
Genetic classification of crude oil families in the Eastern Venezuelan Basin

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Abstract

Four families of crude oils were identified in the Eastern Venezuelan Basin (EVB) by analyzing sulfur composition, absolute V and Ni concentrations and V/Ni ratios in whole oils. Source rock depositional conditions for two oil families were inferred using the V/V+Ni versus S diagram and additional GC and GC-MS data support different source rocks with marine and terrestrial organic matter in EVB. Three oil families were recognized from the Orinoco Oil Belt by calculating the V/Ni ratios of biodegraded oils in which n-paraffins are altered. Differentiation of these families, with marine source rock, may respond to regional changes of organic facies in the Cretaceous source rocks towards the east and the west in the Eastern Venezuelan Basin. Also, it was possible to corroborate previous studies pointing to Tertiary terrestrial organic matter source rocks.

Post-accumulation alteration processes introduce important heterogeneities in the saturated hydrocarbon content in crude oils from the Oveja and Ostra fields. Nevertheless, V/Ni ratios are constant for the oils from both fields, indicating a common and unique source rock. The results of this study confirm the reliability of V/Ni ratio parameter for genetic correlation.

Key words: vanadium, nickel, biomarkers, Eastern Venezuelan Basin, crude oil families, Orinoco Oil Belt.

Resumen

Cuatro familias de crudos fueron delimitadas geográficamente mediante el análisis de V, Ni y el cálculo de la relación V/Ni en muestras de crudos. Se infirieron las condiciones de sedimentación de la roca madre para dos familias usando el diagrama V/V+Ni vs S y los datos de GC and GC-MS soportaron la existencia de rocas madres con materia orgánica marina y rocas madres con materia orgánica terrestre. En la Faja petrolífera del Orinoco se delimitaron tres familias mediante la relación V/Ni, medida sobre crudos biodegradados cuyas n-parafinas se encuentran alteradas. La diferenciación de estas familias, con materia orgánica de tipo marino, pudiera responder a cambios laterales (este-oeste) de las facies orgánicas en las rocas madres del Cretácico. También fue posible corroborar estudios previos que apuntan hacia rocas madres terciarias con materia orgánica de origen terrestre.

Procesos de post-acumulación inducen heterogeneidades moleculares en la fracción de hidrocarburos saturados (n-parafinas) en los crudos procedentes de los campos adyacentes Oveja y Ostra. Sin embargo, la relación V/Ni permanece constante en cada caso, indicando una roca madre común, lo cual confirma la confiabilidad de la relación V/Ni para identificar correlaciones genéticas.

Palabras claves: vanadio, níquel, biomarcadores, Cuenca Oriental de Venezuela, Faja petrolífera del Orinoco.

Introduction

Application of intermetallic ratios are very useful and cost effective for genetic classification of crude oils in a sedimentary basin (James 1990; Hamilton and Cameron 1989; Ellrich et al. 1985; Hodgson 1954). They allow oil-source rock correlation and reconstruction of source rock depositional environments (Lewan 1984; Lewan and Maynard 1982).

Thermal stability of the organo-metallic complexes and their biodegradation resistance, water flushing and weathering (Yen 1975; Davis and Gibbs 1975; Constantinides et al. 1959) indicate that metallic ratios in crude oils, especially V/Ni, are mainly determined by the depositional conditions of the source rock (Lewan 1984). Therefore, trace metals are useful for genetic oil groupings in complex basins, where the existence of different source rocks is suspected.

Several giant oil fields are located in the Eastern Venezuelan Basin (EVB), and an important proportion of oil from these fields was affected by extensive biodegradation. Oil families of regional significance in the EVB, were defined by analysing V and Ni contents in 131 crude oil samples with a quick low-cost (screening) method. Representative crude oils of these families were further analyzed by GC-MS to corroborate the preliminary genetic oil groupings and infer their source rock characteristics. The validity of genetic oil classification using V and Ni was demonstrated in two complex adjoining fields where more detailed studies on crude oils indicate a single family.

Methodology

V and Ni determinations were made on whole oils (free of water and sediments), using a Phillips PW-1410 X-ray fluorescence spectrometer furnished with a molybdenum anode. The spectrometer was operated at 60 kV and 20 seconds of sampling time, performing all measurements on the $K\alpha$ signal. The concentration of V and Ni was determined taking into account the mass coefficient of each sample and its sulfur concentration. Detection limits were 1 ppm for V and 0.8 ppm for Ni, the instrumental error for both V and Ni being $\pm 3\%$.

Sulfur was determined by a KEVEX X-ray fluorescence spectrometer, furnished with a secondary source of Ti, with a voltage of 45 kV and 20 seconds of excitation time. Other operating

parameters were 50 % of dead time, 0.9 mA of intensity and a detection limit of 0.2 % in sulfur, the instrumental error being $\pm 7\%$.

Calibration curves were developed with standard crude oils and analyzed by the Sulphate Ashes Method, according to Milner et al. (1952), using a Perkin Elmer, model 560-X60 atomic absorption spectrophotometer.

Specially selected crude oils were separated into saturated hydrocarbon, aromatic hydrocarbon, resin and asphaltene fractions. The asphaltene fraction was precipitated with cold n-heptane and the maltene portion was separated by column chromatography using silica gel/alumina. The saturated and aromatic hydrocarbon fractions and the resins were eluted with n-hexane, toluene and methanol, respectively.

The saturated hydrocarbon fraction was analyzed by gas chromatography (GC) using a Hewlett Packard 5880 chromatograph with a fused-silica cross-linked (methyl silicone) 25 m (0.2 mm internal diameter) column.

Gas chromatography / mass spectrometry (GC-MS) was performed with a Hewlett Packard 5890II chromatograph and a Hewlett Packard 5971 mass spectrometer. Experimental conditions were DB-5, 60 m, 0.25 mm, 0.25 μ column, helium carrier gas, GC-MS interphase at 320 °C, oven program at 160 °C for 5 minutes, 3 °C/min. increment until 325 °C was reached and maintained for 7 minutes. Selected ions were 191, 218, 217, 177, 259, 125, 232, 412, 163, 231.

Crude oil samples were recolected in glass bottles from well head in Jusepin, Orocuai, and Quiriquire fields at the northern part of E.V.B., Nigua, Nipa, Chimire, Soto Este, Limón, Trico, Oficina, Miga, Yopales, Melones, Adas, Dacción, Jobo and Oritupano fields at the Greater Oficina Area and eastern part of Greater Oficina Area, La Ceiba at Greater Anaco Area and Quiamare at northern part of Greater Anaco Area (Fig. 1). Finally, Orinoco Oil Belt crude oils were supplied by geochemical section of INTEVEP S.A.

Geological Setting

The Eastern Venezuelan Basin (EVB) covers an approximate area of 164,000 square kilometers. Hydrocarbons produced range from extraheavy oils to gas and condensates. El Furrial and the Orinoco Belt are two giant fields located in the northern and southern flanks respectively of this basin.

The EVB is typically asymmetric, with a

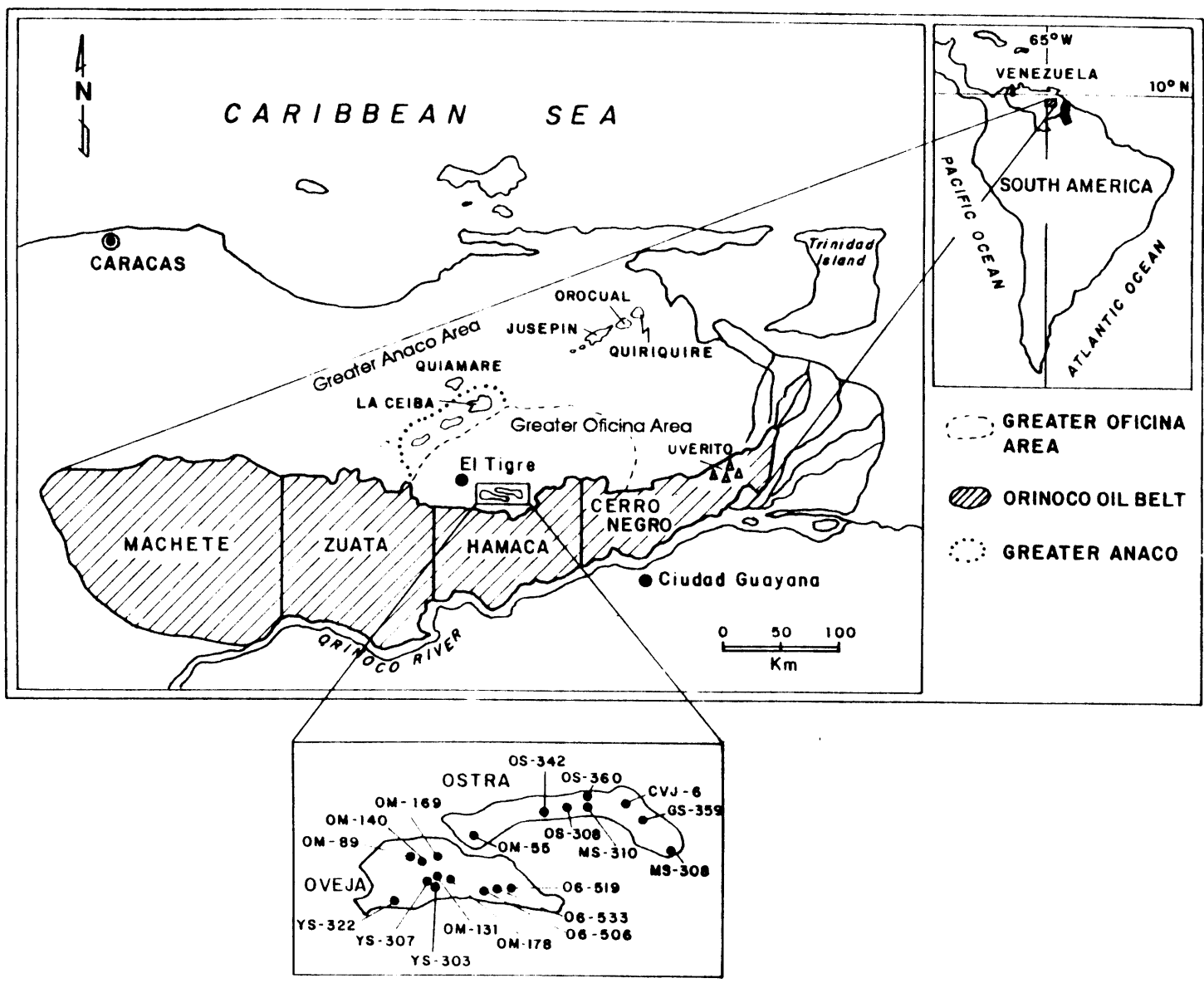


Figure. 1
Geographic location of the study areas and crude oils

compressive northern flank and a passive, tensional southern flank. This basin was a passive margin from Neocomian to Eocene times, when a thick sequence of sediments was deposited on a stable platform. The Guayuta Group was deposited during the maximum transgression in the upper Cretaceous (Cenomanian-Coniacian), and is the principal oil source rock of the basin. This group comprises a thick finegrained carbonate-shale sequence with vertical and lateral variations in organic facies. Terrestrial organic matter and oxidizing environments of deposition increase laterally toward the south and vertically toward the top of the sequence (Talukdar et al. 1987; Alberdi y Lafague 1993, Alberdi et al. 1993).

Based on maturity profiles and basin model

reconstructions, the Guayuta Group seems to have generated hydrocarbons from different kitchens, showing petroleum migration from different fronts southward along the monocline that ascends onto the Guayana Shield (from the northwest, Audemard 1993; from the north, Talukdar et al. 1987, Parnaud 1991; from the northeast, Georges and Socas 1994). During more recent phases of generation, other entrapments occurred within the fold thrust belt.

The principal reservoirs of the basin are the Tertiary systems of alluvial fans and fluvial channels. In the southern flank of the basin (Orinoco Oil Belt and Greater Oficina Area) this thick Tertiary sequence has several sandstones with many interbedded shales (Flores 1988). The Tertiary-

Cretaceous unconformity has been proposed as the principal path of migration for crude oil from north to south (Zamora and Zambrano 1982).

Based on bulk composition, the Eastern Venezuelan Basin contains two types of crude oils. The main family of crude oils is distributed throughout the basin, showing naphthenic-paraffinic characteristics, and is correlated with Cretaceous source rocks (Meneven-Gulf 1982, Audemard et al. 1986, Talukdar et al. 1987). The second family has paraffinic characteristics, being associated with the Greater Anaco Area (Fig. 1) and may be related to Tertiary source rocks which reached adequate maturity close to the Anaco Area (Meneven-Gulf 1982, Audemard et al. 1986)

Results and Discussion

Regional Crude Oil Families

The Vanadium (ppm) vs Nickel (ppm) diagram (Fig. 2) and V/Ni ratios (Table 1) indicate three families with the following characteristics:

The first family, identified as **A**, is defined by the equation $[V] = 2.25 + 3.52 [Ni]$, and has a mean V/Ni ratio of 3.6 (Table 2). Absolute concentrations of V and Ni range from 8 to 561 ppm and 3 to 140 ppm respectively (Table 1). This family includes the crude oils from the northern part of the basin (Jusepín, Orocuál, Quiriquire), most of them coming from the Greater Oficina Area and neighboring fields (Yopales, Melones, Adas, Dacción, Jobo, Oritupano, Miga) and the rest from the east-central part of the Orinoco Oil Belt; Hamaca area (Figs. 2, 3).

Trace metals are associated to resins and asphaltenes in the crude oil (Yen 1975). The relative concentration of these fractions is dependent, among other geochemical processes, of maturity of oils and post-accumulation processes into the pool. Absolute concentration of trace metals in family **A** (Fig. 2), probably is related to maturity changes within a wide geographical distribution of the samples.

The second family, identified as **B**, is defined by the equation $[V] = -48.5 + 5.55 [Ni]$, and has a mean V/Ni ratio of 5.21 (Table 2). Absolute concentrations of V and Ni range from 507 to 1022 ppm and from 105 to 181 ppm respectively, considerably higher than the world average for V (63 ppm) and Ni (18 ppm) (Tissot and Welte 1978). This family includes the western crude oils from the Zuata and Machete areas located

in the western Orinoco Belt (Figs. 2, 3). Most of these samples are heavy biodegraded oils with different intensities of alteration (Mendez et al. 1994). Variations in absolute concentration of trace metals (Fig. 2) are probably related with biodegradation processes.

The third family, identified as **C**, is defined by the equation $[V] = -23.75 + 0.93 [Ni]$, and has a mean V/Ni ratio of 0.73 (Table 2). Absolute concentrations of V and Ni range from 54 to 91 ppm and from 81 to 121 ppm respectively (Table 1). This family includes heavy crude oils from the Uverito area, located in the far eastern part

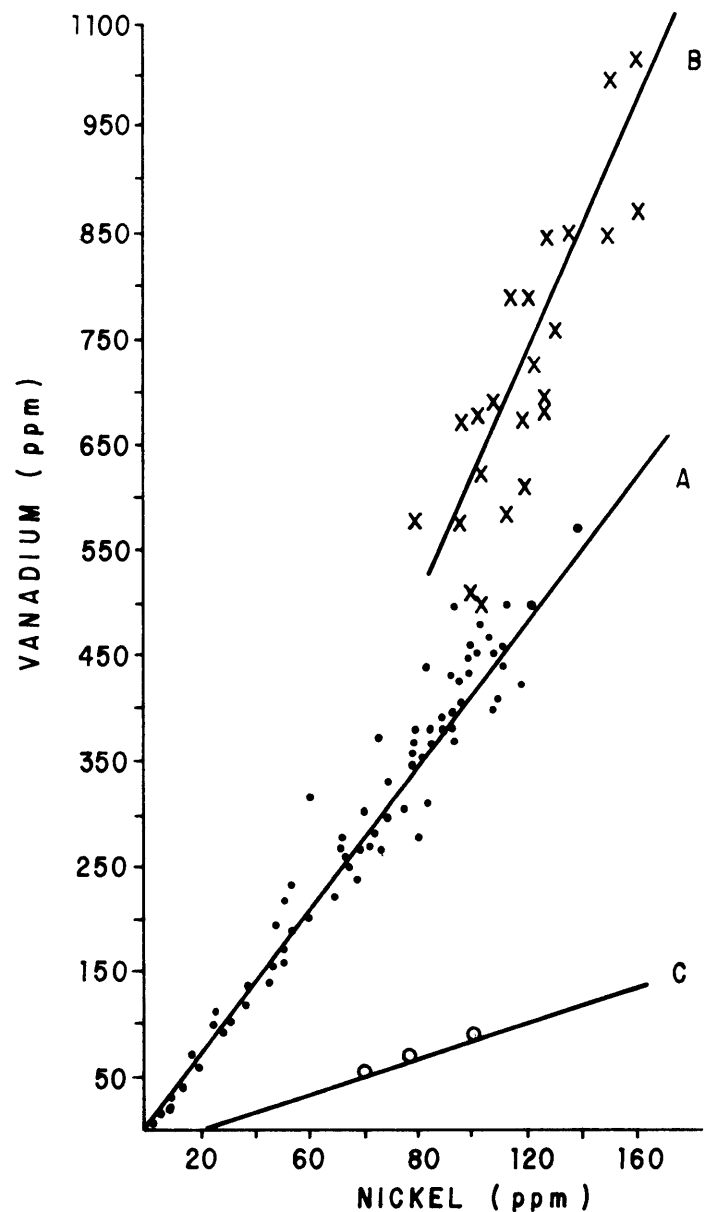


Figure 2

Vanadium vs nickel concentrations in whole oils, discrimination of families

FAMILY	A	B	C	D
n	98	22	3	23(1)
Equation	$[V]=2.25+3.52[Ni]$	$[V]=-48.5+5.55[Ni]$	$[V]=-23.8+0.93[Ni]$	<1
Wx (V/Ni)	3.6	5.2	0.73	0.3
Wx + 2s	2.7 < w < 4.5	4.2 < w < 6.2	0.6 < w < 0.8	0 < w < 0.7
Confidence	3.5 < < 3.7	5.0 < < 5.4		
limit (90%)				
V (range,ppm)	561-8	1022-507	91-54	6.9-0
Median	286	727	65	0.5
Ni (range,ppm)	140-3	181-105	121-81	14-1.1
Median	77	140	99	2.1
%S (range,%)	6.8-0.7	6.4-4.1	2.1-1.4	0-1.0
Median	3.4	5.1	1.7	
Lewan's Reg.	III	Biodegr.	Biodegr.	I+II
W = mean s = standard deviation			= population mean	
(1) Data from Simoza et al. 1985				

Table 2

Statistical parameters of crude oil families defined by vanadium and nickel concentrations. Sulfur concentrations averages in each family

	Ts/Tm (1)	C35 Hop. Index (2)	Oleana. Ind. (3)	C29/C30 Hop (4)	22S (5)	Diast. Ind. (6)	20 S (7)
Family A	0.31	13%	5%	0.94	62%	44%	50%
Family B	0.32	14%	0%	0.83	57%	33%	54%
Family C	0.79	12%	12%	0.67	58%	68%	51%
Family D	0.22(?)	0%	51%	0.63	59%	57%	low conc.

(1) Ts/Tm = 18 α (H) trisnorhopane/ 17 α (H) trisnorhopane

(2) C₃₅-homohopane index = C₃₅ homohopane (20S+20R)/C₃₁₋₃₅ homohopanes (22S+22R) x 100

(3) Oleanane index = 18 α oleanane/ C₃₀ $\alpha\beta$ hopane x 100

(4) C₂₉ $\alpha\beta$ norhopane/ C₃₀ $\alpha\beta$ hopane

(5) 22S = C₃₂ hopane (22S) / C₃₂ hopane (22S) + C₃₂ hopane (22R) x 100

(6) Diasterane index = C₂₇ $\alpha\beta$ diasterane (20R) + C₂₇ $\beta\alpha$ diasterane (20S) x 100/ C₂₇ $\alpha\alpha\alpha$ diasterane (20S) + C₂₇ $\alpha\alpha\alpha$ diasterane (20R).

(7) 20S = C₂₉ $\alpha\alpha\alpha$ (20S) / C₂₉ $\alpha\alpha\alpha$ (20R) + C₂₉ $\alpha\alpha\alpha$ (20S)

Table 3

Biomarker ratios and indices for each family of oils and Guayuta Group bitumen.

Sample	Depth	C30hop/C29ste	%C27/%C29 ster	C23-3/C24-3	C23-3/C21-3	%22S	%bb	%20S
OS-342	4450'	1.61	1.05	2.16	3.41	57	60	63
MS-308	4169'	1.40	1.01	1.96	3.20	60	64	77
Ys-322	3453'	1.50	1.05	1.93	3.10	56	59	56
OM-131	3362'	1.40	1.15	1.76	2.82	53	59	60

Table 4

Biomarker ratios for selected crude oils from Oveja and Ostra fields.

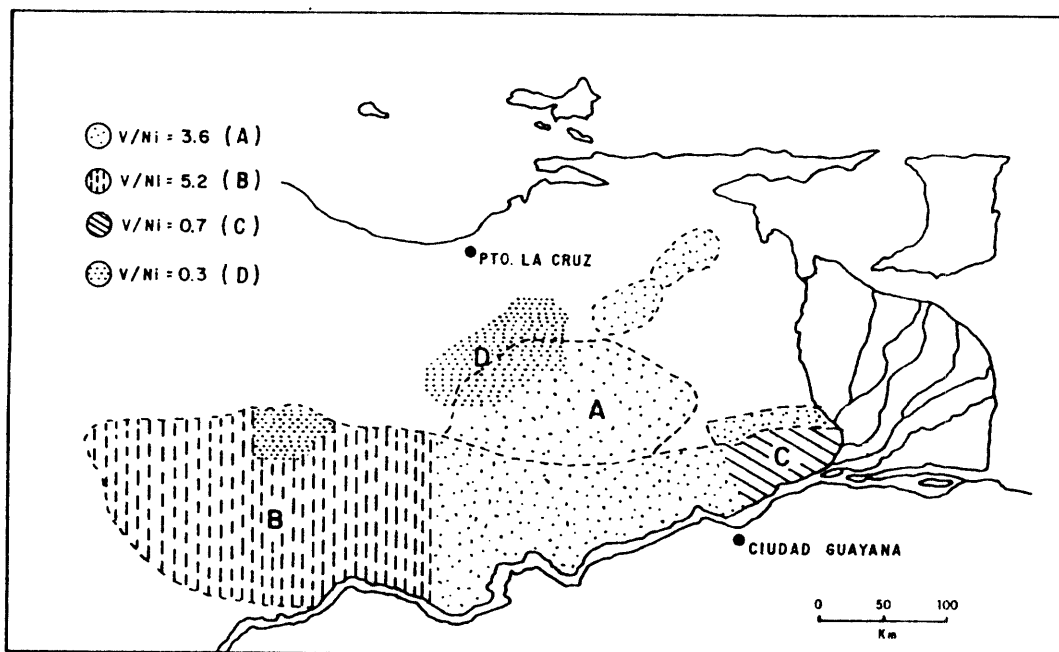


Figure.3
Geographic location of genetic families in the Eastern Venezuelan Basin

of the Orinoco Oil Belt (Figs. 2, 3). They are located in an exploration frontier area near the Orinoco delta.

The fourth family, identified as *D* and characterized by very low V and Ni concentrations and a typical mean V/Ni ratio of 0,3 ppm (Table 2), was defined for the first time by Simoza et al. (1985) in Greater Anaco Area. Absolute concentrations of V and Ni lower than 6.9 ppm and 14 ppm respectively were found. Crude oils coming from La Ceiba and Quiamare fields (Figs. 1, 3) evidenced V and Ni concentrations below the detection limit of the X-ray fluorescence apparatus. This family is associated with the Greater Anaco area fields (Figs. 1, 3) and with two crudes (3-8X and 3-9X) from the northern part of the Machete area (Fig. 3) the latter having similar metal content levels but showing biodegradation in their n-paraffins. Cassani (1985) propose a mix of two types of crude oils to explain these two different samples within Machete area.

Sulfur concentrations for families A, B and C are 0.7-6.8%, 4.1-6.8% and 1.4-2.1%, respectively. For family D, it was always under 1% (Table 1, 2). For the heavily biodegraded crude oils from the Orinoco Oil Belt, the original sulfur concentration must undoubtedly have been lower than the level currently found.

The V/V+Ni ratios and %S of a non

biodegraded subset of family A oils, a non biodegraded subset of the D oils family, of similar maturity, were plotted on a V/V+Ni vs % S diagram (Fig. 4). This diagram was first proposed by Lewan (1984) using a large set of oils from different basins in the world, in order to infer the depositional conditions (Eh-pH) of the source rocks from which the oils were expelled.

Regime I (Fig. 4) represents basic conditions ($\text{pH} > 7$) and $\text{Eh} > 0,2$ under which vanadyl cations would not be available for metallation, conversely nickelous cations would be available for metallation and the proportionality of vanadium to nickel would be low in the organic matter ($\text{V/Ni} < 1$) and its later expelled crude oil. The sulfide ion availability is likely to be hindered by sulfide oxidizing bacteria or the precipitation of iron sulfides.

Regime III represents the most reducing conditions. The availability of nickelous cations would be reduced by the formation of aqueous sulfide complexes, yet vanadyl and trivalent vanadium hydroxide cations are available. Crude oils expelled from rocks deposited in Regime III are expected to have high sulfur contents in addition to high V/Ni ratios (Lewan 1984). Regime II represents mixed conditions between the I and III regimes previously mentioned.

Source rock of family A oils (Regime III) was deposited under most reducing environments (Fig. 4). However, the distribution of the samples shows

Vanadium (ppm), nickel (ppm), sulfur (%) and V/Ni ratios in the crude oils analyzed in the Eastern Venezuelan Basin.

Table 1

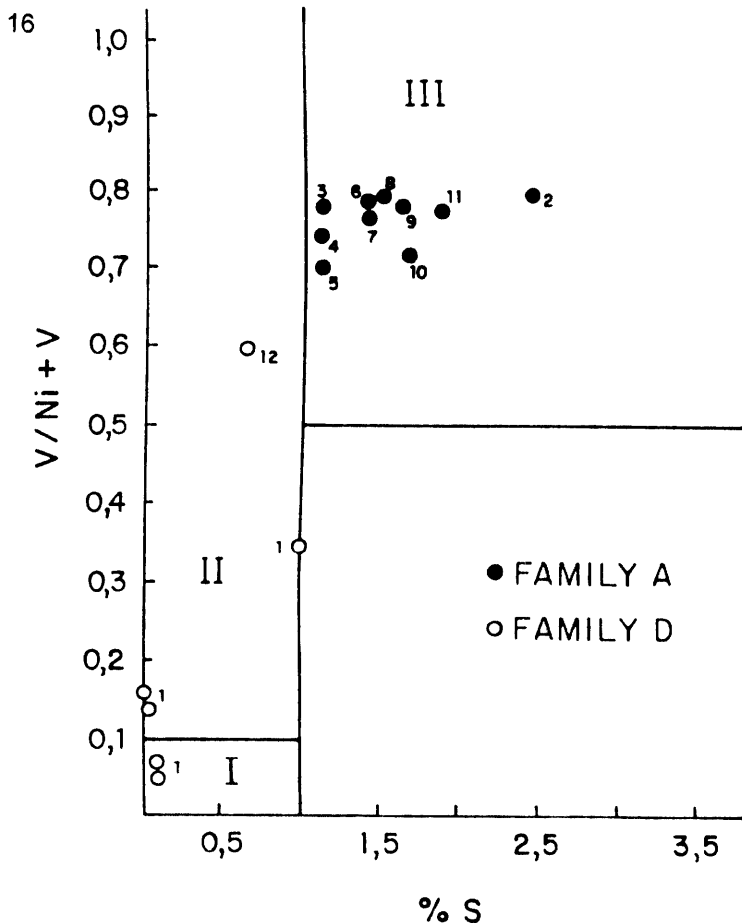
FAMILY A						FAMILY A					
sample	field	V (ppm)	Ni (ppm)	V/Ni	%S	Sample	field	V (ppm)	Ni (ppm)	V/Ni	%S
CN-161	Cerro Negro	473	127	3.7	4.5	CAZ-504	Caracoles	28	5	5	0.7
CN-96	Cerro Negro	484	125	3.9	5.2	M-10-14	Mata	22	7	3.3	0.8
CNX-11	Cerro Negro	440	120	3.7	4.5	SCJ-110	Freites	8	3	3.3	0.7
CNX-15	Cerro Negro	453	124	3.6	4	Casma-6	Casma	39	12	3.3	0.8
CN-121	Cerro Negro	418	118	3.5	3.9	JU-254	Jusepin	24	7	3.3	1.1
CNX-34	Cerro Negro	443	134	3.4	4.4	JU-278	Jusepin	40	14	3	1.4
CNX-50	Cerro Negro	460	123	3.7	3.7	JU-277	Jusepin	19	8	2.3	1.1
CN-38	Cerro Negro	505	123	3.9	5	JU-454	Jusepin	64	19	3.4	1.4
CN-75	Cerro Negro	436	122	3.6	4.4	JU-256	Jusepin	23	6	2.9	1.4
CNX-12	Cerro Negro	426	122	3.5	4.7	JU-453	Jusepin	63	20	3.1	1.4
GG-8	Guara Oeste	212	60	3.5	1.8	JU-246	Jusepin	19	6	3.3	1.7
GS-25	Guara Oeste	72	17	4.2	1.1	OS-360	Ostra	268	76	3.5	2.5
GG-12	Guara Oeste	8	3	3.1	0.7	OM-55	Ostra	156	44	3.6	1.9
OS-322	Trico	309	96	3.2	3.9	MS-310	Ostra	327	94	3.5	4
OG-463	Ofic. Central	322	63	4.9	3.4	MS-308	Ostra	296	91	3.3	4.4
GM-44	GM-4	106	30	3.6	1.5	OS-342	Ostra	373	115	3.2	4.9
MG-581	Miga	286	85	3.3	3.3	OS-308	Ostra	408	110	3.7	5.1
Ys-50S	Yop. Central	234	48	5	3	OM-169	Oveja	336	90	3.7	3.6
Ys-439	Yop. Sur	304	87	3.5	3.1	OM-178	Oveja	159	49	3.2	2
MM-437	Melones	315	93	3.4	2.9	OM-140	Oveja	266	88	3.0	3.9
Ys-64	Yop. Central	93	28	3.3	1.7	OG-533	Oveja	272	82	3.3	3.9
MM-447	Melones	457	133	3.4	5.4	YS-307	Oveja	241	79	3.1	3.5
MG-613	Melones	364	104	3.5	3.9	OG-519	Oveja	297	92	3.2	3.9
ADM-323	Adas	396	131	3	3.7	YS-303	Oveja	223	69	3.2	3.3
ADM-358	Adas	423	140	3	3.9	OM-139	Oveja	107	30	3.6	1.3
LG-247	Daccion	137	37	3.7	1.9	YS-322	Oveja	193	54	3.6	2.3
GS-122	Daccion	277	76	3.6	3.2	OM-131	Oveja	209	59	3.5	3.1
NZ-118	Nipa	40	10	4	1	CVJ-6	Ostra	281	73	3.9	2.9
JOA-94	Jobo	444	125	3.6	4.3	OG-506	Oveja	303	81	3.7	3.3
ORM-67	Oritupano	312	105	3	3.8	GS-359	Oveja	362	102	3.6	3.3
						OM-120	Oveja	375	112	3.30	4

FAMILY	A	B	C	D
n	98	22	3	23(1)
Equation	$[V]=2.25+3.52[Ni]$	$[V]=-48.5+5.55[Ni]$	$[V]=-23.8+0.93[Ni]$	<1
Wx (V/Ni)	3.6	5.2	0.73	0.3
Wx + 2s	2.7 < w < 4.5	4.2 < w < 6.2	0.6 < w < 0.8	0 < w < 0.7
Confidence limit (90%)	3.5 < μ < 3.7	5.0 < μ < 5.4		
V (range,ppm)	561-8	1022-507	91-54	6.9-0
Median	286	727	65	0.5
Ni (range,ppm)	140-3	181-105	121-81	14-1.1
Median	77	140	99	2.1
%S (range,%)	6.8-0.7	6.4-4.1	2.1-1.4	0-1.0
Median	3.4	5.1	1.7	
Lewan's Reg.	III	Biodegr.	Biodegr.	I+II
<p>W = mean s= standard deviation (1) Data from Simoza et al. 1985</p> <p style="text-align: right;">μ = population mean</p>				

Table 1 continuación

Table 1 continuación

FAMILY A						FAMILY B					
sample	field	V (ppm)	NI (ppm)	V/NI	%S	sample	field	V (ppm)	NI (ppm)	V/NI	%S
QQ-652	Quiriquire	273	83	3.3	2.08	NZZ-25	Zuata	684	140	5.1	5.8
QQ-641	Quiriquire	177	49	3.6	2.08	SDZ-4	Zuata	507	115	4.4	5.3
QQ-77	Quiriquire	99	26	3.7	1.36	NZZ-125	Zuata	687	147	4.7	6.1
QQ-349	Quiriquire	133	37	3.6	1.6	IZZ-150	Zuata	616	140	4.7	6.1
QQ-599	Quiriquire	158	45	3.5	1.6	NZZ-19	Zuata	701	147	4.8	6.3
ORS-30	Orocual	383	106	3.6	3.7	IZZ-40	Zuata	767	148	5	6.4
ORC-24	Orocual	221	51	4.3	1.8	SDZ-86	Zuata	511	120	4.2	5.2
ORS-13	Orocual	109	26	4.2	1.7	SDZ-78	Zuata	590	133	4.1	5.8
ORC-13	Orocual	241	63	3.8	2.2	MCH-7-16	Machete	679	118	5.7	4.1
ORS-6	Orocual	38	9	4	1.3	MCH-7-9	Machete	1022	181	5.7	5.7
ORS-34	Orocual	197	49	4.1	1.5	MCH-1-2	Machete	875	180	4.9	6
MFL-1s	Hamaca	427	116	3.7	4.3	MCH-7-1	Machete	798	135	5.9	4.4
MFL-6S	Hamaca	561	139	4	6.8	MCH-12-6	Machete	626	124	5.1	4.6
MFL-50-S	Hamaca	384	99	3.9	3.8	MCH-12-4	Machete	727	140	5.2	4.6
MFL-38-S	Hamaca	388	115	3.4	3.5	MCH-11-2	Machete	679	123	5.6	4.2
MFB-48	Hamaca	353	106	3.3	3.7	MCH-8-4	Machete	583	105	5.6	4.1
MFB-37	Hamaca	302	93	3.3	4	MCH-6-5	Machete	853	156	5.5	5.4
MFB-14	Hamaca	380	110	3.5	3.9	MCH-11-6	Machete	852	170	5	5.6
MFA-31	Hamaca	458	130	3.5	5.2	MCH-10-2	Machete	693	130	5.3	4.6
MFH-3	Hamaca	419	124	3.4	4.3	MCH-7-3	Machete	853	147	5.8	5.1
MFF-3S	Hamaca	372	102	3.6	4.3	MCH-7-7	Machete	1000	169	5.9	5.6
MFD-5	Hamaca	386	112	3.5	4.6	MCH-6-2	Machete	795	140	5.7	4.5
MFK-1S	Hamaca	407	114	3.6	4.5	FAMILY C					
MFI-3S	Hamaca	400	116	3.4	5.1	Sample	field	V (ppm)	NI (ppm)	V/NI	%S
SDZ-43	Zuata	460	122	3.8	5.2	UV-142	Uverito	65	99	0.7	1.7
NZZ-32	Zuata	375	88	4.3	4.2	UV-202	Uverito	54	81	0.7	1.4
SDZ-61	Zuata	370	106	3.5	4.4	UV-164	Uverito	91	121	0.8	2.1
NZZ-29	Zuata	432	114	3.8	4.8	FAMILY D					
SDZ-64	Zuata	499	125	4	5	Sample	field	V (ppm)	NI (ppm)	V/NI	%S
NZZ-1	Zuata	125	38	3.4	2.5	LCV-3	Ceibita	1.8	2.4	<1	0.6
LG-223	Daccion	140	46	3.1	2	LCV-46	Ceibita	<1	<0.8	n.d	0.3
OG-462	Ofic. Central	253	77	3.3	4	CG-23	Ceiba	<1	<0.8	n.d	<0.2
NS-601	Nigua	86	25	3.5	1.8	CG-25	Ceiba	<1	<0.8	n.d	<0.2
NS-605	Nigua	86	23	3.7	1.7	CG-43	Ceiba	<1	<0.8	n.d	<0.2
OZ-312	Chimire	39	11	3.6	1.8	CG-13	Ceiba	<1	<0.8	n.d	<0.2
SM-15	Soto Este	15	3	5	0.9	MCH-3-8	Machete	<1	8	<1	2(?)
LM-851	Limon	146	36	3.9	2.4	MCH-3-9	Machete	<1	8	<1	0.8



(1) Data from Simoza et al. (1985)

Figure 4
Diagram of V/V+Ni vs % S, showing depositional environments on source rocks

variations in the physicochemical conditions of depositional environment of source rock (variations in V/Ni+V ratios), maturity, and probably the post-accumulation process (changes of %S). More oxidizing conditions could be inferred for family D, because all the samples of this family with detectable V and Ni concentrations fall in regime I and II. Supporting the conclusions from Figure 4, Pr/Ph ratios in family A oils are close to one, indicating reducing environments (Fig. 5), while Pr/Ph ratios > 4 in family D oils show oxidizing environments (Fig. 5).

The GC analyses show chromatograms of family D oils with an important contribution of terrestrial organic matter as evidenced by the high concentrations of n-paraffin

between C₂₄ and C₃₂. Family A oils, on the other hand, show predominant C₂₀-C₂₆ n-paraffins and a hump of naphthenes, supporting predominant contribution of marine organic matter (Fig. 5).

GC-MS analyses of a crude oil produced in La Ceiba field (Figs. 1 and 6), representative of family D, show very low quantities of steranes (the C₂₁ sterane being absent), very low quantities of triterpanes, and a remarkable signal of 18 α (H)oleanane. These results support crude oil generation from organic matter with a high terrestrial component; the abundance of 18 α (H)oleanane pointed to Tertiary source rocks (Moldowan et al. 1994). The high diasterane index (Table 3) presumably indicates a clastic lithology. All of these biomarker characteristics were found in Tertiary source rocks analysed in the northcentral part of the basin (Tocco et al. 1993) and support a good correlation between paraffinic crude oils in the Greater Anaco Area and organic matter in Tertiary source rocks analyzed in previous work of Meneven-Gulf (1982) and Audemard et al. (1986).

Oils representative of family A, from Oveja, Ostra fields and Hamaca area in the Orinoco Oil Belt show very different distributions of steranes and terpanes. High sterane concentrations, complete signatures of triterpanes and high C₂₁ steranes, support marine organic matter in the original source rock (Figure 6). Also, low signals of diasteranes (Table 3) and high sulfur content (Table 2) in these samples indicate marine source rocks, with carbonate lithology.

Hamaca area in the Orinoco Oil Belt belongs to family A and V and Ni analyses define two additional families: Family C in Uverito Area (Figs. 2, 3) and family B in the Machete area (Figs. 1, 2, 3). The oils of these areas are all biodegraded

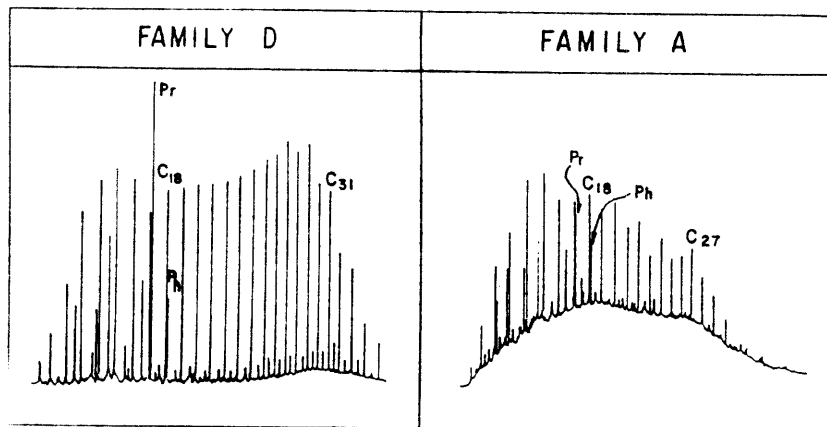
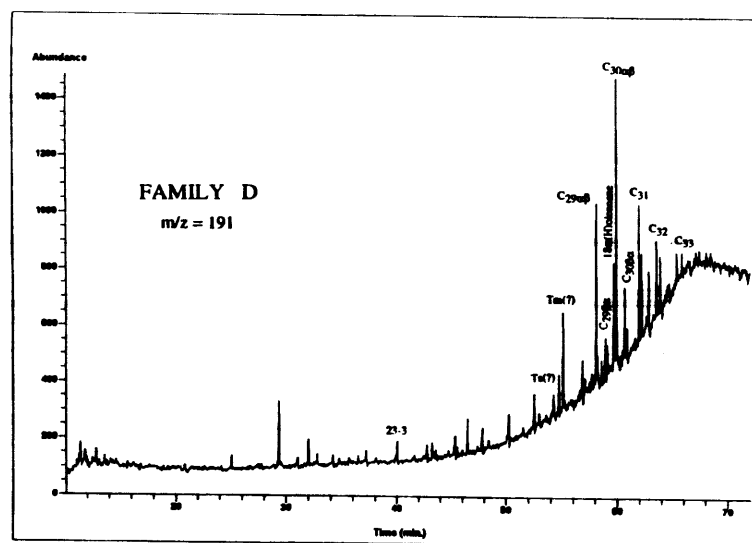
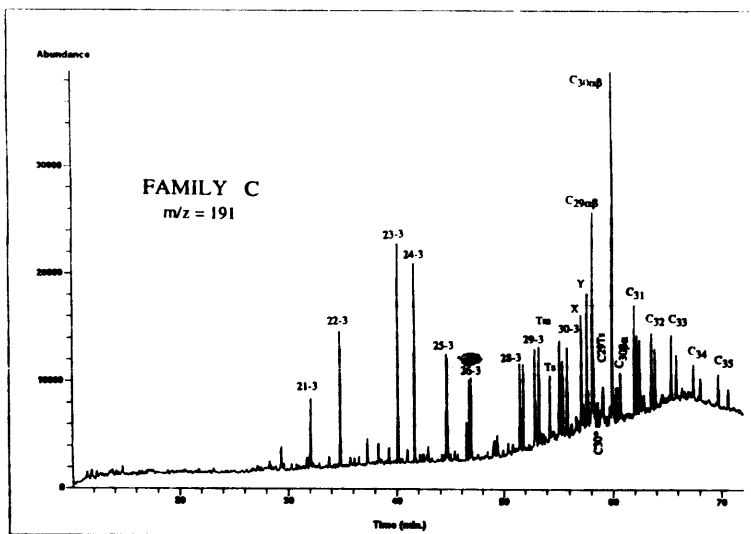
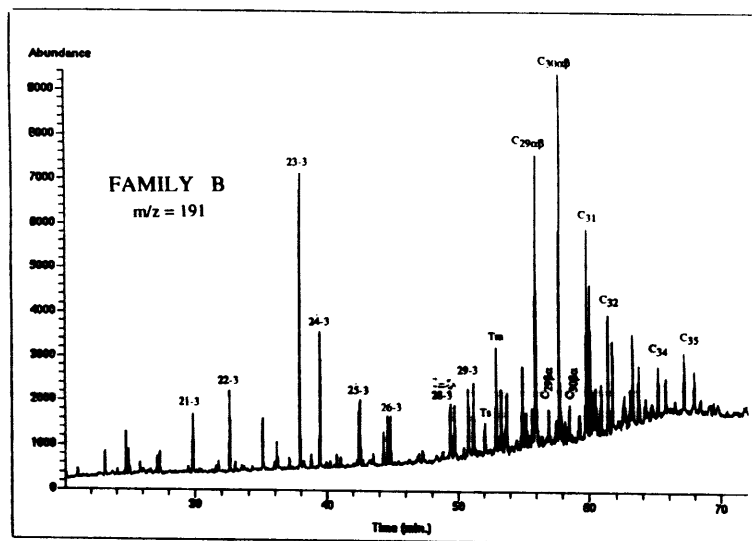
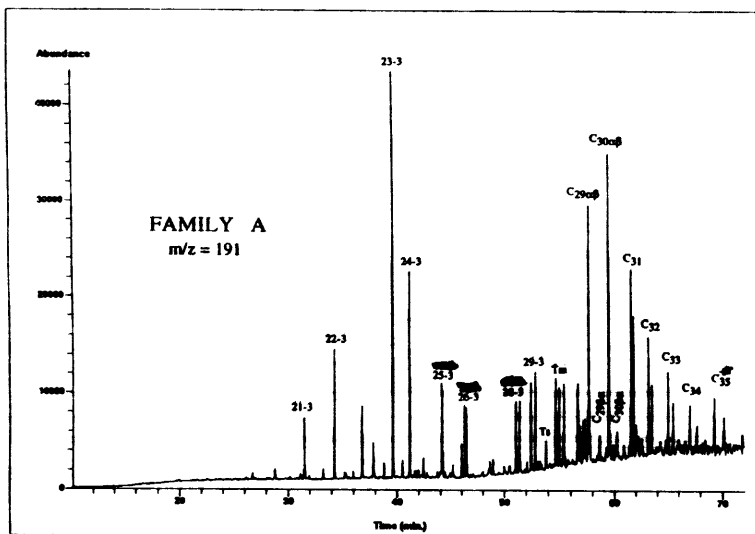


Figure 5
Gas chromatograms showing n-paraffin distribution, pristane and phitane in selected oils from Family A and Family D.

Figure 6
Mass chromatograms ($m/z=191$) of selected oils from each family



in several intensities. Family B in the Machete area was previously examined by means of GC-MS on pyrolyzates of asphaltenes (Cassani and Eglinton 1991). Previous studies of Cassani (1985) point to a different genetic origin for this group of oils and the V/Ni ratios in this study corroborate this conclusion and show that these crude oils are mixed with family A in the Zuata area.

High V/Ni ratios (Table 2) and high C_{35}/C_{34} hopane ratios (Fig. 6) in family B, indicate that the source rock depositional environment was anoxic or euxinic (Peters and Moldowan 1991). Trace metals studies on carbonate rocks of the Guayuta Group (Alberdi and Lafargue 1993) found similar V/Ni ratios (approximately 5) in the bottom of this sedimentary sequence, similar to V/Ni ratio of family B, where an euxinic depositional condition was well established. The Guayuta Group towards the top was deposited under less reducing conditions and V/Ni ratios are between 1.7 and 4, similar to family A characterized by a mean of V/Ni of 3.6. It indicates that the oils from families A and B were generated by the same source rock, but with somewhat different depositional conditions. The last conclusion is also supported by GC-MS data (Table 3). Oils from both families have similar Ts/Tm ratios, similar C_{35} homohopane indices, low diasterane indices, high $C_{29} \alpha\beta$ hopane/ $C_{30} \alpha\beta$ hopane. Biomarker maturity ratios also indicate a similar maturity (generated in early stages).

Based on the geochemical evidence and geographic distribution, both the family B oils in the Machete area (Fig. 3) and the family A oils in the central part of the Orinoco Oil Belt appear to have been generated by the same Guayuta source rock, located toward the north of the basin, with few differences in the organic facies. Family B was probably generated from kitchens in the northwest of the basin (Audemard 1993) and family A from kitchens in the north of the basin (Talukdar et al. 1987).

Lateral variations in organic facies from west to east, reflecting minor changes in depositional conditions may explain the V/Ni ratio changes from family B to family A. V/Ni ratios and biomarker parameters also indicate that family B was generated by a more carbonate-rich source rock, with more marine organic matter deposited under more reducing conditions than family A.

The Uverito oil family, located in a frontier exploration area to the east of the Orinoco Oil Belt (Fig.1), exhibit several molecular differences compared to families A and B. The Uverito oils are characterized by high diasterane index and high Ts/Tm which may indicate more clastic source

rock lithology (Table 3). Several crude oils have little quantities of $18\alpha(H)$ oleanane and Uverito crude oils have a little more concentrations than some samples from families A and B, additionally, Uverito samples have 30 nor-neohopane ($C_{29}Ts$), 17 $\alpha(H)$ -diahopane (C_{30}^*), more tricyclic C-30 terpanes, and two additional compounds X and Y, that we have tentatively identified as C-31 tricyclic terpanes and bisnorhopane. Another organic facies from Guayuta Group could generate this group of oils, but Cretaceous and Tertiary source rocks are not detailed characterized at this time.

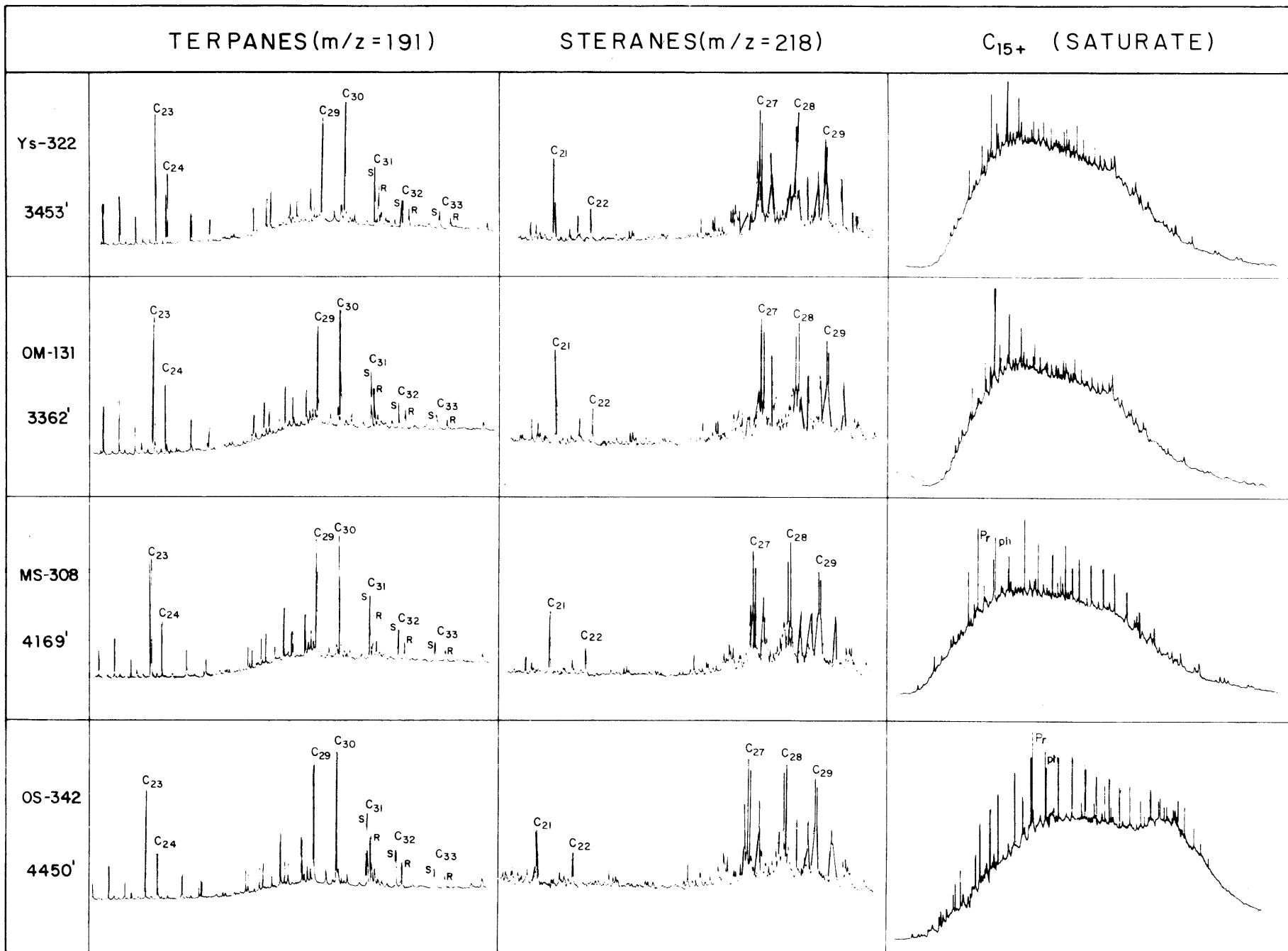
Vanadium and nickel distributions in the Oveja and Ostra crude oils.

The Oveja and Ostra fields are located in the Greater Oficina Aréa (Fig. 1); their reservoirs are Miocene deltaic sands intersected by east-west normal faults (Gonzalez de Juana et al. 1980). Twenty crude oils were sampled from different producing intervals. Similar distributions of steranes and terpanes ($m/z=191$ and $m/z=217$, Fig. 7) and specific $C_{30}\alpha\beta$ hopane/ C_{29} sterane and % $C_{27}/\%C_{29}$ ratios (Table 4) seem to indicate that the oils from the Oveja and Ostra fields belong to the same family and were generated by the same source rock.

GC analyses shows preferential removal of n-paraffins in the most shallow reservoirs and these data suggest effects of biodegradation of oils toward de upper reservoirs (Fig. 7). Vanadium and nickel are preferentially associated with NSO compounds and asphaltenes which appear to be fairly resistant to bacterial attack. When biodegradation proceeds, preferential removal of alkanes could increase the relative concentration of trace metals (ej. OG-169, OG-506, Fig. 8) however, the V/Ni ratios are constant in all the crude oils analyzed in the Oveja and Ostra fields indicating a single source rock (Table 1) according to biomarker ratios (Table 4), nevertheless post-accumulation process.

The increasing trend of vanadium and nickel with depth (Fig. 8) is not clearly explained by biodegradation and suggest additional processes controlling the molecular heterogeneities of the petroleum in its reservoirs. Slight differences in biomarker ratios (C_{23-3}/C_{24-3} , C_{23-3}/C_{21-3} , %22S, %bb and %20S) could be interpreted like slight differences in maturity or organic facies in the same source rock, actually related to inefficient mixing of different oil pools and successive petroleum charges from Cretaceous-Tertiary unconformity.

Figure 7
 Mass chromatograms ($m/z=191$ and $m/z=218$) of oils from Oveja And Ostra fields at different depths in the reservoirs



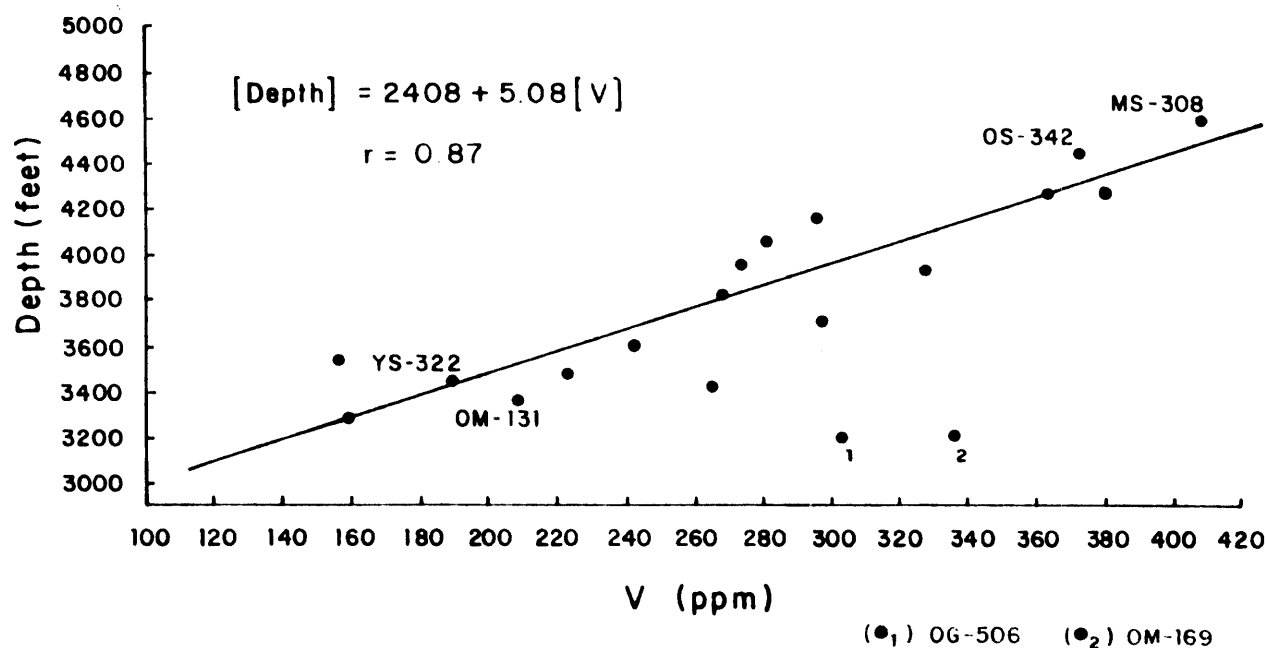


Figure 8
Vanadium concentration (ppm) in whole oils from Oveja and Ostra fields vs depth of the sampling in the reservoirs.

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Conclusions

*V/Ni ratios define four genetic families of crude oils in the Eastern Venezuelan Basin.

*V, Ni and S contents allow the identification of two depositional environments in the source rocks. GC and GC-MS data support very dissimilar organic matter characteristics. Two families (family A V/Ni=3.6 and family B, V/Ni=5.2) were generated from anoxic-euxinic source rock, most likely, Upper Cretaceous but with somewhat different organic facies. Family C in Uvero area (V/Ni=0.73) could be generated from another organic facies with more terrestrial organic matter content. Family D with low concentrations of V and Ni (V/Ni=0.3) support oxic conditions in the environment of deposition of the organic matter and GC-MS data support previous studies which correlate this group of oils with a Tertiary terrestrial source rock.

The neighbouring Oveja and Ostra fields

have biodegraded crude oils, nevertheless V / Ni ratios still maintain the original genetic grouping and variations in V and Ni concentrations are probably related to inefficient mixing of different oil pools.

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