,73	0,64	0,74	0,47	0,38	0,40	0,69	0,80	0,85	0,95	0,83	0,86
14B17B C29/20R C29	1,02	3,02	3,98	3,80	2,84	2,45	2,68	3,42	3,05	0,92	0,89	1,20
C27/C29	0,99	1,06	1,10	1,12	1,04	0,94	1,59	1,57	1,50	0,73	1,18	1,27
C28/C29	0,82	0,74	0,70	0,73	0,73	0,63	1,41	1,22	1,15	0,58	1,13	1,28
Bicadinanes/Hopane											0,24	
phenanthrene/dibenzothiophene	10,40	2,40	3,80	4,40	8,30	7,10	8,00	2,90	8,00	9,60	27,00	n.a.
26/28 triaromatics	1,40	0,63	1,35	1,22	0,92	0,82	0,86	1,63	0,79	0,48	0,82	n.a.
27/28 triaromatics	1,03	1,03	0,51	0,73	0,87	1,22	1,38	0,63	1,02	1,10	1,28	n.a.
phenanthrene/triaromatics	64,00	45,00	27,00	27,00	5,10	2,60	0,13	0,27	30,00	230,00	66,00	n.a.
1,8 / total carbazoles	0,04	0,14	0,25	0,27	n.a.	0,18	0,01		0,16	0,17	0,10	n.a.
1,8 / patial shielded	0,10	0,21	0,33	0,38	n.a.	0,25	0,01		0,21	0,23	0,15	n.a.
1,8 / non shielded	0,07	0,41	1,00	0,95	n.a.	0,59	0,19		0,63	0,61	0,32	n.a.
partial / non shielded	0,73	1,98	3,06	2,46	n.a.	2,36	29,24		2,93	2,68	2,16	n.a.
1 methyl/ non shielded	0,54	0,64	1,05	1,19	n.a.	0,12	18,64		0,70	0,68	0,11	n.a.
Naphalene Comp/1,8 Carba	9,90	7,90	—	—	—	17,00			1,94	3,30	11,30	n.a.

n.a.: not analized

ratio 1.8/total non-shielded carbazoles in general decreases toward the platform area.

The oils from the central foothills area (from wells 1 to 6) and two samples of oil from the central platform area (oils 20 and 21) contain significantly higher amounts of oleanane and bicadinane than those from the other areas of the Llanos Basin do. Conversely, the lowest values are related to most of the oils from the central platform. Also some oils from the foothills (samples 2, 4 and 5) and the samples 20 and 21 show the highest C_{30} hopane/ C_{27} sterane ratio. The highest ratios of pristane/ phytane are found in oils 1, 3, 4, 20 and 21. These oils show the lowest values of sulfur. The carbon isotopic composition of the oils shows a wide variation. Heavy isotopic composition ($d^{13}C$ SATca. $-26^{o}/_{oo}$; $d^{13}C$ ARO around $-25^{o}/_{oo}$) distinguish the oils from the central platform (samples 8 ,13, 14, 17 and 21). The oils from the northern platform show the most negative isotopic composition, whereas the oils from the central foothills exhibit intermediate values.

DISCUSSION

Geochemical Characteristics

The geochemistry of the oils within this basin is extremely complex due to the influence of several different processes, the most important of which is the mixing of oils from different source rocks over different geological times and extensive biodegradative alteration.

Figure 3 shows the level of 25-norhopane versus hopane for each of the oils. As can be seen many oils have abundant 25-norhopane suggesting a significant amount of biodegradation. The 25-norhopane has been associated with oils that have experienced severe bacterial alteration, (Volkman et al. 1983). Many oils, especially those within the central platform show extensive alteration with 25-norhopane/hopane ratios greater than 1. Most of the oils from the southern platform, of which the oil 7 is an example, also show extensive microbial alteration using this parameter. Oils

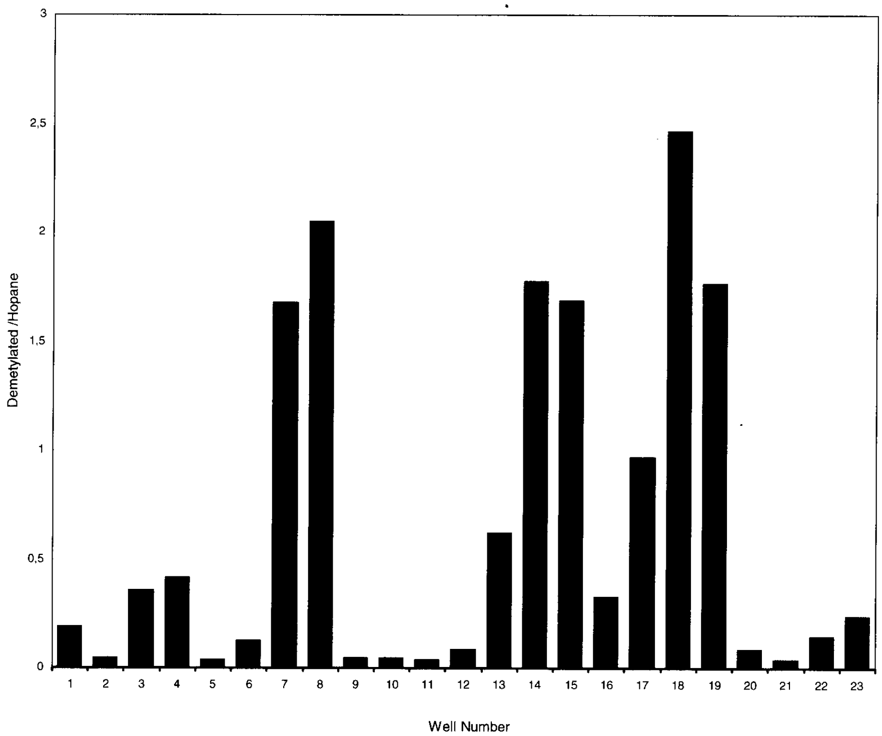

Figure 3. Relative content of 25-norhopane for each of the oils.

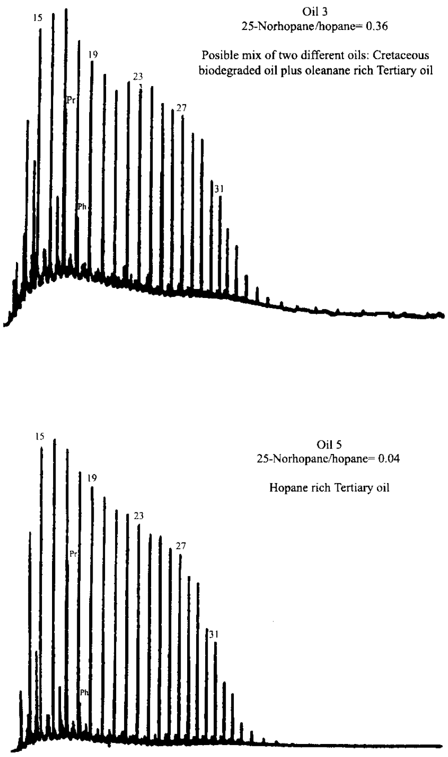

Figure 4. Saturate chromatograms of two representative crude oils from the foothills.
Key: Pr = Pristane; Ph = Phytane; numbers refer to carbon chain length of n-alkanes.

from the northern platform have low values suggesting low alteration. Many oils in this study, including some from the foothills which show moderate to extensive microbial alteration in the triterpane traces, also contain a high abundance of normal and branched chain and isoprenoid alkanes (see Figure 4). According to Talukdar et al. (1986) this suggests that there have been at least two pulses of oil (contributed to the reservoired oil), the first of which suffered extensive microbial alteration.

Oleanane is present in all the oils in varying amounts (see Table 2). Thus oils such as 1 and 3 have oleanane/hopane ratios greater than 0.5 whereas oils such as 9 and 11 have ratios of less than 0.1. Indeed most of the oils in the central platform area have relatively low oleanane/hopane ratios. Oleanane is known to be a triterpane of higher plant origin (Ekweozor et al., 1979), and limits the age of the source rock(s) from Late Cretaceous to Tertiary. The ratio of oleanane/hopane appears to be affected by the degree of biodegradation as is shown in Figure 5 where oleanane/hopane is plotted against 25-norhopane/hopane ratio for all the oils. The oils that show extensive alteration (indicated by high 25-norhopane/hopane ratio) show oleanane/hopane values that increase with higher relative values of 25-norhopane. The oleanane/hopane ratio seems to not be affected in oils with low or limited microbial alteration.

A cross plot of oleanane/hopane versus C_{30} hopane/C_{29} sterane (Figure 6), splits the oils in three groups related to the relative input of eucaryote (algal plus higher plants) or prokaryote (bacterial) organic matter. One group, which shows high C_{30} hopane/C_{29} sterane ratios, indicates, according to Tissot and Welte (1984), oils derived from more terrigenous and microbial reworked organic matter. These oils also present higher than 0.2 oleanane/hopane ratio. According to the observation reported by Moldowan et al. (1994) the oleanane ratio greater than 0.2 implies a significant contribution of a Tertiary source rock. This group with high oleanane and high C_{30} hopane is related to the oils 2, 4 and 5 located in the foothills and the oils 20 and 21 from the platform, and may correspond to oil fields with high contribution from Tertiary source rocks. Another group, the 1 and 3 oils from the foothills, shows the highest oleanane/hopane ratio and a relatively low C_{30} hopane/C_{27} sterane. This may indicate a high input of higher plant organic matter mixed with input of Planktonics and/or benthic algal marine organic matter e.g. Moldowan et al. (1985). These oils, might result from the mixing of Cretaceous and oleanane rich Tertiary oil pulses. The third group has the lowest oleanane/hopane and relatively low C_{30} hopane/C_{27} sterane ratios related to mainly an algal marine organic matter input together with less input of terrigenous organic matter. It may correspond to the Cretaceous oil pulse, which predominates in the central platform.

Some parameters given in Table 1 provide information related to the depositional environment of the source rock. Thus, the sulfur content is relatively low, less than 0.5 in all of the oils of the foothill area. The less biodegraded oils of the central platform also show low sulfur, which could be related to a fairly oxic depositional environment, for example peat swamp or deltaic. The pristane / phytane ratio is higher than 3 in most of the oils of the foothills and in some of the central platform (samples 20 and 21), confirming that for these oils the original depositional environment was oxidizing. Most of the oils of the central platform have relatively low pristane/phytane ratios ranging between 1.5 to 3 indicating that an alternative source rock deposited in less oxidizing environment may be responsible for these oils (samples 8, 9, 10, 11, 12, 14, 16).

The oils in the plot of pristane/ phytane versus sulfur (Figure 7), can be divided in four groups of oils which broadly fit with the oil families A, B, C, D and E identified by Rangel et al. (1991). The first group related to oils of the northern platform (samples 22 and 23) have features indicating that their source is marine with some terrestrial input correlatable with Family A. For example the sulfur content is relatively high (more than 0.5) and the pristane/phytane ratio is relatively low (less than 1.5). The possible source responsible for these oils according to Rangel et al (1991.) is an Upper Cretaceous rock located toward the northern foothills. The second group with high pristane/phytane, (more than 3) and very low sulfur (less than 0.3), is correlatable with Family B, possibly derived from nonmarine reducing/oxidizing environment, related to the oils of the central foothills and some oils of the platform. The third group of oils, correlatable with Family C, shows low sulfur and relatively low pristane/ phytane ratio, related to those oils located in the central platform. Their features indicate a marine terrestrially influenced, slightly oxidized environment. Finally, a fourth group with the highest values of sulfur and pristane/phytane ratio more than 3 is related to biodegraded oils of the central and southern platform correlatable to families D and E. In the central Llanos Basin the oil families B, C and D identified by Rangel et al (1991) may correspond to a mixing in different

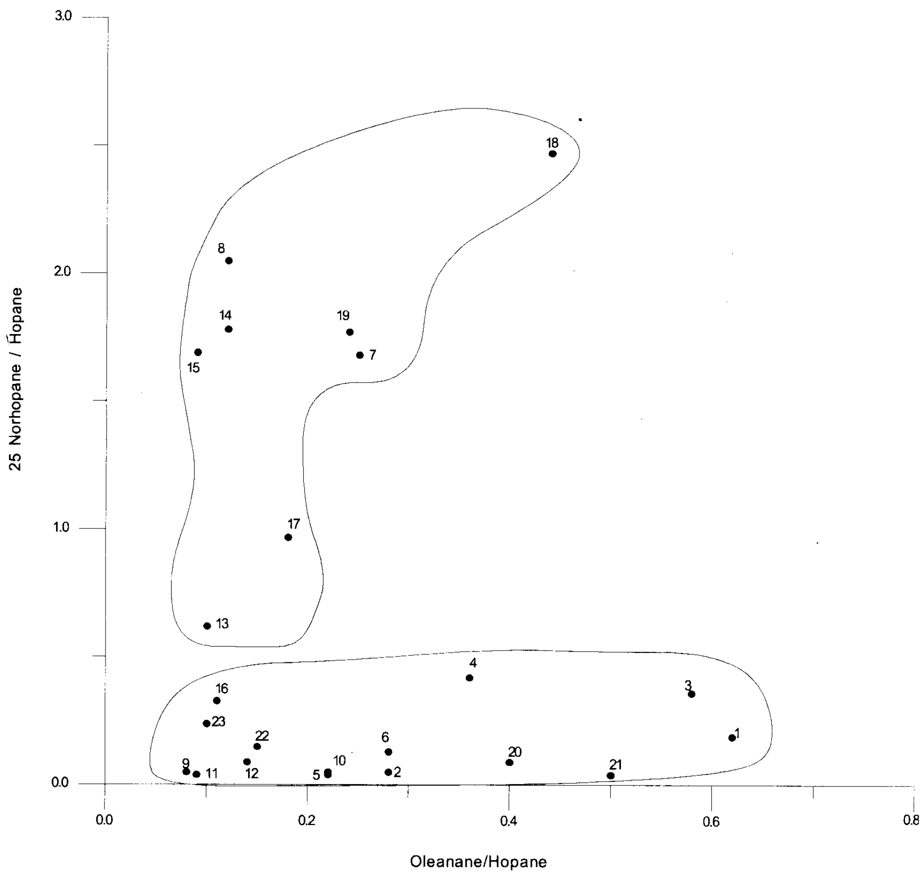

Figure 5. Correlation between relative content of 25-Norhopane and Oleanane.

amounts of three different pulses of oils, the Cretaceous pulse, the oleanane rich Tertiary pulse and the hopane/sterane rich Tertiary pulse. The B family would be related to oils with the highest amount of oleanane rich Tertiary oils and the Family C would correspond to those oils mainly derived from Cretaceous source rock. The Figure 8 shows the distribution of triterpanes and steranes in oils of the three suggested oil phases.

All of the oils, except those of the northern area of the basin, have a high relative abundance of diasteranes (high diasterane/sterane ratio, Table 2) suggesting that they were derived from source rocks rich in siliciclastics and/or high oxicity (Mello et al., 1988; Moldowan et al., 1986)

The C_{24} tetracyclic terpane is relatively abundant (ratio C_{24} tetracyclic/C_{26} tricyclic greater than 1) in the oils of the foothills and in some of the central platform (Table 2). Ekweozor et al. (1981) reported high amounts of C_{24} tetracyclic terpane in oils of deltaic origin. According to Mello et al. (1988) and Philp and Gilbert (1986), the abundance of C_{24} tetracyclic may be marker of higher plant input.

The isotopic compositions of the saturate and aromatic fractions show a wide range of variation of the $d^{13}C$ values. This variation is about 4 per mil in the saturate fractions and 4.5 per mil in the aromatic fractions. A cross plot of $d^{13}C$ saturates versus $d^{13}C$ aromatics (Figure 9) shows three groups with very similar composition, suggesting the existence of at least three families of oils. According to Sofer (1984), the isotopic relationship between the saturate and aromatic hydrocarbon fractions can be used to distinguish marine from non marine derived oils.

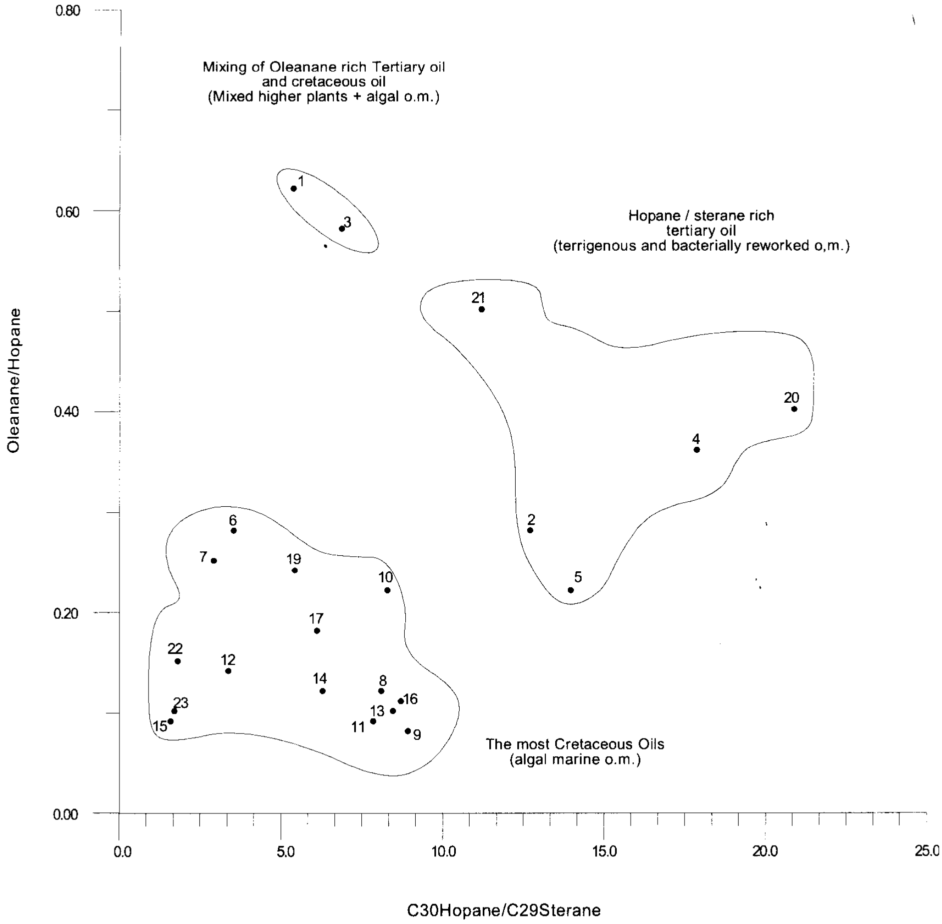

Figure 6. Possible source of the oils interpreted from geochemical parameters.

The oils from the central foothills (oils 1, 3, and 4) plot in the middle of the trend, (Figure 10) above of the Sofer line, in the area of nonmarine crude or near to it. Some of the oils from the central region (oils 20, 21, and 12) also plot in the nonmarine area. These oils may correspond to a mix of oils derived from the Upper Cretaceous source rock plus an important amount of oil derived from Tertiary source rock. The other samples from the central platform (oils 10, 13, 14, 15, 16 and 17) plot in the marine area possibly correspond to a more Cretaceous oil pulse with a minor proportion of Tertiary oil. The upper group in the cross plot, i.e. the most isotopically positive, corresponds to oils from the central platform, some of them above the Sofer line and some of them below it, as discussed above. The lowest value in the plot, i.e. most isotopically negative, is related to an oil of the northern platform.

Possible Source Rock

Total organic carbon, Rock-Eval pyrolisis and visual kerogen analyses published in Palmer and Russel (1986) and Rangel et al. (1991) show that the Tertiary section contains primarily terrestrially-derived humic kerogen (gas prone). These rocks are immature or marginally mature (Ro = 0.4-0.7%) and their organic richness varies from poor to good (TOC = 0.10-1.4%). However, in this study a shale interval in the Mirador Formation was identified (well 24) with high TOC and HI (see Table 3). Figure 10 shows the m/z 191 fragmentogram of this extract and Table 4 shows

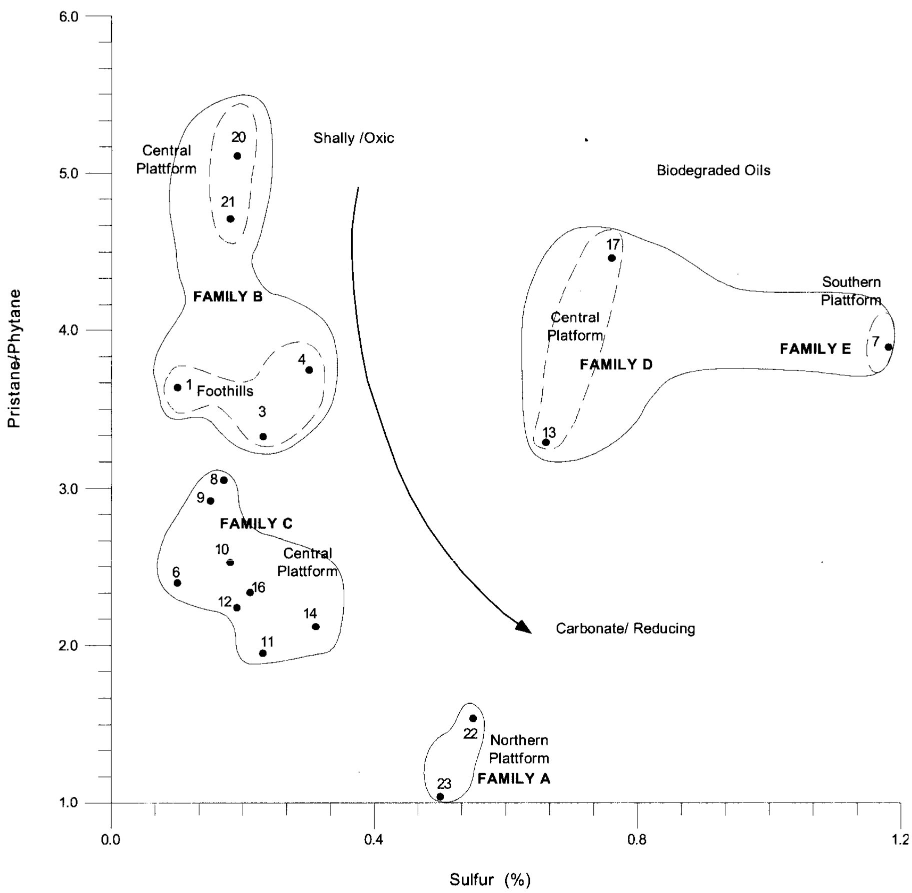

Figure 7. Depositional environment of source rock as interpreted from oil composition.

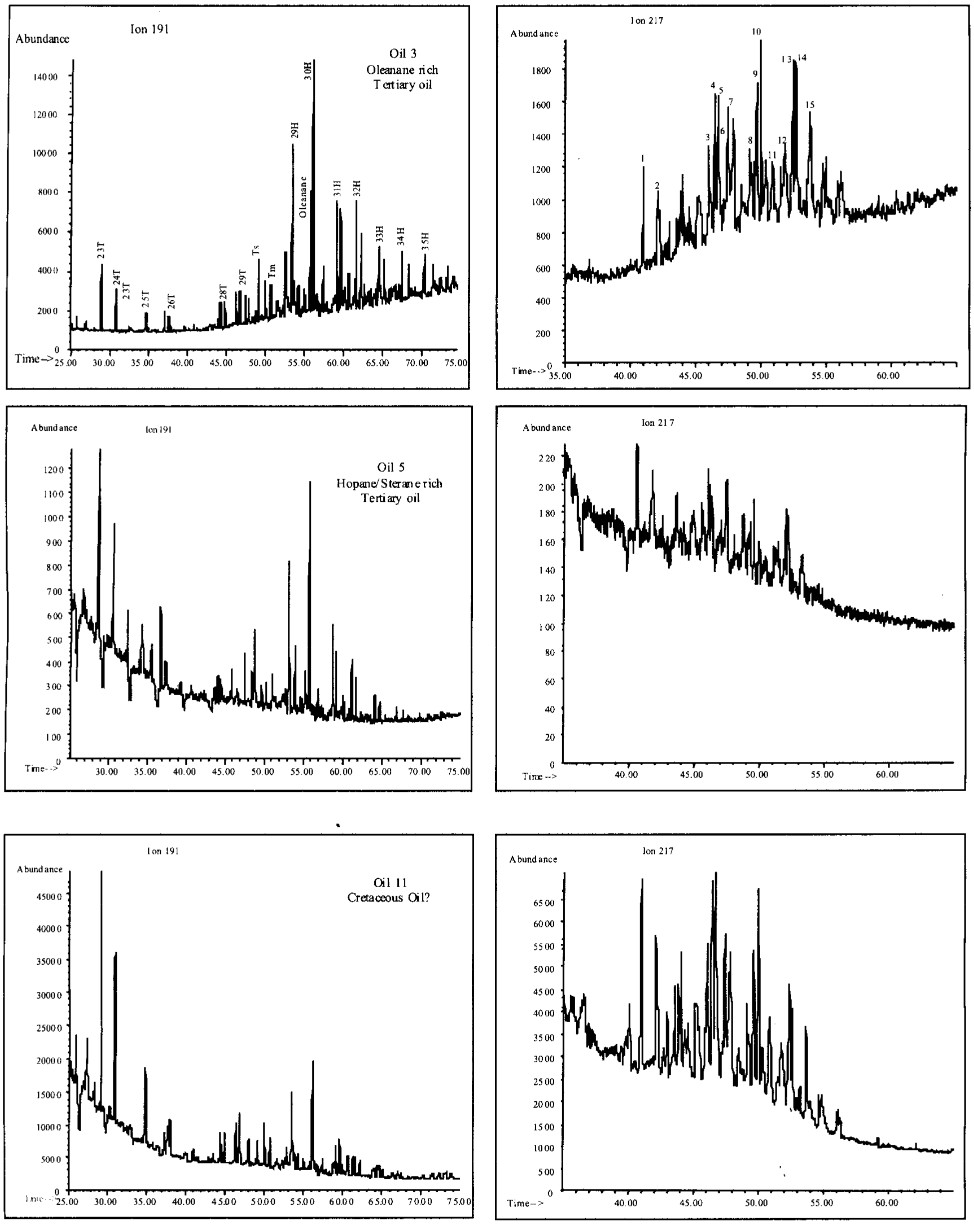

Figure 8. Distribution of triterpanes and steranes in Oils of the three suggested oil phases. (see Tables 5 and 6 for identification)

the biomarker results. This sample shows very high oleanane/hopane ratio (1.1), high C_{24} tetracyclic/ C_{26} tryciclic and low tricyclic/hopane ratio. The geochemical features described above are consistent with the idea that these rocks may be responsible for the terrigenous pulse of oil that mixed with the early Cretaceous (marine) oil.

The Late Cretaceous rocks found in some wells and outcrops of the foothills contain marine oil prone kerogen with some higher plant influence, Palmer and Russel (1986), Rangel et al.(1991). The biomarker results related to these rocks indicate effective a source rock. The extract analysis for oil - source rock correlation indicates relatively low oleanane/hopane ratio, moderate pristane/phytane ratio, hopane signature and isotopic composition very similar to some oils from the platform (the more Cretaceous pulse).

Extent of mixing

Most of the oils in the central foothills and central platform areas, which show moderate to extensive microbial alteration in the triterpane traces and moderate to high 25-norhopane/hopane ratio, are also abundant in normal and branched chain and isoprenoid alkanes. As was mentioned before, this suggests at least 2 pulses of oil (two different oil phases) contributed to the reservoired oil, the first of which suffered microbial alteration.

Tegelaar et al. (1995) interpreted that the biodegraded and non-biodegraded contributions in Cusiana and Cupiagua oils (located in the foothill area), were derived from different source rocks and represent different pulses of hydrocarbon generation. In that case, the relative abundance of 25-norhopane positively correlate with the C_{30} sterane (marine marker, Moldowan et al. , 1990) and inversely correlate with bicadinane.

From the discussion of the geochemical characteristics of the oils it can be inferred that in

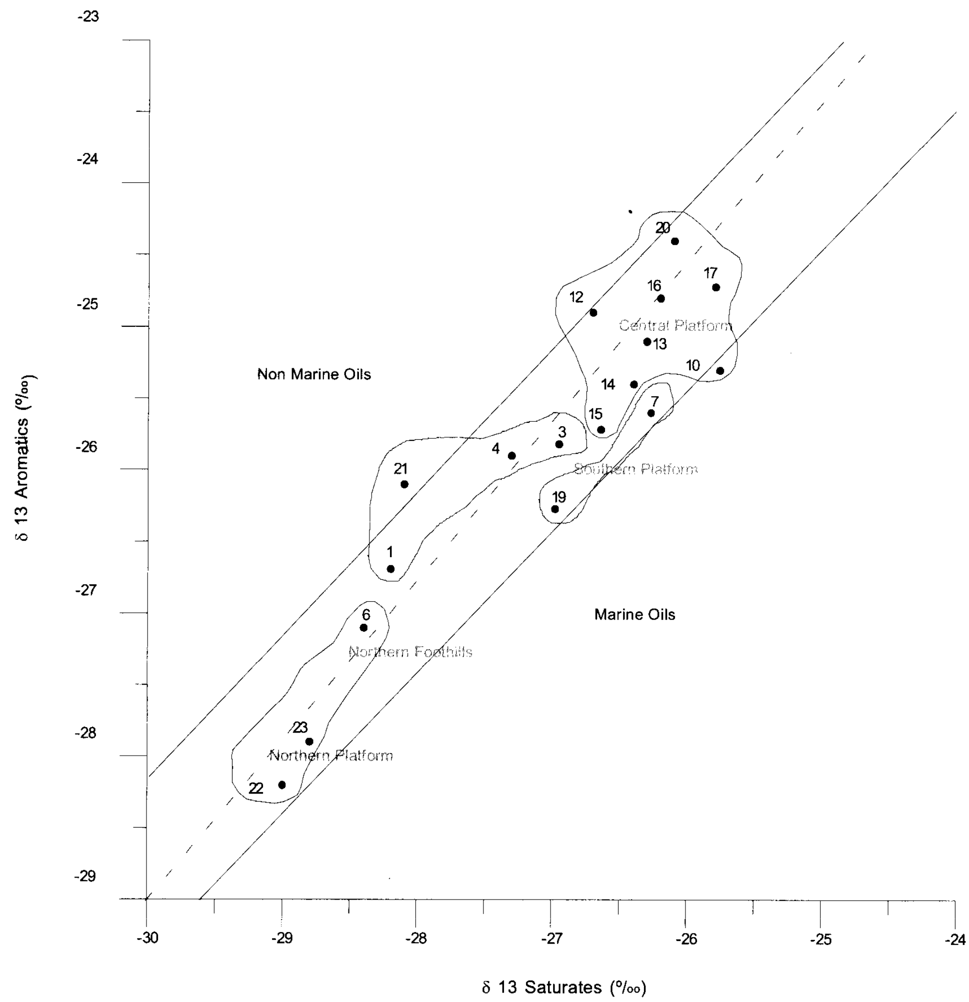

Figure 9. Stable carbon isotopes of oils in the Llano Basin.

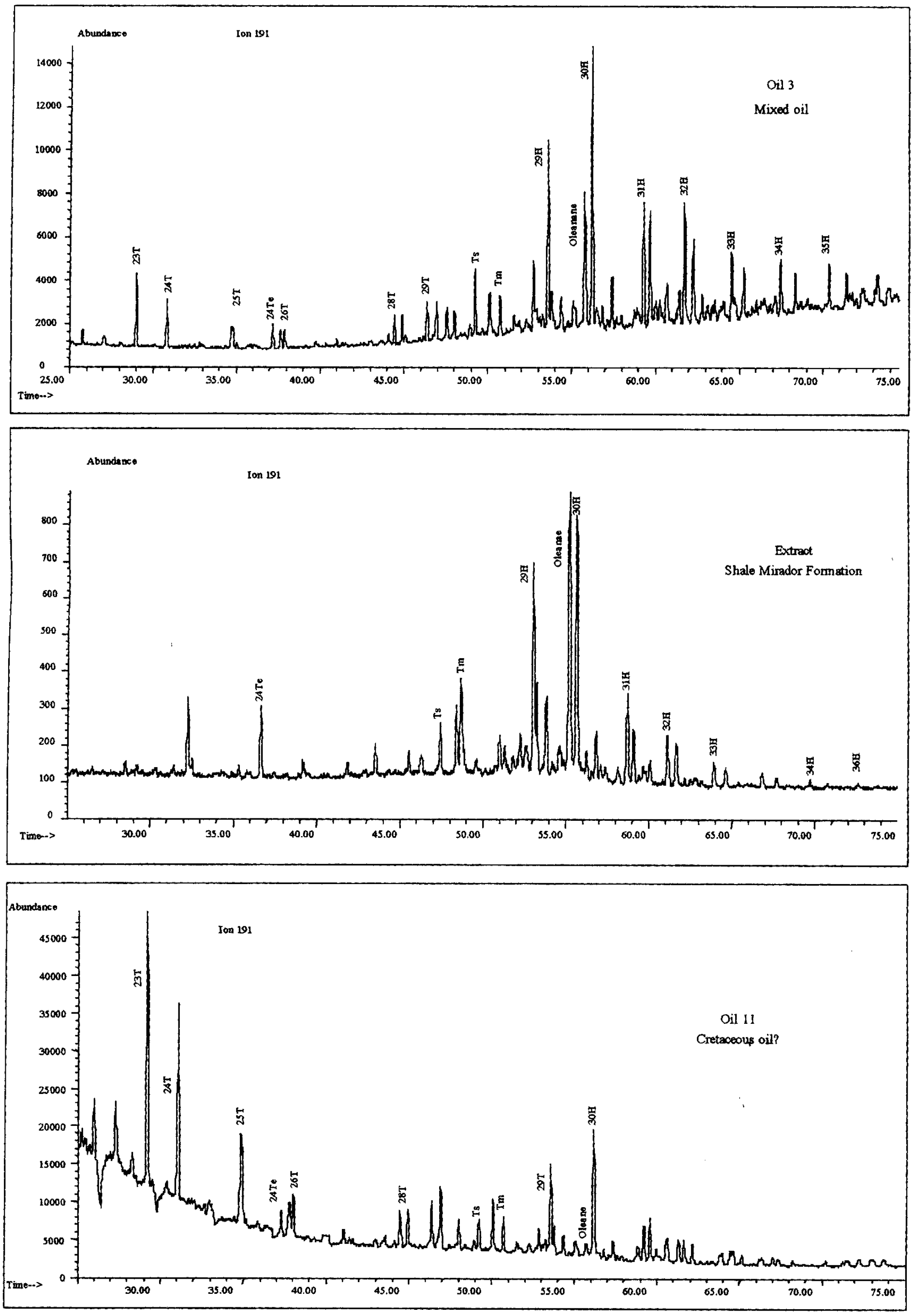

Figure 10. Distribution of triterpanes in the rock extracts from the Mirador Formation, in oil 11 (possible pure cretaceous oil) and in Oil 3 (mixed oil).

the central Llanos Basin there have been three different oil pulses mixed in different proportions depending on the reservoir location within the basin. The first pulse which could be related to Upper Cretaceous source rocks exhibits an oleanane/hopane ratio of around 0.1, high C_{23} tricyclic/hopane ratio (higher than 1), low C_{24} tetracyclic/C_{26} tricyclic terpane ratio, pristane/phytane less than 2, and diasterane/ sterane ratios of less than 1.5. The oils 11,15, 22 and 23 are representative of this phase and may correspond to a typical Upper Cretaceous relatively more carbonate oil.

On the other hand, there is a second group of oils with a high oleanane/hopane ratio (greater than 0.58) which could have a contribution from a Tertiary and Upper Cretaceous source rocks. The samples 1 and 3 from the central foothills are related to this group. The Tertiary source rock(s) contributing to these oil fields have not been definitively identified to date. However, a shale within the Mirador Formation (Tertiary) with very high oleanane/hopane ratio (1.1), high C_{24} tetracyclic/C_{26} tryciclic and low tricyclic/hopane ratio seems to be consistent with the idea that these rocks are responsible for the oleanane rich pulse of oil that mixed with the Upper Cretaceous oil.

Table 3. Results of pyrolysis Rock-Eval, TOC and vitrinite reflectance on shale samples *from the Mirador Formation*

Formation	Depth (Feet)	TMAX	S1	S2	S3	PI	S2/S3	PC	TOC	HI	OI	Ro%
Mirador	14652	447	1,01	11,91	0,21	0,08	56,71	1,07	2,91	409	7	0,60
Mirador	14787	447	0,74	11,00	0,16	0,06	68,75	0,97	3,45	319	5	0,60

Table 4. Biomarker parameters in the rock extract from Mirador Formation

Sample	Extract of Mirador Formation (shale interval)
Well	24
Ts/Tm	0.55
C23 Tricyclic/Hopane	0,10
C24 Tetracyclic/Hopane	0,27
C24 Tetracyclic/C26 Tricyclic	13,50
C29 /Hopane	0,82
C29X/C29 Norhopane	0,42
Bisnorhopane/Hopane	n.a.
Oleanane/Hopane	1,10
C31 22R/22S	0,60
C35 /C34 Hopane	0,50
25-Norhopane/Hopane	---
C30 Hopane/C27 Sterane	30,00
Dia C27/20R C27	—

n.a. : not analized

Thirdly, some oils of the foothills, i.e. wells 2 and 5, display some unusual characteristics which are not present in the other oils of the same area. These oils have very high hopane/C_{27} sterane ratio, high oleanane/hopane, high C_{24} tetracyclic/C_{30} hopane (more than 4) ratios, very low tricyclic/hopane ratios (less than 0.2) and high diasterane/sterane ratios. Part of these oils was probably generated from a different Tertiary source rock or from a more siliciclastic Upper Cretaceous source rock. These oils appear to be restricted to some areas of the foothills.

Estimation of the contribution of the two main pulses (the Cretaceous pulse and the Tertiary

Table 5 . Identification of the major terpanes present in the m/z 191 fragmentograma

22T	C22 Tricyclic Terpane
23T	C23 Tricyclic Terpane
24T	C24 Tricyclic Terpane
25T	C25 Tricyclic Terpane
24Te	C24 Tetracyclic Terpane
26T	C26 Tricyclic Terapne (22R)
	C26 Tricyclic Terpane (C22S)
Ts	C27 18a(H) Trisnorhopane (Ts)
Tm	C27 17A(H) Trisnorhopane (Tm)
30T	C30 Tricyclic Terpane (C22R)
DM	C29 17a(H), 21b(H) 25-Norhopane
29H	C29 17a(H), 21b(H)-Norhopane
OLEANANE	
30H	C30 17a(H), 21b(H)-Hopane
31H	C31 17a(H) 21b(H)-Homohopane (22S)
	C31 17a(H) 21b(H)-Homohopane (22R)
GAMMACERANE	
32H	C32 17a(H) 21b(H)-bishomohopane (22S)
	C32 17a(H) 21b(H)-bishomohopane (22R)
33H	C33 17a(H) 21b(H)-trishomohopane (22S)
	C33 17a(H) 21b(H)-trishomohopane (22R)
34H	C34 17a(H) 21b(H)-tetrahomohopane (22S)
	C34 17a(H) 21b(H)-tetrahomohopane (22R)
35H	C35 17a(H) 21b(H)-pentaomohopane (22S)
	C35 17a(H) 21b(H)-pentaomohopane (22R)

Table 6. Identification of the major steranes present int the m/z 217 fragmentogram

1	C27 ba Diasterane (20S)
2	C27 ba Diasterane (20R)
3	C27aaaa Sterane (20S)
4	C27abb Ster (20R)+ C29 ba Diaster
5	C27abb sterane (20S)
6	C27 aaa Sterane (20R)
7	C29 ba Diasterane (20R)
8	C28aaa Sterane (20S)
9	C28abb Sterane (20R)
10	C28abb Sterane (20S)
11	C28aaa Sterane (20R)
12	C29aaa Sterane (20S)
13	C29abb Sterane (20R)
14	C29abb Sterane (20S)
15	C29aaa Sterane (20R)

pulse rich in oleanane) to a mixed oil production, was estimated by measuring the relative abundance of oleanane/hopane in two inferred end members (the oil 11 for the Upper Cretaceous oil, and extract of the shaly unit of the Mirador Formation for the Tertiary) and plotting these values in a mixing diagram (Figure 11).

Oil 11 located in the central platform, can be considered a quite pure Cretaceous oil phase, because of its relatively low Pr/Ph (<2), high relative abundance of the C_{27} steranes, high Ts/Tm, moderate proportions of steranes to hopanes, relatively low oleanane/ hopane ratio (0.09), high C_{23} tricyclic/hopane ratio (higher than 1), low C_{24} tetracyclic/C_{26} tricyclic terpane ratio, and

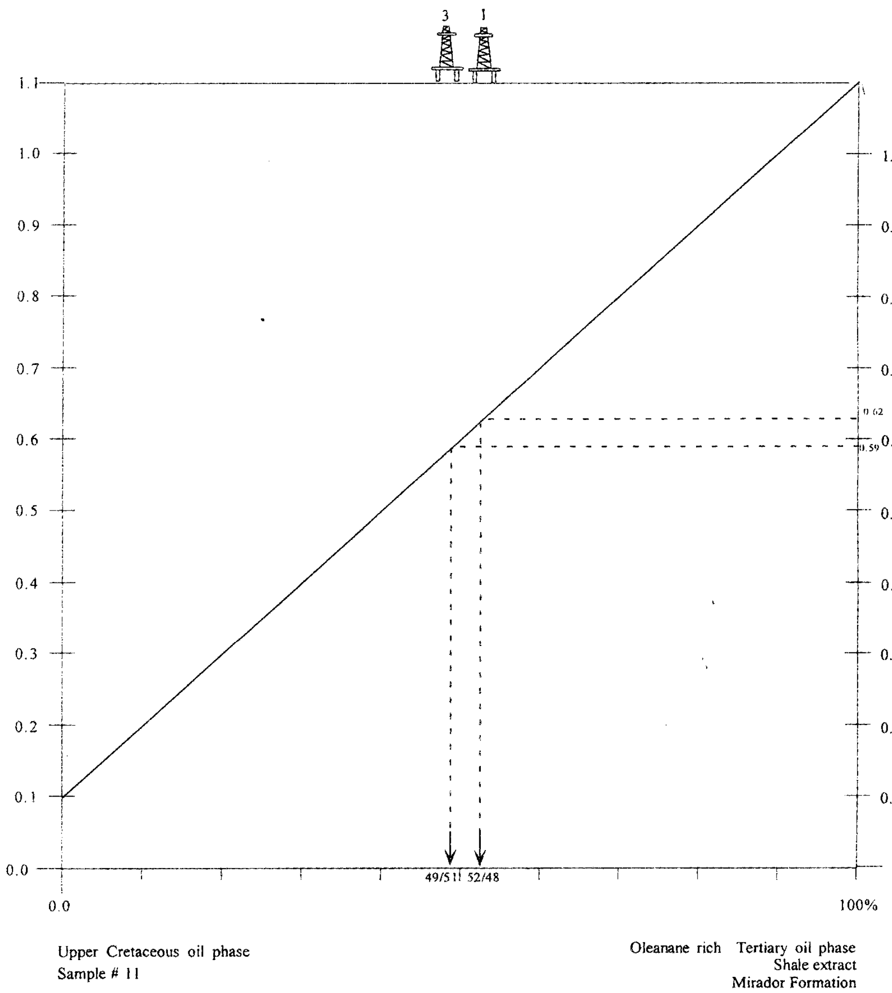

Figure 11. Mixing diagram for the two most important phases of oil in the foothills of the Llanos Basin.

diasterane/ sterane ratios of less than 1.5. These geochemical features may be interpreted as indicative of marine terrestrially influenced source rock probably of Upper Cretaceous age.

Plotting a mixing curve in this diagram allows an estimate of the contribution of each phase in those mixed production wells in which these two phases seem to be present. In the foothills the contribution of the oleanane rich Tertiary phase can be as high as 52% (Figure 11).

Migration Pathway

In order to make some possible inferences concerning secondary migration; the NSO fractions were analyzed for C2 carbazoles by GC-MS. According to Li et al. (1992) these aromatic nitrogen compounds are potential indicators of migration. Figure 12 shows a typical carbazole trace for two of the oils, one of the less migrated oils and one of the more migrated oils. The peak identifications were based on the elution order given by Ignatialis et al. (1995). In this study it is possible to see that, in general, the more migrated oils are relatively enriched in shielded and partially shielded isomers (Figure 13). However, there is no very good positive relationship since it is possible that the migration pathway is not in a straight line from the foothills to the platform. An integrated geochemistry-structural geology study is in progress to address this matter further.

CONCLUSIONS

1. The ubiquitous occurrence of oleanane in all of the oils studied is interpreted as indicative of their origin from Upper Cretaceous and/or Tertiary source rocks.

2. In the central Llanos Basin there appear to be at least three different oil generation phases with various amounts of mixing. The extent of the mixing depends on the location of the wells within the basin. The first phase was derived from carbonate shale, Upper Cretaceous source rock. This pulse is widely spread in the central platform. The second phase originated from a Tertiary source rock, probably the shale level of the Mirador Formation and predominates in the central foothills; and the third phase was probably generated from a different Tertiary unit or a more siliciclastic Upper Cretaceous source rock. These phases are located in the central foothills and central platform.

3. The depositional environment of the source rocks inferred from the oil geochemistry

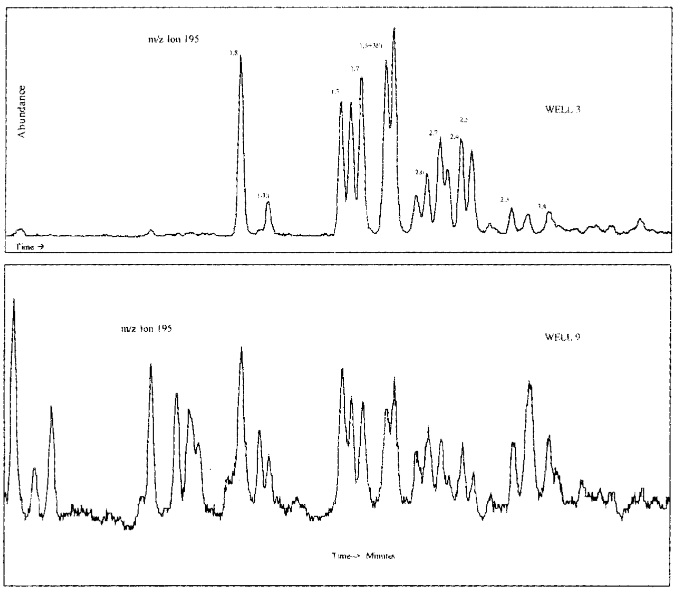

Figure 12. Comparison of the carbazole distribution between two different migrated oils.

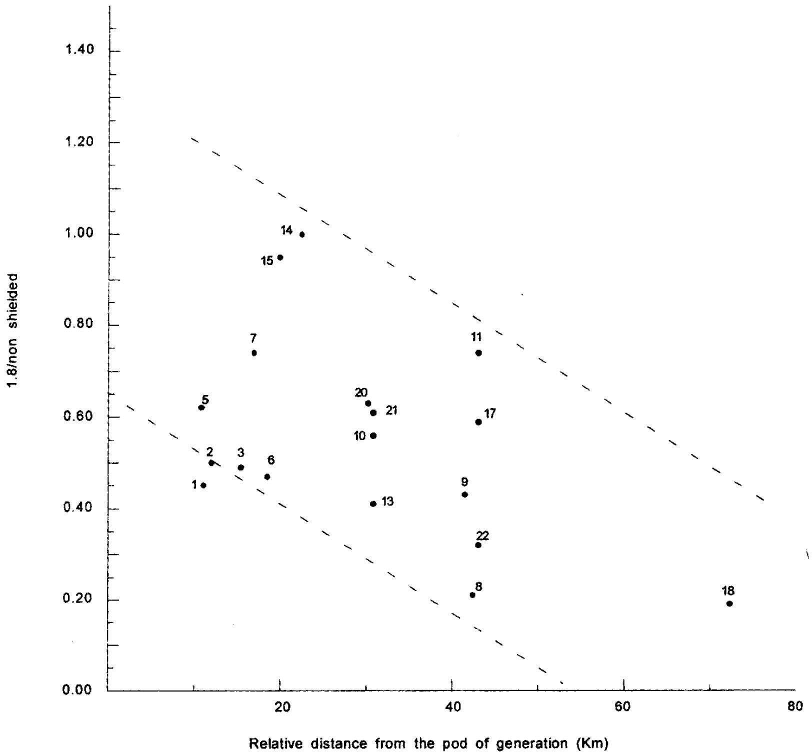

Figure 13. Correlation curve between the relative content of shielded carbazoles and possible distance of migration.

indicates for the Tertiary source rocks a fairly oxic and mainly siliciclastic environment ranging from peat swamp to deltaic, whereas for the Cretaceous source rock the depositional environment is clastic poor, marine-reducing.

4. In the foothills the contribution of the oleanane rich Tertiary phase can be as high as 52 % of the oil.

5. The use of carbazoles as potential indicators of migration distance appears to work to some extent in this area. In general the more migrated oils show higher relative amounts of shielded and partially shielded isomers.

REFERENCES

Cooper M.A., Addisson F.T., Alvarez R., Coral M., Graham R.H., Hayward A.B., Howe S., Martinez J., Naar J., Peñas R., Pulham A.J. & Taborda A. 1995 Basin development and tectonic history of the Llanos Basin, Eastern Cordillera and Middle Magdalena Valley, Colombia. American Association Petroleum Geologists *Bulletin.* **79**(10): 1421-1443.

Droz R.J. & Piggot N. 1995 The geochemistry of the Cusiana field oils. IN: Fourth Latin American Congress on Organic Geochemistry, *Procceedings,* Bucaramanga-Colombia, p.58-66

Ekweozor C.M., Orogun J.I., Ekong D.E.U. & Maxwell J.R. 1979 Preliminary organic geochemical studies of samples from Niger Delta (Nigeria). I. Analyses for shale derivatives. *Chemical Geology*, **27**: 11-29

Ekweozor C.M., Orogun J.I., Ekong D.E.U. & Maxwell J.R. 1981 C24-C27 degraded triterpanes in Nigerian petroleum: Novel molecular markers of source/ input on organic maturation. *J. Geochemical Exploration*, **15**:653-662

Fajardo A.A. 1995 *4 -D Stratigraphic architecture and 3-D reservoir fluid -flow model of the Mirador Formation, Cusiana Field, Foothills Area of the Cordillera Oriental, Colombia.* M.Sc.

Thesis, Colorado School of Mines. 171 p.

Haq, B.U., J. Hardenbol, & P.R Vail. 1978 Chronology of fluctuating sea levels since the Triassic: *Science,* **235**:1156-1166.

Ignatialis L. Schmitter J.M. & Arpino P. 1995 *J. Chromatography* **324**: 87-111

Li M., Larter S.R., Stoddart D.& Bjoroy M. 1992 Liquid chromatographic separation schemes for pyrrolic and pyridine nitrogen aromatic heterocyclic fractions from crude oils suitable for rapid characterization of chemical samples. *Anal. Chem.* **64:**1337-1344

Mello M.R., Telnaes N., Gaglianone P.C., Chicarelli M.I., Brassel S.C. & Maxwell J.R. 1988 Organic geochemical characterization of depositional paleoenvironments in Brazilian marginal basin. *Organic Geochemistry*, **14**: 529-542.

Miller, T. 1979 The geology of the Eastern Cordillera between Aguazul-Sogamoso- Villa de Leiva, part I, **In:** Geological Field Trips, Colombia 1959-1978: Colombian Society of Petroleum Geologists and Geophysicists, Geotec Ltd., Bogota, p.349-396.

Miller D.E. 1994 Crude oils geochemistry and migration history in the Llanos Basin, Colombia.IN: Fourth Latin American Congress on Organic Geochemistry, *Abstracts*, Bucaramanga- Colombia, p.24.

Moldowan J.M., Seifert W.K. & Gallegos E.J. 1985 Relationships between petroleum composition and depositional environment of petroleum source rocks. American Association of Petroleum Geologists, *Bulletin*. **69**:1255-1268.

Moldowan J.M., Sundararaman P. & Schoell M. 1986 Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of S.W. Germany. *Organic Geochemistry* , **10**: 915-926

Moldowan, J.M., Fago, F.J., Lee. C.Y., Jacobson,S.R., Watt,D.S., Slougui, N.E., Jeganathan, A. & Young, D.C. 1990 Sedimentary 24-n-propylcholestane, molecular fossils diagnostic of marine algae. *Science*, **247**: 309-312.

Moldowan J.M., Dahl J., Huizinga B.J., Fago F.J., Hickey L.J., Peakman T.M. & Taylor D.W. (1994) The molecular fossil record of oleanane and its relation to angiosperms. *Science*, **265**:.768-771.

Notestein, F.B., C.W. Hubman, & J.W.Bowler. 1994 Geology of the Barco concession, Republic of Colombia: *Geological Society of America Bulletin*, **55**:1155-1218.

Palmer S.E. & Russel J.A. 1988 The five oil families of the Llanos Basin. IN: III Simposio Bolivariano: Exploración Petrolera de las Cuencas Subandinas. *Procceedings*, Caracas, Marzo 13-16, 1988, p.724-754.

Philp R.P. & Gilbert T.D. 1986 Biomarker distribution in oils predominantly derived from terrigenous source material. **In**: Leythaeuser D. & Rullkotter J., Eds., *Advances in Organic Geochemistry*, 1985, Pergamon Press, p. 73-84.

Rangel A.V., Giraldo B.N., Córdoba F. & Ramón J.C. 1991 Evaluación geoquímica de la Cuenca de los Llanos Orientales. IN: IV Simposio Bolivariano: Exploración Petrolera en las Cuencas Subandinas. *Memorias*, Bogota-Colombia, Marzo 10-13, 1991..1(9):26.

Reyes A. 1996 *Sedimentogy and stratigraphy and its control on porosity and permeability Barco Formation, Cusiana Field, Colombia.* M.Sc. Thesis, University of Reading. 47 p.

Sofer, Z. 1984 Stable carbon isotope compositions of crude oils: Applications to source depositional environments and petroleum alteration. American Association Petroleum Geologists, *Bulletin*, **68**:31-49.

Talukdar, S.,Gallango, ° & M. Chin A-A Ven. 1986 Generation and migration of hydrocarbons in the Maracaibo Basin, Venezuela. An integrated basin study. **In**:. Leythaeuser, D. & Rullkotter, J. Eds, *Advances in Organic Geochemistry.* 1985 Pergamon Press. pp. 261-280.

Tegelaar E.W., Zaugg P., Hegre J. & Rangel A.V. 1995 Petroleum system of the Southern Llanos and Putumayo Basin. IN: VI Congreso Colombiano del Petróleo, Bogotá, 1995

Tissot B.P.& Welte D.H. 1984 *Petroleum formation and occurrence.* Springer-Verlag, New York, 699p.

Volkman, J. P., Alexander, R., Kagi, R.I., & Woodhouse, G.W. 1983 Demethylated hopanes in crude oils and their application in petroleum geochemistry. *Geochimica et Cosmochimica Acta*, .**47:** 785-794.