



Vanadium, nickel and sulfur in crude oils and source rocks and their relationship with biomarkers: Implications for the origin of crude oils in Venezuelan basins



Liliana López*, Salvador Lo Mónaco

Instituto de Ciencias de la Tierra, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela

ARTICLE INFO

Article history:

Received 27 May 2016

Received in revised form 6 November 2016

Accepted 22 November 2016

Available online 6 January 2017

Keywords:

Vanadium

Nickel

Sulfur

Crude oil

Source rock

Saturated biomarkers

Venezuelan basins

ABSTRACT

This work presents a study of vanadium, nickel and sulfur concentrations and biomarkers in a suite of crude oils and source rocks from three Venezuelan basins (Maracaibo and Eastern basins and Barinas sub-basin). Crude oils range from unaltered to altered by biodegradation, and source rocks are characterized by having different kerogen types (Type II, III or IV) and maturity levels (early mature to post-mature). Vanadium, nickel and sulfur concentrations, V/Ni or V/(V + Ni) and saturate biomarkers were used to classify the oils and source rocks based on inferred paleo-redox environment, lithology and maturity of the source rock. Oils are classified into five groups based on V/Ni ratios; they appear to be related to variations in the paleo-redox environment (from suboxic-dysoxic to anoxic-suboxic) of source rocks with variable lithological composition and organic matter input, regardless of their maturity or biodegradation level. These five groups are also classified based on biomarkers related to maturity, organic matter type, paleo-redox environment and source rock lithology. In source rocks, vanadium, nickel and sulfur concentrations, together with V/Ni or V/(V + Ni) ratios, provide information about the paleo-redox environment and are related to lithology, regardless of their maturity. These results also indicate variable paleo-redox conditions during the sedimentation of Venezuelan source rocks. All this suggests that, while the main source rocks in Venezuelan basins are well established, there are still uncertainties regarding their lateral and vertical variations in organic and inorganic facies and paleo-redox conditions. The presence of other source rocks contributing to the accumulation of hydrocarbons in the Venezuela basins is also a possibility.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

For decades, the study of trace metals (such as vanadium (V) and nickel (Ni)) in crude oils and source rocks (bitumen, kerogen) has been of great interest to the field of petroleum geochemistry. V and Ni are the most abundant trace metals in crude oils, bitumen and kerogen. The association of these elements with organic matter in organometallic complexes with porphyrin-type structures is well established, although non-porphyrin tetrapyrrole complexes such as pseudo-aromatic and highly aromatic compounds can also be present (Filby, 1975, 1994; Lewan and Maynard, 1982). The association of V and Ni with organic matter depends on several factors related to diagenesis, including possible biological sources or

the incorporation of water or sediment. This incorporation is controlled by paleo-redox conditions (pH and Eh) in the sedimentary environment and organic matter type, the latter of which is related to the formation of organometallic complexes (Lo Mónaco et al., 2002).

The abundance and distribution of V and Ni have been studied here in order to determine their application in interpreting the geochemical processes associated with the paleo-redox environment during source rock formation and petroleum generation and migration, as well as their application in oil–oil and oil–source rock correlation studies (Curiale, 1985; Branthaver and Filby, 1987; Greibrokk et al., 1994; Alberdi et al., 1996; López et al., 1998; Alberdi-Genolet and Tocco, 1999; Xu et al., 2012).

In source rocks, V and Ni concentrations are useful in evaluating the paleo-redox environment (Lewan, 1984; Tribouillard et al., 2006) and the processes and conditions that control vanadium accumulation in carbonaceous rocks (Breit and Wanty, 1991). Additionally, some indexes (Ni/Cr, V/Co and Ni/V) have been

* Corresponding author. Fax: +58 212 6051152.

E-mail addresses: liliana.lopez@ciens.ucv.ve (L. López), salvador.lomonaco@ciens.ucv.ve (S. Lo Mónaco).

compared to interpret paleo-redox conditions in argillaceous sedimentary rocks. V/Cr and Ni/Co were found to be reliable indexes for interpreting paleo-oxygenation conditions (Jones and Manning, 1994). Specific metal ratios such as V/(V + Ni) and Mo/(Mo + Cr) in kerogen and bitumen have been used to determine lithofacies (siliceous shales vs phosphatic shales) in source rocks (Odermatt and Curiale, 1991). Other studies have determined the distribution of trace metals in rocks and their fractions, such as carbonates, silicates, sulfides and organic matter (Hirner and Xu, 1991; Lo Mónaco et al., 2002).

In crude oils, V and Ni abundance and the V/(V + Ni) ratio are used to determine paleo-redox conditions during source rock deposition. In addition, they are very useful in classifying crude oils (Hitchon and Filby, 1984). In oil–oil correlations, similar V/Ni or V/(V + Ni) ratios are related to source rock sedimentation under the same paleo-redox conditions and can be used as evidence of a common origin among oils (Simoza et al., 1985; Alberdi et al., 1996). V and Ni concentrations have also been determined in oil fractions (saturated and aromatic hydrocarbons, NSO and asphaltenes) and discussed in terms of possible metal–organic associations and their usefulness in oil–oil correlations (Ellrich et al., 1985; López et al., 1991).

Sulfur content in crude oils and bitumen is related to paleo-redox conditions and source rock lithology (Tissot and Welte, 1984). Additionally, during biodegradation the residual oil is enriched with NSO compounds and asphaltenes, which result in higher concentrations of sulfur, vanadium and nickel and lower API gravity (Peters et al., 2005; Larter et al., 2006). Therefore, the sulfur content together with V and Ni concentration (using V/Ni or V/(V + Ni) ratios) may be used to determine paleo-redox conditions or biodegradation, when accompanied by a biomarker analysis for assessing the level of biodegradation.

The oils and source rocks from Venezuelan basins are characterized by having a high vanadium, nickel and sulfur content. Their distribution in oils and bitumen and the V/Ni or V/(V + Ni) ratios have proved to be useful in inferring paleo-redox conditions and as an efficient correlation parameter. This study compiles information on V, Ni and S in rocks and crude oils from Venezuelan basins and includes the main Cretaceous source rocks: La Luna (Maracaibo Basin), Querecual and San Antonio (Eastern Basin) and the Tertiary sequence from the Naricual Formation. The oils (biodegraded and non-biodegraded) come from the Maracaibo Basin, Eastern Basin and Barinas sub-basin. Vanadium, nickel and sulfur were studied in these basins, and some of the results presented in previous works are cited in this article. The concentrations of these three elements and V/Ni or V/(V + Ni) ratios are used to classify the source rocks and crude oils from Venezuelan basins according to paleo-redox sedimentation conditions (from suboxic–dysoxic to anoxic–suboxic), organic matter input (marine, terrigenous or mixtures), lithology (shale, marl or carbonate) and maturity (immature to post-mature). These results were compared with those obtained through the use of biomarkers to determine organic matter type, sedimentation environment and maturity. In addition to crude oils, vanadium, nickel and sulfur concentration, along with biomarkers, were also used to identify the biodegradation process and possible secondary charge.

2. Study area

Venezuela has three important oil provinces: the Maracaibo Basin, the Eastern Basin and the Barinas sub-basin (Fig. 1) (González et al., 1980). These basins are characterized by the presence of mainly marine, terrigenous and mixed (marine and terrigenous) oils. Additionally, some oils are heavy to extra heavy as the result of biodegradation (Cassani and Eglinton, 1986, 1991;

Gallango and Cassani, 1992; Alberdi et al., 1996; López and Lo Mónaco, 2010). The principal marine organic matter source rocks are the Cretaceous La Luna and Querecual formations from the Maracaibo and Eastern basins, respectively (Talukdar et al., 1985; Talukdar and Marcano, 1994). In the Eastern Basin the secondary source rocks are the San Antonio Formation (López, 1997). Tertiary source rocks with terrigenous organic matter have also been identified (Tocco et al., 1994; Quintero et al., 2012). However, in the Barinas sub-basin the source rock is not well established (Tocco et al., 1997; López et al., 1998).

3. Samples and methods

A total of 189 oils and 50 rock samples from Venezuelan basins were analyzed for V, Ni and S (López et al., 1998; Lo Mónaco et al., 1999; López and Lo Mónaco, 2004, 2010; López, 2014; López et al., 2015). The oils come from the Mara, Mara Oeste, Boscán, Los Manueles, Lagunillas and La Paz fields (Maracaibo Basin); the Socororo, Junín, Ayacucho and Carabobo fields (Eastern Basin), and the La Victoria, Guafita, Caipe, Silvestre, Sinco, Silván, Palmita, Hato and Maporal fields (Barinas sub-basin). Before the analysis of S, V and Ni in crude oils, samples were mixed with toluene (2:1, v: v) followed by centrifugation (20 min at 5000 rpm) to separate water and sediment; subsequently the solvent was removed by evaporation under reduced pressure. This was done to decrease the contamination level by elements in sediment or water associated with crude oil. The rocks come from outcrops of La Luna (Cretaceous, Maracaibo Basin), Querecual and San Antonio (Cretaceous, Guayuta Group, Eastern Basin), and a core from the Naricual Formation (Tertiary, Eastern Basin) (Table 1, Fig. 1). In rocks from outcrops, the weathered surfaces were removed with a rock hammer and pick. They were then cut with a diamond saw in the laboratory to further remove the weathered surfaces; lastly, they were pulverized. Previous studies have reported results on V, Ni and S in oils. This work includes new information on oils from the Boscán, Los Manueles, Lagunillas and La Paz fields (Maracaibo Basin) and the main source rocks in Venezuela. Additionally, the SARA composition (saturate, aromatic, resin and asphaltene) was determined in selected samples of oils and bitumens, and a biomarker analysis was performed for the saturate fraction. The results on the origin, maturity and biodegradation of the oils obtained with the use of biomarkers were compared with those obtained with V, Ni and S concentrations.

3.1. Elemental composition

Several methods were used to determine V, Ni and S in crude oils: (1) X-ray fluorescence energy dispersive technique with a KEVEX equipment (model 7000) in oils from the Mara, Mara Oeste and La Paz fields; (2) X-ray fluorescence technique with a Phillips (PW1410) in oils from the Junín field; (3) inductively coupled plasma spectrometry (Jobin-Yvon JY-24) in oils from the Ayacucho, Carabobo, La Victoria, Guafita, Caipe, Silvestre, Sinco, Silván, Palmita, Hato, Maporal and Los Manueles fields and (4) inductively coupled plasma mass spectrometry (ICP/MS, Thermal Jarrel Ash ENVIRO II) in oils from the Lagunillas, Socororo and Boscán fields. In Methods 1 and 2 a modified version of the Reynolds (1963) method was used, and sulfur content was determined by X-ray fluorescence. In Methods 3 and 4, sulfur content was determined using a LECO SC-432 sulfur analyzer. In the whole rock, V and Ni were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermal Jarrel Ash INVIRO II) and sulfur content was determined using a LECO SC-432 sulfur analyzer.

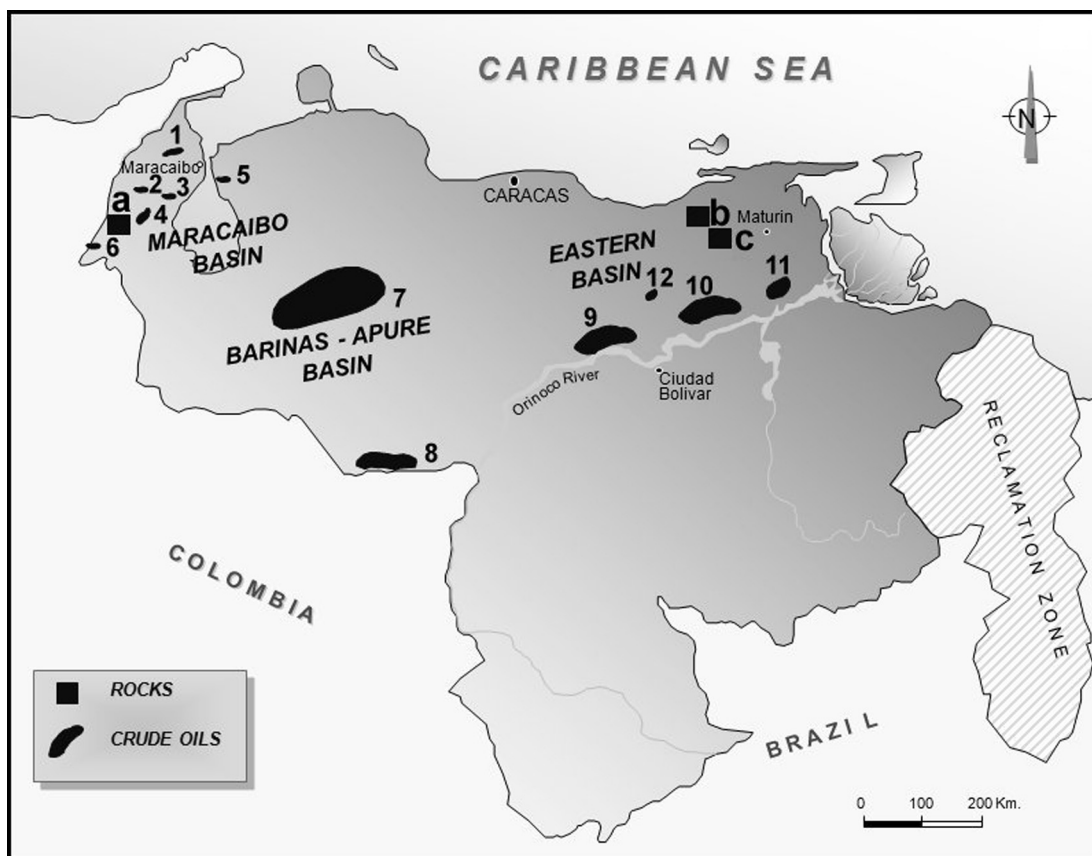


Fig. 1. Location of oil fields and source rocks for which vanadium, nickel and sulfur were determined. a: La Luna Formation, Maraca ravine; b: Querecual and San Antonio formations, Querecual River; c: Narical Formation, La Vieja-1 well; 1: Mara Oeste; 2: Mara; 3: La Paz; 4: La Concepción; 5: Boscán; 6: Los Manueles; 7: Caipe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo and Maporal; 8: La Victoria and Guafita; 9: Junín; 10: Ayacucho; 11: Carabobo; 12: Socororo.

Table 1

Crude oils and source rock samples analyzed in order to determine V, Ni and S concentration.

Sample types	Basin	Wells and rock analyzed samples ^a
Crude oils	Barinas	La Victoria (4) Guafita (16) Caipe (4) Silvestre (8) Sinco (7) Silván (6) Palmita (1) Mingo (5) Hato (5) Maporal (9)
	Maracaibo	Mara Oeste (5) Mara (10) Los Manueles (7) Lagunillas (20) La Paz (6) Boscán (16)
	Eastern	Junín (20) Carabobo (9) Ayacucho (20) Socororo (11)
Rocks	Maracaibo	La Luna Formation (15 outcrop samples)
	Eastern	Querecual (18 outcrop samples) and San Antonio (7 outcrop samples) formations Narical Formation (10 core samples)

^a Number of samples in parentheses.

3.2. Whole rock analysis and bitumen extraction

In whole rock, mineralogical composition was determined by X-ray diffraction (Siemens XD-8 Advance). The total carbon (TC) content was determined using a carbon analyzer (LECO, C-144). Carbonate carbon was measured using Bernard's calcimeter method (Hesse, 1971) and total organic carbon (TOC) was determined by difference. Kerogen type and maturity level were determined on a Rock-Eval 6 pyrolysis instrument under standard conditions following basic methods for whole rock analysis (Behar et al., 2001). Bitumen was extracted with dichloromethane in a Soxhlet extractor using pulverized rocks.

3.3. SARA composition

In crude oil and bitumen samples, the maltene fraction was separated into its saturated, aromatic and resin fractions by means of

adsorption chromatography using packed columns (20 cm long × 1.5 cm in diameter) with alumina as the stationary phase (20 g). The saturated hydrocarbons were eluted with *n*-hexane (30 mL), the aromatic hydrocarbons with toluene (20 mL), and a mixture (15 mL) of toluene:MeOH (70:30, v:v) was used to elute NSO compounds. The saturated hydrocarbon fraction was purified twice by liquid chromatography using packed columns as described above.

3.4. Saturated biomarkers

The saturated biomarkers were analyzed in selected crude oils from the Eastern Basin (20), Maracaibo Basin (12) and Barinas sub-basin (43), and in bitumen extracts from the Querecual (5), San Antonio (10), Narical (2) and La Luna (14) formations. The analyses were performed using gas chromatography–mass spectrometry (GC–MS) by coupling the gas chromatograph to a 5975

Agilent Technologies mass spectrometer operated in single ion monitoring mode. The GC system was equipped with DB-1 fused silica capillary columns (60 m × 0.25 mm × 0.25 μm) to analyze the saturated fractions. The monitored ions were: $m/z = 113, 191, 177, 218, 217$ for *n*-alkanes, acyclic isoprenoid alkanes (pristane and phytane), terpanes, steranes and diasteranes, respectively. In crude oils from Los Manueles field and oils from the Barinas sub-basin, the gas chromatography of the saturated fractions was carried out on a 5890 HP gas chromatograph using a flame ionization detector.

4. Results and discussion

4.1. Crude oil type

Table 2 shows the API classification and SARA composition for the analyzed oils. Using these parameters, it was possible to identify different oil types throughout the Venezuelan basins. The oil samples are characterized by having variable API gravity (6.4–32.8° API), hence they can be classified as extra heavy (6.4–9.9° API), heavy (10.0–21.6° API), medium (22.4–29.4° API) and light (31.6–32.8° API) crude oils or as paraffinic–naphthenic, aromatic–naphthenic or aromatic–asphaltic oils depending on their SARA compositions. The different oil types are specified in the ternary SARA composition diagram (Fig. 2). This variability in crude oil composition is the result of different origins and biodegradation processes, which are discussed below taking into account vanadium, nickel and sulfur concentrations and biomarker distributions.

4.2. Source rock type

In the Eastern Basin, the Guayuta Group of the Cretaceous is represented by the Querecual (late Albian–Santonian) and San Antonio (Turonian) formations. The limestones of the Querecual

Formation are considered to be the source rocks that generated most of the crude oils of the Eastern Basin (Talukdar et al., 1985). The limestones, calcareous shales and cherts of the San Antonio Formation are considered to be secondary source rocks in the Eastern Basin (López, 1997). Mineralogical analyses showed the presence of calcite, dolomite, quartz, pyrite and siderite in the Querecual Formation. In the San Antonio Formation, the mineralogical composition in limestone and calcareous shale is quartz, calcite, dolomite and pyrite. The Querecual Formation is characterized by the presence of marine organic matter (Type II kerogen), as evidenced by a visual study of the kerogen, which indicates a prevalence of amorphous marine organic matter with few vitrinite particles. The hydrogen index (HI) measured in sections of varying maturity (0.5–1.3 %Ro) suggests a high generation potential for this formation (Talukdar et al., 1985). The Naricual Formation (late Oligocene–early Miocene) is characterized by the presence of quartz, kaolinite, illite and pyrite. The organic matter studied in the stratigraphic sequence from the Naricual Formation is mixed source (Type II–III kerogen), although some samples were classified as Type IV kerogen. The analysis of biomarkers and Rock-Eval pyrolysis determined that this sequence has a maturity near the peak of the oil window (Quintero et al., 2012). In the Maracaibo Basin, the La Luna Formation (Cenomanian–Campanian) represents the main source rock. The mineralogical analysis showed the presence of calcite, quartz, pyrite and illite. The study section of the La Luna Formation (Maraca ravine) is Type II kerogen with a maturity near the peak of the oil window. Table 3 shows the generation potential and maturation of these rocks based on TOC (wt%), kerogen type and T_{max} (°C).

4.3. V, Ni and S concentrations in oils and source rocks

Table 4 shows the maximum, minimum and average concentrations of vanadium, nickel and sulfur, together with V/Ni and V/(V + Ni) ratios, in the crude oils analyzed. Oils with the lowest V con-

Table 2
Oil classification based on API gravities and SARA composition and for oil samples from Venezuela basin.

Basin	Oil field	API classification	SARA ^A (wt%)	Oil classification
Barinas sub-basin ^{a,b}	La Victoria, Guafita	Light and intermediate oils	S: 44–64 A: 25–32 R + A: 5–22	Paraffinic–naphthenic
	Caípe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo, Maporal	Medium oils	S: 30–43 A: 25–37 R + A: 19–42	Aromatic–naphthenic
Eastern Basin	Socororo ^c	Heavy oils	S: 17–37 A: 32–39 R + AR: 30–46	Aromatic–asphaltic
	Junín ^d	Extra heavy oils	S: 5–11 A: 14–45 R + A: 49–75	Aromatic–asphaltic
	Ayacucho ^e	Extra heavy oils	S: 5–13 A: 27–49 R + A: 45–73	Aromatic–asphaltic
	Carabobo ^e	Extra heavy oils	S: 5.2–10.5 A: 14–31 R + A: 63–75	Aromatic–asphaltic
Maracaibo Basin ^c	Boscán	Extra heavy oils	S: 12 A: 36 R + A: 52	Aromatic–asphaltic
	Mara ^f	Heavy to medium oils	S: 38–59 A: 13–22 R + A: 18–25	Aromatic–naphthenic
	Mara Oeste ^f	Heavy oils	S: 18–40 A: 23–25 R + A: 34–49	Aromatic–asphaltic
	La Paz	Light oils	S: 36–60 A: 22–32 R + A: 9–22	Paraffinic–naphthenic
	Los Manueles	Light oils	S: 48–70 A: 19–26 R + A: 11–28	Paraffinic–naphthenic
	Lagunillas	Extra heavy oils	S: 20–25 A: 15–25 R + A: 55–64	Aromatic–asphaltic

^A S: Saturated, A: Aromatic, R: Resins or NSO compounds and A: Asphaltenes.

^{a,b} López et al. (1998), Lo Mónaco et al. (1999).

^c López et al. (2015).

^d López (2014).

^e López and Lo Mónaco (2010).

^f López and Lo Mónaco (2004).

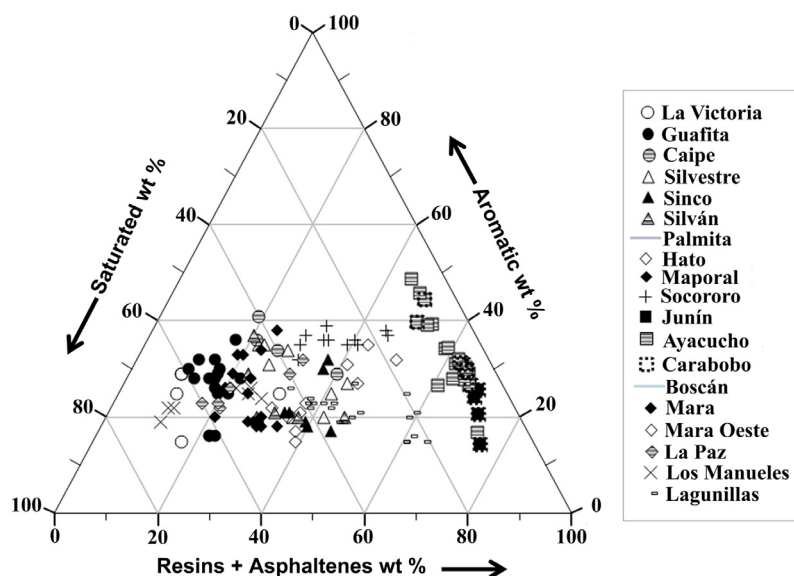


Fig. 2. Ternary diagram showing the bulk SARA (saturate, aromatic, resins and asphaltenes) composition of crude oil samples from Venezuelan basins.

Table 3

Source rocks lithology, total organic carbon (TOC), kerogen type and maturity parameters (T_{\max} °C).

Formations	Lithology	TOC	Kerogen type	T_{\max} (°C)
Querecual bottom (8)	Limestone	0.2–5.6	II	539–542
Average ± SD		2.5 ± 1.7		542 ± 2
Querecual top (10)	Limestone	0.2–4.2	II	514–537
Average ± SD		1.4 ± 1.2		525 ± 10
San Antonio (7)	Limestones, calcareous shales	0.8–4.6	II	430–521
Average ± SD		2.4 ± 1.1		486 ± 40
Naricual (10)	Shales	1.1–12.8	II–III–IV	428–448
Average ± SD		4.5 ± 3.8		433 ± 3
La Luna (15)	Limestone	0.7–7.3	II	434–442
Average ± SD		4 ± 2		440 ± 2

Naricual Formation: [Quintero et al. \(2012\)](#).

Number of samples in parentheses. SD: standard deviation.

centrations (< 26 ppm) occur in the Guafita, La Victoria and Caipe fields in the Barinas sub-basin, and in Los Manueles (two oils) in the Maracaibo Basin ($V < 21$ ppm). Oils with the highest V concentrations occur in Mara Oeste (954–999 ppm) and Boscán (995–1417 ppm) in the Maracaibo Basin. In other fields, V ranges from 108 ppm (oil from Palmita, Barinas sub-basin) to 654 ppm (oil from Junín, Eastern Basin).

Nickel concentration ranges from 2.4 ppm (Los Manueles) to 156 ppm (Carabobo area); only one crude oil (Sinco) has a Ni concentration > 200 ppm (291 ppm). This element is found in concentrations > 100 ppm (maximum of 156 ppm) in crude oils from Boscán, Junín, Ayacucho, Carabobo, Silvestre, Sinco, Silván, Mingo, Hato and Matoral. Concentrations < 100 ppm were observed in crude oils from La Victoria, Guafita, Caipe, Palmita, Hato, Matoral, Mara, Mara Oeste and Los Manueles.

Sulfur is < 2% in all crude oils from the Barinas sub-basin and in oils from Los Manueles (Maracaibo Basin). This element has concentrations of 9.3–12.8% in oils from the Boscán field, and 2.0–5.7% in crude oils from the Orinoco Oil Belt (with some exceptions in the Carabobo area). Mara, Mara Oeste, La Paz, Lagunillas and Socororo have sulfur concentrations of 1.9–3.5%.

Based on their vanadium, nickel and sulfur concentrations, the oils can be divided into three groups, regardless of their location (Table 4): (1) oils from Boscán and Mara Oeste (Maracaibo Basin), with the highest concentrations of V (995–1417 ppm), Ni (91–

139 ppm) and S (5.6–12.8%); (2) oils from La Victoria and Guafita (Barinas sub-basin), with lower concentrations of V (6–17 ppm), Ni (25–69 ppm) and S (0.3–0.8%) and (3) oils from Caipe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo and Matoral (Barinas sub-basin); Mara, Los Manueles, Lagunillas and La Paz (Maracaibo Basin) and Junín, Carabobo, Ayacucho and Socororo (Eastern Basin), with V, Ni and S concentrations between the ranges described for the first two groups. These differences in V, Ni and S concentrations are the result of paleo-redox sedimentation conditions, lithology and maturity of the source rock, as well as secondary processes such as biodegradation.

Fig. 3 shows that API gravity increases with decreasing sulfur content. This inverse correlation between oil API gravity and sulfur content is typically observed in biodegraded crude oils ([Hunt, 1996](#)). Additionally, non-biodegraded crude oils have low sulfur concentrations and API gravities higher than those of biodegraded crude oils. Furthermore, immature crude oils are characterized by lower API gravities and high sulfur content ([Vandenbroucke and Largeau, 2007](#)). As shown in Fig. 3, API gravity decreases with increasing sulfur content, and the location of oils on the graph is the result of one of two processes: maturation or biodegradation. The first process accounts for the immature oils from the Boscán field ([Talukdar et al., 1986](#)), which have a high sulfur content (9.3–12%) and low API gravities (8.7–11.2° API), and immature crude oils from the Mara Oeste field, which also show

Table 4
Concentration ranges of V, Ni (ppm), S (wt%), V/Ni and V/(V + Ni) ratios in crude oils from Venezuelan basins.

Field	V	Ni	S	V/Ni	V/(V + Ni)
La Victoria (4)	6–26	25–69	0.4–0.8	0.2–0.4	0.186–0.273
Average ± SD	12 ± 9	39 ± 20	0.5 ± 0.2	0.3 ± 0.1	0.22 ± 0.04
Guafita (16)	10–17	33–52	0.3–0.6	0.3	0.210–0.252
Average ± SD	13 ± 2	44 ± 7	0.56 ± 0.08	0.30 ± 0.02	0.231 ± 0.009
Caípe (4)	3–244	3–71	0.4–1.7	1.1–3.5	0.518–0.780
Average ± SD	151 ± 106	44 ± 30	1.2 ± 0.6	3 ± 1	0.7 ± 0.1
Silvestre (8)	158–355	77–124	0.6–1.5	2.0–2.9	0.669–0.740
Average ± SD	247 ± 74	97 ± 21	1.1 ± 0.3	2.5 ± 0.3	0.71 ± 0.02
Sinco (7)	252–575	95–291	1.5–2.1	2.0–2.8	0.664–0.737
Average ± SD	320 ± 114	133 ± 70	1.7 ± 0.2	2.5 ± 0.3	0.71 ± 0.03
Silvan (6)	132–282	50–109	0.8–1.9	2.3–2.6	0.697–0.725
Average ± SD	172 ± 58	69 ± 22	1.2 ± 0.4	2.5 ± 0.1	0.71 ± 0.01
Palmita (1)	108	43	1.1	2.5	0.716
Mingo (5)	270–333	94–129	1.8	2.4–2.9	0.710–0.743
Average ± SD	299 ± 5	112 ± 15	1.8 ± 0	2.7 ± 0.2	0.73 ± 0.01
Hato (5)	158–255	65–102	1.1–1.5	2.4–2.7	0.10–0.728
Average ± SD	214 ± 35	85 ± 14	1.3 ± 0.2	2.52 ± 0.09	0.716 ± 0.007
Maporal (9)	118–286	47–111	1.4–1.7	2.2–2.9	0.685–0.745
Average ± SD	194 ± 59	75 ± 20	1.6 ± 0.1	2.6 ± 0.2	0.72 ± 0.02
Mara Oeste (5)	954–999	90–96	2.5–3.0	10.3–12.6	0.912–0.926
Average ± SD	981 ± 18	19 ± 2	5.9 ± 0.2	10.6 ± 0.3	0.914 ± 0.002
Mara (10)	176–260	14–24	2.5–3.0	10.3–12.6	0.912–0.926
Average ± SD	219 ± 25	19 ± 3	2.7 ± 0.2	11.3 ± 0.7	0.919 ± 0.005
Los Manueles (7)	21–137	2–22	0.4–1.1	6.3–8.5	0.863–0.895
Average ± SD	74 ± 50	11 ± 8	0.8 ± 0.3	7.2 ± 0.9	0.88 ± 0.01
Lagunillas (20)	442–512	69–85	2.0–3.4	6.1–6.5	0.858–0.866
Average ± SD	476 ± 22	76 ± 5	2.7 ± 0.4	6.3 ± 0.1	0.863 ± 0.003
La Paz (6)	157–426	11–34	1.9–3.0	9.5–14.5	0.905–0.936
Average ± SD	274 ± 92	23 ± 9	2.6 ± 0.6	12 ± 2	0.92 ± 0.01
Boscán (16)	995–1417	93–139	9.3–12.8	9.5–11.0	0.901–0.917
Average ± SD	1204 ± 87	120 ± 11	12 ± 1	10.1 ± 0.5	0.910 ± 0.004
Junín (20)	229–654	65–124	3.4–5.7	3.5–5.8	0.779–0.853
Average ± SD	524 ± 111	108 ± 16	4.3 ± 0.7	4.8 ± 0.6	0.83 ± 0.02
Carabobo (9)	158–639	125–156	0.8–4.1	1–5	0.556–0.836
Average ± SD	492 ± 135	141 ± 11	3 ± 1	3 ± 1	0.76 ± 0.08
Ayacucho (20)	361–606	53–155	3.3–3.9	3.4–4.8	0.773–0.828
Average ± SD	471 ± 94	119 ± 27	3.2 ± 0.5	4.0 ± 0.4	0.80 ± 0.02
Socororo (11)	133–287	33–63	2.0–3.5	3.6–4.6	0.784–0.820
Average ± SD	187 ± 56	45 ± 10	2.5 ± 0.5	4.1 ± 0.4	0.80 ± 0.02

Number of samples in parentheses. SD: standard deviation.

Barinas sub-basin: López et al. (1998), Lo Mónaco et al. (1999). Mara and Mara Oeste fields: López et al. (1991, 1995). Lagunillas field: López et al. (2011). Junín, Ayacucho and Carabobo fields: López and Lo Mónaco (2010). Socororo field: López et al. (2015).

biodegradation (López and Lo Mónaco, 2004) and have a sulfur content of 2.5–3.0% and low API gravities (11.2–15.8° API). The second process accounts for the biodegraded oils from the Orinoco Oil Belt and Socororo field, with API gravities of 6.4–16.2° API and a variable sulfur content (0.8–5.7%) (López and Lo Mónaco, 2010; López et al., 2015). Other groups from the Mara and Sinco fields (15–20° API and sulfur < 3%) are crude oils altered and unaltered by biodegradation (López et al., 1991, 1998) and are included in Fig. 3 in the biodegraded Mara oils. Lastly, crude oils with API gravities > 20° and sulfur content < 3% are not biodegraded and belong to the Mara field, together with the oils from La Victoria, Guafita, Caípe, Silvestre, Silván and Palmita located in the Barinas sub-basin (López et al., 1998). In summary, three trends are shown in Fig. 3: (1) increased sulfur content and decreased API gravity in immature oils from Boscán and Mara Oeste; (2) increased sulfur content and decreased API gravities resulting from biodegradation in crude oils from Junín, Ayacucho, Carabobo, Socororo, Mara and Mara Oeste and (3) decreased sulfur content and increased API

gravities in unaltered crude oils from La Victoria, Guafita, Caípe, Silvestre, Silván, Palmita and La Paz.

The graphs for V and Ni concentrations vs API gravity also group crude oils according to their origin and secondary processes (Fig. 4). Immature oils from Boscán and Mara Oeste and biodegraded oils from the Orinoco Oil Belt, Lagunillas and Socororo have high V and Ni concentrations and lower API gravities. This trend is expected because V and Ni are found mainly in NSO and asphaltene fractions, whose concentration is higher in heavy and extra-heavy crude oils (Table 2, Fig. 2), whether as a result of having been generated by an immature source rock or of being biodegraded. Note that Boscán and Mara Oeste oils have the highest V concentrations compared to other oils, but their nickel concentrations are similar to those obtained in biodegraded oils from the Orinoco Oil Belt. Moreover, with decreasing V and Ni concentrations the API gravity increases, as is usually the case in non-biodegraded crude oils generated by mature source rocks. In this crude oil type, the saturated and aromatic hydrocarbons content increased relative to

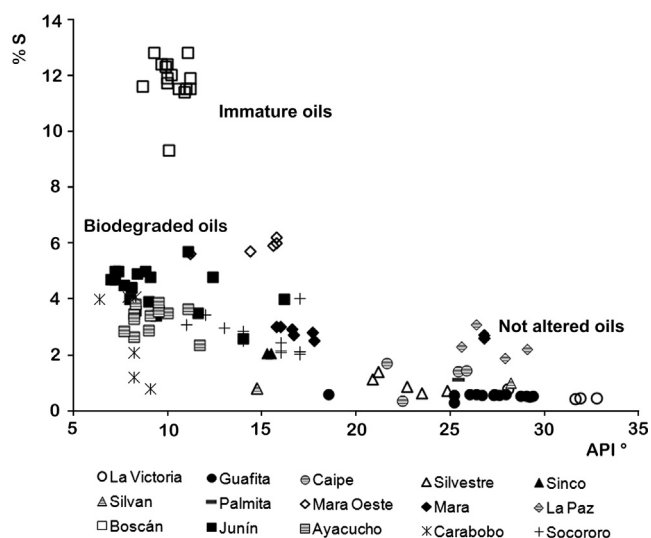


Fig. 3. Sulfur content (wt%) vs API gravity in crude oils from Venezuelan basins. Includes only those crude oils for which API gravity data were available.

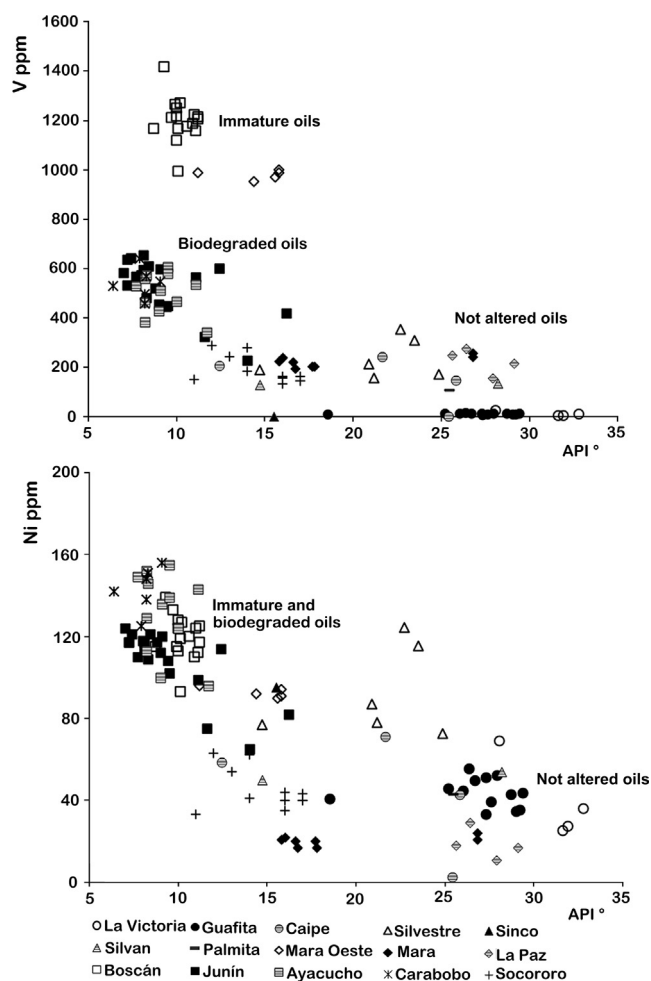


Fig. 4. Vanadium and nickel (ppm) concentration vs API gravity in crude oils from Venezuelan oil basins. Includes only those crude oils for which API gravity data were available.

NSO and asphaltene compounds (Table 2, Fig. 2) and, therefore, V and Ni are in lower concentrations. Additionally, in non-biodegraded crude oils, V and Ni concentration and V/Ni or V/(V

+ Ni) ratio are the result of the source rock paleo-redox sedimentation conditions.

Another way to discuss these results is through the Lewan (1984) diagram shown in Fig. 5a, which represents the $V/(V + Ni)$ ratio vs sulfur content. In this graph, oils from La Victoria and Guafita are located in regime II, with $V/(V + Ni) < 0.273$ and low sulfur content (0.3–0.8%). Regime II, with $V/(V + Ni) < 0.4$ and $S < 1\%$, may be associated with the sedimentation of marine shales in suboxic conditions. Additionally, eleven oils from Carabobo (1), Los Manueles (4), Caípe (1), Silvestre (4) and Silván (1) are also located in regime II. These oils are characterized by having $S < 1\%$ and $V/(V + Ni) > 0.7$, which is typical of anoxic conditions, and may be related to marine marls or carbonate source rocks. Regime III includes oils from the Barinas sub-basin and the Los Manueles ($V/(V + Ni) > 0.8$ and $S > 1\%$), La Paz and Mara fields from the Maracaibo Basin ($V/(V + Ni) > 0.9$ and $S > 1.7\%$). These characteristics in the crude oils from La Paz and Mara are associated with marine carbonate deposited in anoxic environments.

On the other hand, oils from the Barinas sub-basin (Caípe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo and Maporal) are included in regimes II and III due to their variable sulfur content and higher $V/(V + Ni)$ ratio compared to oils from La Victoria and Guafita. This too may be associated with more anoxic sedimentation conditions in the source rock facies that originated the crude oils located in Caípe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo and Maporal compared to less anoxic facies in the source rock that originated the crude oils in La Victoria and Guafita.

Fig. 5a shows crude oils from Junín, Carabobo, Ayacucho and Socororo. The biodegradation of these crude oils produces a relative increase in sulfur content. Therefore, they are only included in this diagram for the purpose of comparing $V/(V + Ni)$ values. These oils have $V/(V + Ni) \approx 0.8$ and $S \leq 4\%$, a limit proposed by Lewan (1984) for the sulfur content of crude oils with API gravities $\geq 20^\circ$. However, in many Venezuelan oils sulfur is $\leq 4\%$, but API gravities may be $\leq 20^\circ$ (Fig. 3). Using only $V/(V + Ni)$ ratios for crude oils from Junín, Carabobo, Ayacucho and Socororo with values ≈ 0.8 , it is possible to relate the main source rock of these oils to marls or carbonate source rocks, such as the Querecual Formation. Oils from Boscán, Mara Oeste and some from Junín are not included in this diagram because sulfur is $> 4\%$.

Table 5 shows the minimum, maximum and average V, Ni and S concentrations and V/Ni and $V/(V + Ni)$ ratios in source rocks. These concentrations include V, Ni and S incorporation into organic matter (kerogen and bitumen) and mineral sediment fractions, such as sulfides (pyrite: FeS_2 , millerite: NiS, sphalerite: ZnS , chalcocite: Cu_2S and covellite: CuS) and vanadium silicates as part of the clays–mica structure. Consequently, V/Ni or $V/(V + Ni)$ ratios determined in crude oils are consistent with these ratios in the bitumen, but differ from those determined in the whole rock (Breit and Wanty, 1991). However, we can make inferences regarding the crude oils and their source rocks based on sulfur, vanadium and nickel concentrations determined in whole rock.

The highest concentrations of V (values > 1500 ppm) were obtained for the La Luna and Querecual (toward the bottom) formations, which is characteristic of anoxic–euxinic paleoenvironments. Moreover, in the Querecual (top), San Antonio and Narical formations V concentrations that do not exceed 161 ppm are related to less anoxic environments (Table 5). The highest nickel concentrations were observed in the Querecual and La Luna formations. Because they are limestone, they have low levels of the iron needed to form sulfides (Tribouillard et al., 2015) and, therefore, part of the nickel is present as a sulfide phase, which was confirmed in both formations through electron microscopy (Lo Mónaco et al., 2007). Sulfur content has an inverse trend: higher concentrations were obtained in some samples from the

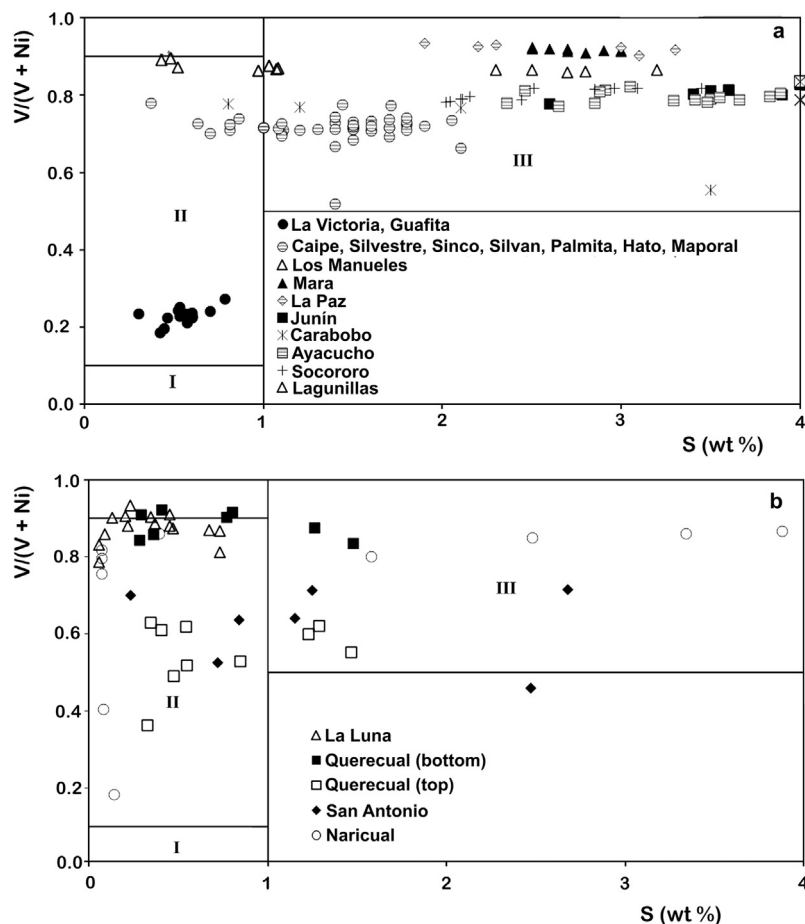


Fig. 5. Lewan diagram (1984) for: (a) crude oils and (b) source rocks from Venezuelan oil basins.

Table 5

Concentration ranges of V, Ni (ppm), S (wt%), V/Ni and V/(V + Ni) ratios in source rocks from Venezuelan basins.

Formations	Ni	V	S	V/Ni	V/V + Ni
Querecual bottom (8)	45–135	240–1630	0.3–1.3	5.1–12.0	0.837–0.923
Average ± SD	95 ± 35	830 ± 474	0.7 ± 0.5	8.3 ± 2.7	0.88 ± 0.03
Querecual top (10)	35–127	27–127	0.3–1.5	0.6–1.7	0.362–0.629
Average ± SD	55 ± 14	71 ± 29	0.7 ± 0.4	1.3 ± 0.4	0.55 ± 0.08
San Antonio (7)	29–72	57–108	0.2–2.7	0.9–2.5	0.461–0.716
Average ± SD	49 ± 14	84 ± 21	1.3 ± 0.9	1.8 ± 0.7	0.6 ± 0.1
Naricual (10)	22–62	14–161	0.1–3.9	0.2–6.6	0.187–0.868
Average ± SD	32 ± 13	115 ± 56	1.2 ± 1.5	4.1 ± 2.2	0.7 ± 0.2
La Luna (15)	25–275	123–1932	0.1–0.7	3.7–13.9	0.787–0.933
Average ± SD	145 ± 80	1078 ± 624	0.3 ± 0.2	7.6 ± 2.6	0.874 ± 0.04

Number of samples in parentheses. SD: standard deviation. La Luna Formation: Lo Mónaco et al. (2002).

Naricual and San Antonio formations because in these shales sulfur appears mainly as pyrite. However, V/Ni and V/(V + Ni) ratios (Table 5) suggest anoxic–euxinic sedimentation conditions for the La Luna and Querecual (toward the bottom) formations, compared to V/Ni and V/(V + Ni) ratios in the Querecual (top), San Antonio and Naricual formations, which are related to anoxic–suboxic sedimentation conditions.

Fig. 5b shows the Lewan (1984) diagram for source rocks from the Maracaibo and Eastern basins. Based on V/(V + Ni) > 0.787 (Table 5), it can be inferred that sedimentation conditions for La Luna and Querecual (toward the bottom) were anoxic–euxinic. These sequences are carbonate source rocks with low iron content, hence they will form nickel sulfide, while vanadium (VO²⁺) and the

excess of sulfur is incorporated into organic matter. In the Querecual (top) and San Antonio formations, where V/(V + Ni) ratios are between 0.362 and 0.716 and the lithology is characterized by marl and shale, the paleoenvironment was anoxic–suboxic. Therefore, vanadium was present as vanadate ion (VO₄²⁻), which is not incorporated into organic matter. In this case, iron is available for the formation of sulfides, and nickel will incorporate into organic matter. The V/(V + Ni) ratio is variable for shales from the Naricual Formation, between 0.187 and 0.868 (average 0.7 ± 0.2). This is due to the presence of these elements in mineral phases, such as nickel sulfides and vanadate in clay minerals, and therefore their ratio does not reflect the addition of V and Ni to organic matter.

Table 6

Saturated hydrocarbon biomarker source parameters determined in selected oils and bitumen samples from Venezuelan petroleum basins.

Samples	Biomarker parameter	GI ^a (%)	OI ^b (%)	Pr/Ph ^c	C ₃₅ /C ₃₄ ^d	C ₂₄ /C ₂₃ ^e	C ₂₂ /C ₂₁ ^e	C ₂₆ /C ₂₅ ^e	C ₃₁ 22R/C ₃₀ Hop ^f	
Oils	La Victoria, Guafita	28–38	14–16	1.1–1.5	1.03–1.59	0.77–0.92	ND	0.71–0.83	0.23–0.26	
	Caípe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo, Maporal	18–40	9–15	1.0–1.2	0.58–1.23	0.12–0.97	0.22–0.29	0.61–1.55	0.27–0.32	
	Socororo	NC	NC	NCB	0.89–1.37	0.47–0.55	1.39–2.54	0.47–0.70	0.38–0.52	
	Junín	12–19	3–10	NCB	1.11–1.42	0.42–0.49	0.48–0.66	1.33–1.46	0.43–0.51	
	Ayacucho	15–28	5–11	NCB	1.22–1.19	0.42–0.50	0.54–0.62	1.41–1.50	0.43–0.49	
	Carabobo	24	8	NCB	1.70	0.4	0.60	1.38	0.46	
	Boscán	NC	NC	0.6	1.11	0.48	1.36	1.44	0.54	
	Mara	NC	NC	0.8–1.0	0.81–0.84	0.30–0.32	ND	0.82–1.84	0.35–0.56	
	Mara Oeste	NC	NC	0.6	0.84–1.36	0.27–0.33	ND	0.76–1.86	0.42–0.50	
	La Paz	NA	NA	0.6–0.7	NA	NA	NA	NA	NA	
	Lagunillas	NC	NC	NCB	0.82	0.49	0.28	1.35	0.19	
	Los Manueles	18	11	1.2–2.5	0.97	0.59	0.56	1.67	0.39	
	Source rocks	Querecual	NC	NC	1.0–1.6	NCOM	0.10	NCOM	NCOM	0.27–0.67
		San Antonio	NC	3–16	0.5–1.5	0.90–1.31	0.37–0.60	NCOM	NCOM	NCOM
Naricual		NC	23–24	1.2–8.2	0.36–0.40	ND	ND	ND	0.21–0.28	
La Luna		9–21	NC	0.4–0.9	0.53–1.23	0.33–0.54	0.37–0.62	0.74–1.10	0.31–0.43	

NC: Not calculated in oils and source rocks where oleanane and gammacerane were not detected.

NA: Not analyzed.

NCB: Not calculated in biodegraded oils.

NCOM: Not calculated in overmature source rocks.

ND: Not determined in oils and source rocks where tricyclic terpanes were not detected.

^a GI Gammacerane Index = [gammacerane]/(gammacerane + 17 α ,21 β -C₃₀hopane) \times 100 (Moldowan et al., 1985).^b OI Oleanane Index = [(18 α (H)-oleanane)/(18 α (H)-oleanane + 17 α ,21 β -C₃₀hopane)] \times 100 (Moldowan et al., 1994).^c Pr/Ph = Pristane/Phytane (Tissot and Welte, 1984).^d C₃₅/C₃₄ = homohopane index (Peters and Moldowan, 1991; Peters et al., 2005).^e C₂₄/C₂₃, C₂₂/C₂₁ and C₂₆/C₂₅ = tricyclic terpane ratios.^f C₃₁22R/C₃₀Hop = 17 α ,21 β -homohopane (22R)/C₃₀17 α ,21 β -hopane (Peters et al., 2005).

4.4. Biomarkers: organic matter type and sedimentation environment

Table 6 shows the saturated hydrocarbon biomarker source parameters determined in the selected oil and bitumen samples. Fragmentograms of selected samples are presented in Figs. 6–9. In general, all crude oil samples are characterized by having predominantly marine organic matter input determined by the presence of: (a) abundant tricyclic terpanes (cheilanthanes), which maximize at C₂₃; (b) abundant C₂₇ regular steranes relative to C₂₉ steranes (Moldowan et al., 1985) and (c) C₃₀ steranes (Peters et al., 2005), which have a higher relative abundance in crude oils from the Maracaibo Basin (Fig. 6).

18 α (H)-Oleanane and gammacerane were detected in oils from Los Manueles (Table 6), although 18 α (H)-oleanane is not commonly observed in crude oils from the Maracaibo Basin (Alberdi and López, 2000). Additionally, these compounds were detected in all oils from the Barinas sub-basin and Orinoco Oil Belt (Table 6), which suggests input from angiosperms (Moldowan et al., 1994) and stratification of the water column (Moldowan et al., 1985), respectively. The oleanane index values (Table 6) are related to limited higher plant input (from angiosperms) during organic matter deposition, and suggest variations in terrigenous organic matter input during the deposition of the source rock of these oils. Similarly, gammacerane index values suggest variations in stratification conditions in water column. In rocks, 18 α (H)-oleanane was detected in some shale intervals from the San Antonio Formation (not shown in Fig. 9) and shales from the Naricual Formation (Fig. 9). The highest oleanane index was determined in the latter formation of Tertiary age (OI between 23% and 24%). Gammacerane was only detected in some samples from the La Luna Formation (not shown in Fig. 9).

When identifying paleo-redox conditions, 17 α ,21 β -28,30-bisnorhopane (BNH) was detected with variations in signal intensity in all crude oils and source rocks (Figs. 6–9). High BNH concentrations are related to clay-poor source rocks that are deposited under anoxic conditions and result in Type IIS kerogen formations (Peters

et al., 2005). Variations in BNH signal intensity suggest differences in the redox conditions during deposition, but could also be due to: (a) maturity, since the concentration of BNH decreases with maturity (Peters et al., 1989), for example the Querecual Formation (Fig. 9) and (b) biodegradation (Peters et al., 2005), for example the oil from Lagunillas (Fig. 8).

The pristane/phytane ratio (Pr/Ph) was \leq 1 in crude oils from the Maracaibo Basin (Boscán, Mara, Mara Oeste and La Paz) and bitumen from the La Luna Formation, a value associated with anoxic environments. Some of these samples have Pr/Ph < 0.8, which is typical of anoxic conditions in carbonate environments (Didyk et al., 1978). Note that in this basin, crude oils from Los Manueles have Pr/Ph values between 1.2 and 2.5, which suggests a source rock deposited in suboxic–dysoxic conditions with terrigenous organic matter input. It has been suggested that Los Manueles has a mix of oils resulting from a source rock with marine organic matter input (La Luna Formation) and a source rock with terrigenous organic matter input (Talukdar and Marciano, 1994). Crude oils from the Barinas sub-basin have Pr/Ph in the range 1.0–1.5, which suggest suboxic sedimentation conditions. In the bitumen from the Querecual and San Antonio formations, Pr/Ph suggests suboxic sedimentation conditions, and in the Naricual Formation Pr/Ph reflects suboxic–dysoxic conditions and terrigenous organic matter input (Table 6).

The homohopane index was also calculated (Table 6) to interpret paleo-redox conditions. All crude oils and rocks from the Querecual, San Antonio and La Luna formations have homohopane indexes with values of C₃₅/C₃₄ \approx 1, which suggests anoxic–suboxic conditions during source rock deposition (Peters and Moldowan, 1991). Only the bitumen from the Naricual Formation has C₃₅/C₃₄ < 1 related to suboxic–dysoxic conditions (Fig. 9).

The source rock lithology of analyzed crude oils revealed a higher relative abundance of C₂₉ 17 α ,21 β -hopane when compared to C₃₀ 17 α ,21 β -hopane in oils from the Mara and Mara Oeste fields (Fig. 6) and bitumen from the La Luna Formation (Fig. 9). The greater abundance of C₂₉ over C₃₀ hopane is attributed to the

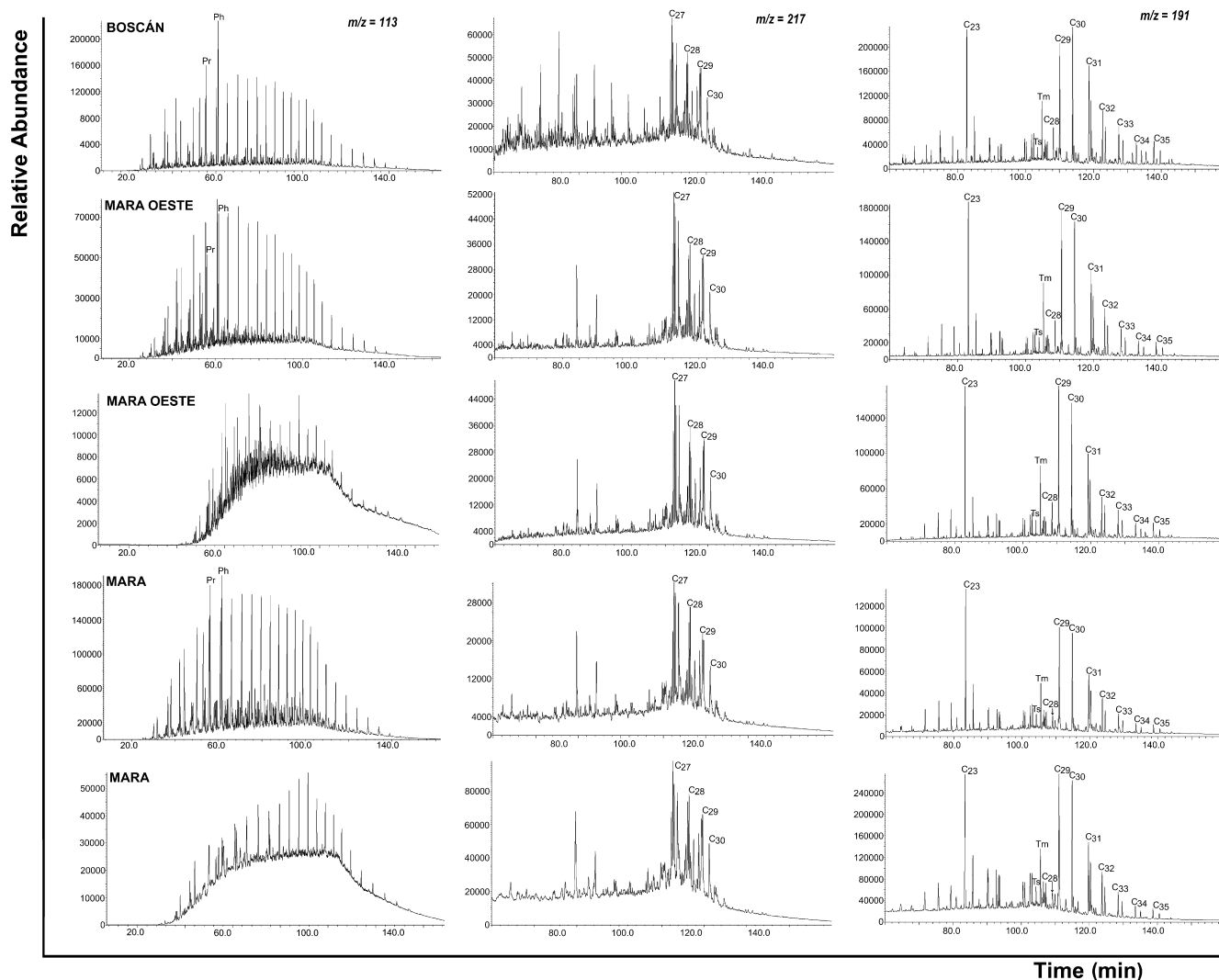


Fig. 6. Mass fragmentograms showing *n*-alkanes and isoprenoid alkanes pristane and phytane in *m/z* 113, steranes in *m/z* 217 and terpanes in *m/z* 191 from selected oil samples from the Maracaibo Basin.

carbonate source rock (Connan et al., 1986). Zumberge (1984) reports $C_{29} > C_{30}$ hopanes for the La Luna Formation in the Magdalena Valley (Colombia). These values are similar to those observed in the La Luna Formation in the Maracaibo Basin.

The C_{24}/C_{23} , C_{22}/C_{21} and C_{26}/C_{25} tricyclic terpane ratios and the $C_{31}22R/C_{30}Hop$ ratio were used to determine the source rock lithology of crude oils (carbonate, marine shale or marl source rocks). Crude oils from the Barinas sub-basin have $C_{24}/C_{23} > 0.6$. In this group, only two oils have $C_{24}/C_{23} < 0.6$ (Caípe = 0.12 and Sinco = 0.14), $C_{22}/C_{21} = 0.22–0.29$, $C_{26}/C_{25} = 0.61–1.55$ and $C_{31}22R/C_{30}Hop = 0.23–0.32$. Crude oils from the Eastern (Socororo, Junín, Ayacucho and Carabobo) and Maracaibo basins (Boscán, Mara, Mara Oeste and Lagunillas) and source rocks have $C_{24}/C_{23} < 0.6$ (Los Manueles has a value close to 0.6), $C_{22}/C_{21} = 0.37–2.54$, $C_{26}/C_{25} = 0.47–1.86$ and $C_{31}22R/C_{30}Hop = 0.27–0.67$ (Table 5). According to Peters et al. (2005), oils from carbonate source rocks are characterized by low C_{24}/C_{23} (< 0.6), high C_{22}/C_{21} (> 0.5), low C_{26}/C_{25} (< 1.1) and $C_{31}R/C_{30}Hop$ ratios greater than 0.30. Therefore, the values obtained for the C_{24}/C_{23} , C_{26}/C_{25} and $C_{31}22R/C_{30}Hop$ ratios suggest that the oils from the Eastern and Maracaibo basins originated from either a marine carbonate or a marine marl source rock and crude oils from the Barinas sub-basin originated from marine shales. $C_{31}22R/C_{30}Hop$ values for the Narical Formation are more characteristic of marine shales.

4.5. Biomarkers: maturity

Table 7 shows the maturity parameters calculated for a set of selected crude oils and bitumen. The results are shown in the range of determined values (minimum–maximum). Figs. 6–9 show examples of fragmentograms of crude oil and source rock bitumen. The $22S/(22S + 22R)$ ratio for the C_{32} 17 α -hopanes (Seifert and Moldowan, 1980) was calculated for each of the analyzed samples. The C_{32} homohopane isomerization values fall in the 0.53–0.64 range (Table 7), which indicates that the endpoint has been reached (0.55–0.62) and the early phase of oil generation has been reached or surpassed (Peters et al., 2005). Given that this ratio is an indicator of immature or early mature oils or bitumen, because its isomerization occurs at low maturity, it does not differentiate the maturity level of the crude oils and source rocks analyzed.

The Mor/Hop ratio [$C_{30}17\beta,21\alpha(H)$ -moretane/ $C_{30}17\alpha,21\beta(H)$ -hopane] was also used to determine maturity. This ratio has values that decrease from approximately 0.8 in immature rocks to < 0.15 in mature source rocks and reach a minimum of 0.05 (Mackenzie et al., 1980; Seifert and Moldowan, 1980). The Mor/Hop ratio (Table 7) indicates that analyzed oils were generated when the rock reached a maturity near the peak of the oil window (0.06–0.15). On the other hand, the maturity in the La Luna (0.07–0.14) and Narical formations (0.06–0.07) is near the peak of the oil

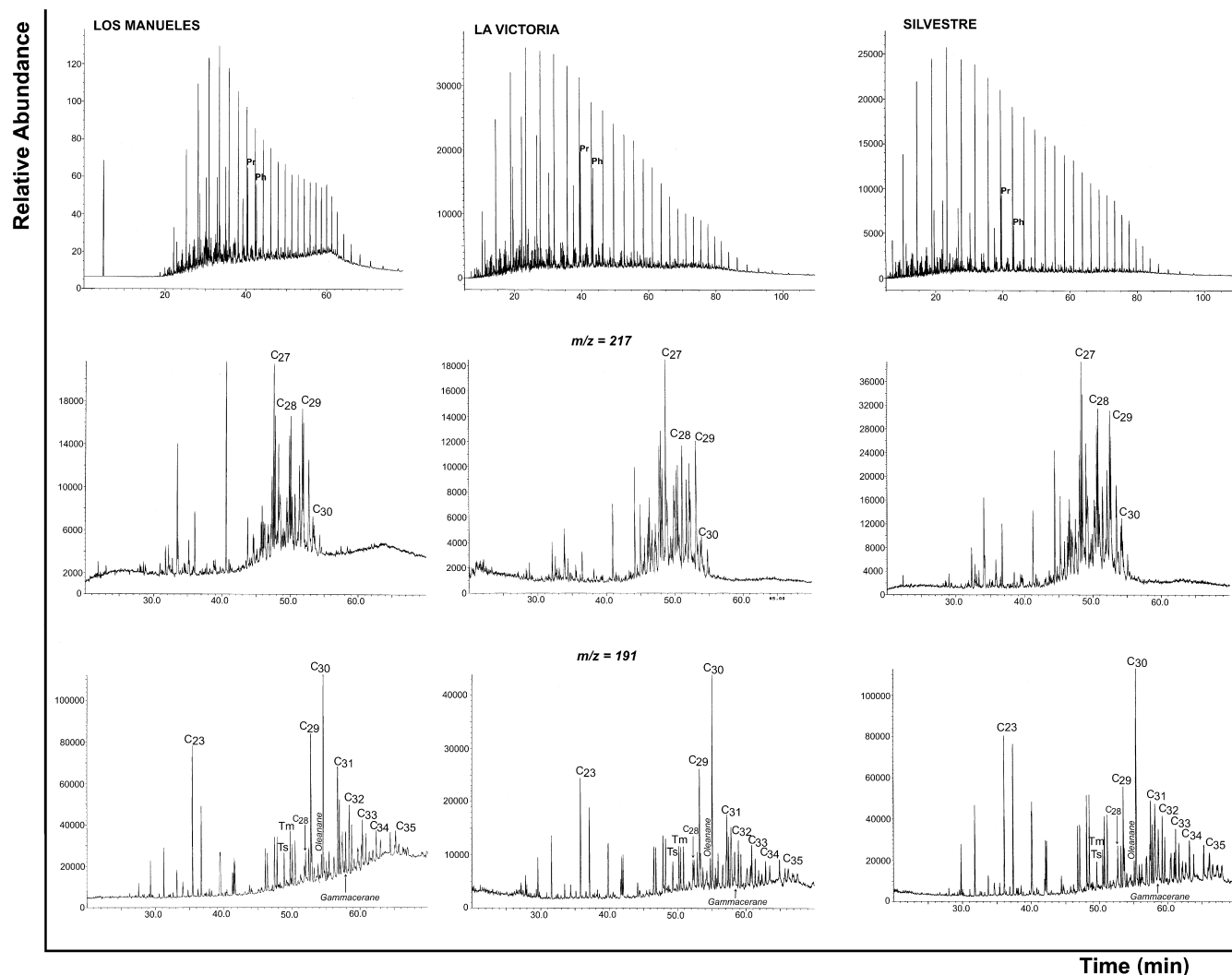


Fig. 7. Mass fragmentograms showing *n*-alkanes and isoprenoid alkanes pristane and phytane in *m/z* 113, steranes in *m/z* 217 and terpanes in *m/z* 191 from selected crude oil samples from the Maracaibo Basin and Barinas sub-basin.

Table 7

Saturated hydrocarbon biomarker maturity parameters determined in selected oils and bitumen samples from Venezuelan petroleum basins.

Samples	Biomarker parameter	$C_{32}22S/C_{32}22(S+R)^a$	Mor/Hop ^b	Ts/(Ts + Tm) ^c	%C ₂₉ 20S ^d	%C ₂₉ ββ ^e
Oils	La Victoria, Guafita	0.53–0.60	0.10–0.15	0.38–0.50	38–44	36–43
	Caípe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo, Maporal	0.56–0.60	0.08–0.11	0.34–0.50	44–50	45–50
	Socororo	0.57–0.64	0.06–0.08	0.14–0.31	36–55	46–59
	Junín	0.58–0.61	0.08–0.10	0.19–0.24	NCB	NCB
	Ayacucho	0.59–0.62	0.09	0.21	65	38
	Carabobo	0.57	0.12	0.21	NCB	NCB
	Boscán	0.56	0.11	0.13	52	51
	Mara	0.59–0.60	0.08–0.13	0.20–0.28	43–56	39–60
	Mara Oeste	0.60–0.62	0.06–0.14	0.16–0.21	43–52	45–70
	Lagunillas	0.55	0.09	0.44	NCB	NCB
	Los Manueles	0.58	0.15	0.38	50	60
	Source rocks	Querecual	0.53–0.63	0.05–0.09	0.38–0.54	NCOM
San Antonio		0.56–0.62	0.05–0.07	0.35–0.53	NCOM	NCOM
Naricual		0.58–0.60	0.06–0.07	0.30–0.40	48–58	46–50
La Luna		0.58–0.62	0.07–0.14	0.21–0.36	42–51	44–56

NCB: Not calculated in biodegraded oils.

NCOM: Not calculated in overmature source rocks.

^a $C_{32}22S/C_{32}22(S+R)$ = homohopane isomerization (Seifert and Moldowan, 1980).

^b Mor/Hop: Moretanes/Hopanones = $C_{30}17\beta(H), 21\alpha(H)$ -moretane/ $C_{30}17\alpha(H), 21\beta(H)$ -hopane (Seifert and Moldowan, 1980).

^c Ts/(Ts + Tm) = $C_{27}18\alpha$ -trisorneohopane/($C_{27}18\alpha$ -trisorneohopane + $C_{27}17\alpha(H)$ -trisorneohopane) (Seifert and Moldowan, 1978).

^d %C₂₉20S: $C_{29}20S/(C_{29}20S + C_{29}20R)$ steranes.

^e %C₂₉αβ: $C_{29}\beta\beta/(C_{29}\beta\beta + C_{29}\alpha\alpha)$ steranes (Seifert and Moldowan, 1978; Mackenzie et al., 1980).

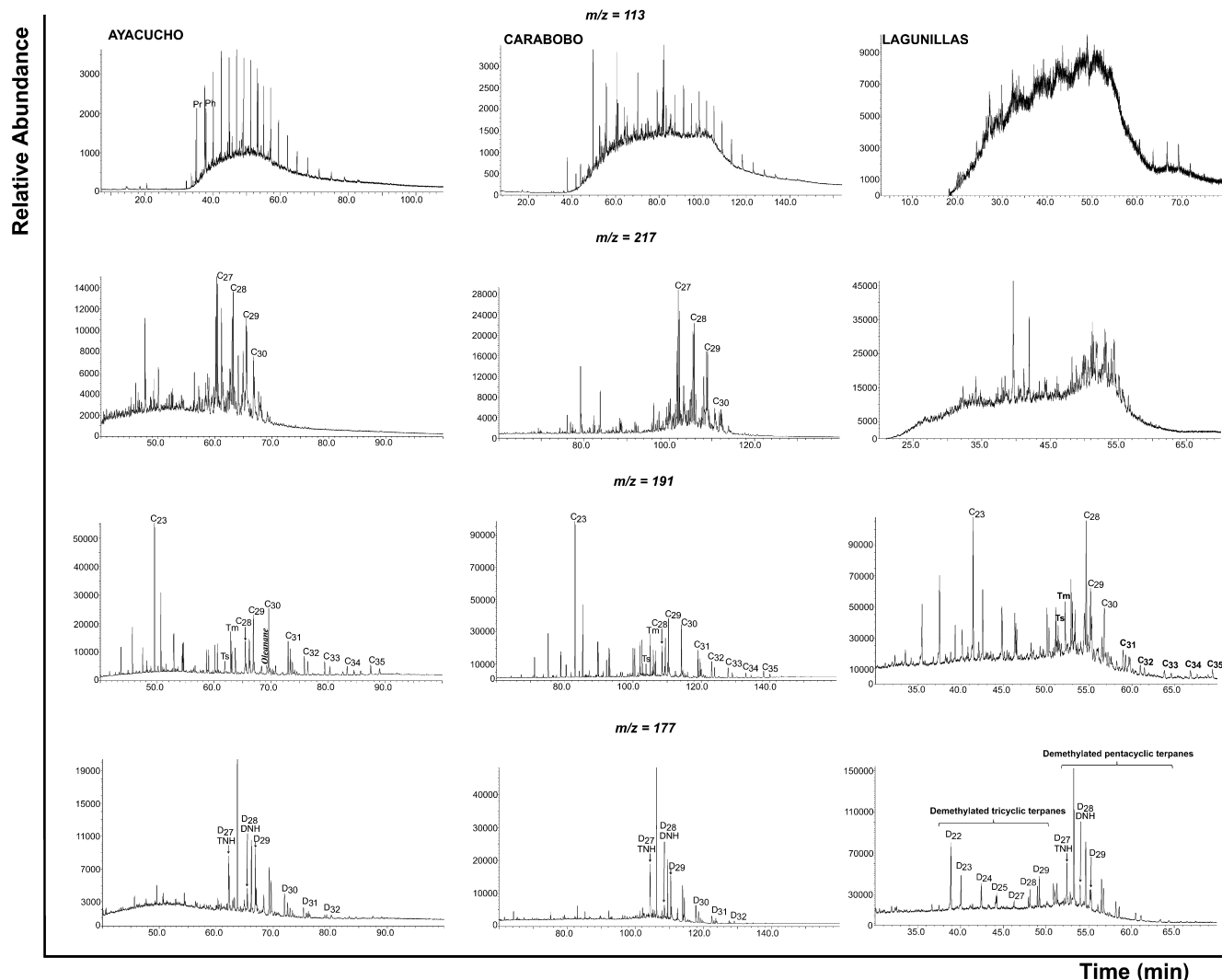


Fig. 8. Mass fragmentograms showing different levels of biodegradation, *n*-alkanes and isoprenoid alkanes (m/z 113), steranes (m/z 217), terpanes (m/z 191), demethylated tricyclic terpanes and hopanes (25-norhopanes) (m/z 177) of selected crude oil samples from the Eastern and Maracaibo basins.

window. In the Querecual (0.05–0.09) and San Antonio (0.05–0.07) formations, Mor/Hop values near 0.05 are related to higher thermal maturity. Vitrinite reflectance values for the Querecual Formation kerogen samples range are in the range 0.9–2.0 %Ro (López and Pasquali, 1997). These data offer additional support for the presence of a thermally mature kerogen along this type section.

The $Ts/(Ts + Tm)$ ratio is based on the lower thermal stability of $17\alpha(H)-22,29,30$ -trisorhopane (Tm) compared to that of $18\alpha(H)-22,29,30$ -trisorneohopane (Ts) (Seifert and Moldowan, 1978). In order to use this ratio in the interpretations that follow, it is necessary to consider that crude oils from carbonate source rocks have unusually low $Ts/(Ts + Tm)$ ratios (≤ 0.25) compared to those from shales representing anoxic environments (0.26–0.34) (Peters et al., 2005). This is the result of different source rock lithology in the samples analyzed. $Ts/(Ts + Tm)$ values (Table 7) for oil samples from Boscán (0.13), Socororo (0.14–0.31), Junín (0.19–0.24), Ayacucho (0.21), Carabobo (0.21), Mara (0.20–0.28) and Mara Oeste (0.16–0.21) are in the 0.13–0.31 range. In this group, one sample from the Socororo field (= 0.31) and one sample from the Mara field (= 0.28) have a $Ts/(Ts + Tm)$ ratio higher than 0.24. Aside from these two exceptions, these crude oils have a $Ts/(Ts + Tm)$ ranging from 0.13 to 0.24, which indicates that the differences in the level of maturity of the oils in this group are small. Additionally, the

values are typical for crude oils derived from carbonate source rock (Peters et al., 2005), as suggested by the other biomarkers (see next section). However, a more detailed comparison of $Ts/(Ts + Tm)$ values for the crude oils described above suggest that the Boscán (0.13) and Mara Oeste (0.16–0.21) oil fields have the lowest maturity, the latter of which has only one oil with a value of 0.21 and the remaining one in the 0.16–0.18 range. In a previous work Talukdar et al. (1986) indicated the lowest maturity for these crude oils. In crude oils from the Barinas sub-basin, $Ts/(Ts + Tm)$ is in the 0.34–0.50 range, but this maturity parameter is not used because, as López et al. (1998) have noted, these crude oils were generated from a source rock with variable lithofacies, and this ratio is maturity and source-dependent (Peters et al., 2005).

The $Ts/(Ts + Tm)$ values from Querecual (0.38–0.54) and San Antonio (0.35–0.53) indicate higher thermal maturity for carbonate source rocks, whereas the values for La Luna (0.21–0.36) indicate the lowest maturity (only one sample has a value of 0.36). In the shale source rock from the Naricual formation (0.30–0.40), these values are the result of rock lithology since shales have higher $Ts/(Ts + Tm)$ ratios than carbonate source rocks (Rullkötter et al., 1985).

C_{29} sterane isomerization ratios [$C_{29}20S/(20S + 20R)$ and $C_{29}(\alpha\beta\beta/\alpha\beta\beta + \alpha\alpha\alpha)$] were calculated for those samples in which

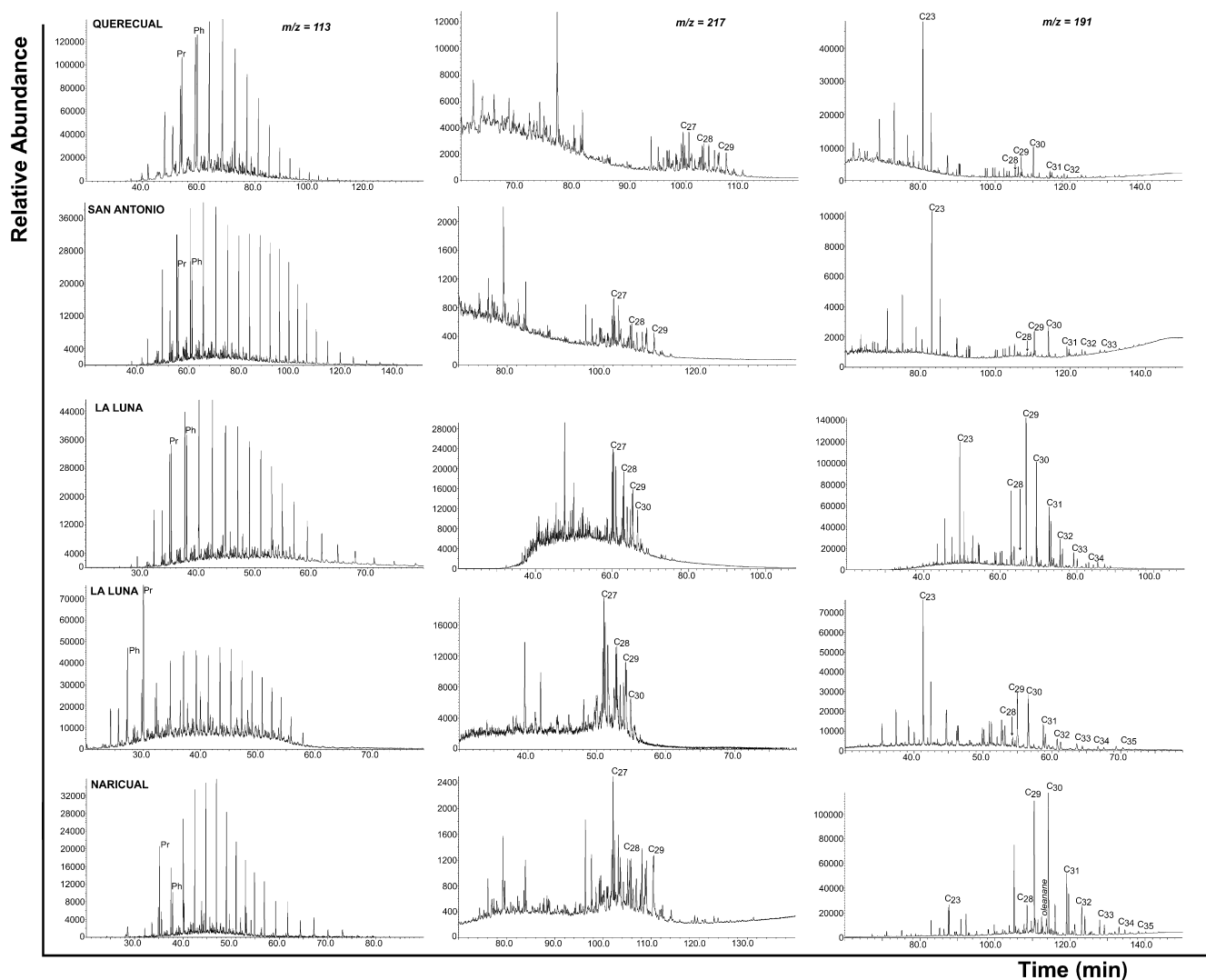


Fig. 9. Mass fragmentograms showing *n*-alkanes and isoprenoid alkanes pristane and phytane in *m/z* 113, steranes in *m/z* 217 and terpanes in *m/z* 191 from selected rock samples from the Eastern and Maracaibo basins.

steranes were unaltered by biodegradation (Table 7). The equilibrium end point of these ratios is 52–55% and 67–71% for $C_{29}20S$ and $C_{29}\beta\beta$, respectively (Peters et al., 2005). Fig. 10 shows the correlation of thermal maturity based on $C_{29}20S$ and $C_{29}\beta\beta$ steranes for a set of selected samples. The values for these ratios indicate that the endpoint has not been reached and suggest that the crude oils were generated by source rocks near the peak of the oil window. Additionally, it is possible that the maturity sequence for the selected crude oils is: La Victoria, Guafita < Caípe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo, Maporal \cong Boscán \cong Mara Oeste \cong Orinoco Oil Belt (Junín, Ayacucho, Carabobo) < Mara \cong Los Manuales. This sequence was also determined based on Mor/Hop ratios.

4.6. Biomarkers: biodegraded oils

Some crude oils from Mara and Mara Oeste are biodegraded even though they contain *n*-alkanes and isoprenoid alkanes (pristane and phytane). They have biodegradation levels from 1–4 (light to moderate) according to the Peters and Moldovan (1993) scale, and there is no evidence for the alteration of steranes and terpanes (Fig. 8). On the other hand, some crude oils from Caípe, Silvestre and Sinco from the Barinas sub-basin have a normal distribution

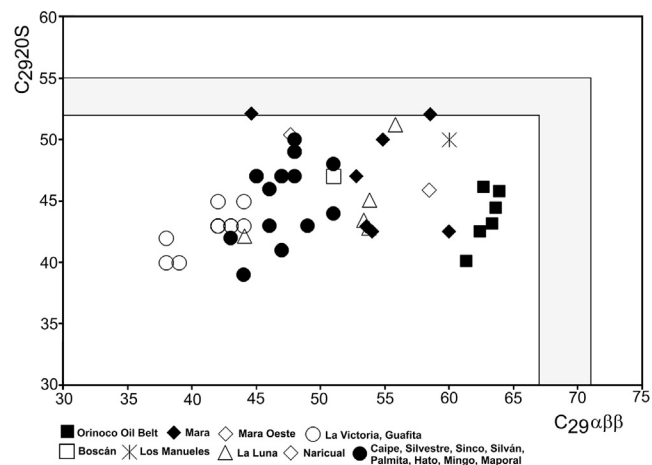


Fig. 10. Thermal maturity based on $C_{29}20S$ and $C_{29}\alpha\beta\beta$ steranes for selected crude oils and source rocks from Venezuelan basins.

of *n*-alkanes, terpanes and steranes. However, in a previous work López et al. (1998) detected the presence of 25-norhopanes, which indicates biodegradation in the 7–8 level. The distribution of these

biomarkers, with the presence of *n*-alkanes, terpanes and steranes together with 25-norhopanes, indicate that these oils are mixtures.

Severely biodegraded oils were identified in the Orinoco Oil Belt, the Socororo field from the Eastern Basin and the Lagunillas field from the Maracaibo Basin (Fig. 8). The oils from the Ayacucho and Carabobo fields contain *n*-alkanes, pristane and phytane. There is no evidence for the alteration of the C₂₇–C₂₉ steranes, but the C₂₉–C₃₀ hopanes and C₃₁–C₃₅ homohopanes are biodegraded, along with the presence of 25-norhopanes. Again, the presence of compounds with different levels of susceptibility to biodegradation indicates that they must be mixtures of two oil charges subjected to biodegradation. Additionally, in crude oils from the Socororo field, the presence of pristane and phytane, along with alteration of hopanes and steranes and the presence of 25-norhopanes, once again indicates that the oils are mixtures with different levels of biodegradation (López et al., 2015). Crude oils from the Lagunillas field have the highest levels of biodegradation (Fig. 8). Oil from Lagunillas is severely biodegraded, as indicated by the depletion of *n*-alkanes, pristane and phytane, the alteration of C₂₇–C₂₉ steranes, C₂₉–C₃₀ hopanes and C₃₁–C₃₅ homohopanes and the formation of 25-norhopanes. Furthermore, this oil contains demethylated tricyclic terpanes (DTT), and the demethylation of tricyclic terpanes occurs with the removal of a methyl group at C-10. 17-Nor-tricyclic terpanes in the C₂₂–C₂₉ range were observed in crude oils from Lagunillas (Fig. 8). These compounds were already identified in sidewall samples from a producing well in this field (Alberdi et al., 2001).

These results show the presence of various migration and reservoir filling events and the subsequent alteration of the accumulated crude oil. The results also point to four different cases: (a) two reservoir filling events with oils generated by the same source rock (La Luna Formation), which occurred at different maturity stages with subsequent light to moderate biodegradation levels in some of the reservoirs (Mara and Mara Oeste); (b) two reservoir filling events with a first, severely biodegraded charge and a later accumulation of an oil generated by a source rock near the peak of the oil window showing no evidence of biodegradation (Caípe, Silvestre and Sinco); (c) two reservoir filling events with oils generated by one source rock (Querecual Formation) and in the same maturity stage (near the peak of the oil window), which suggests that the oil charges happened around the same time (Junín, Ayacucho, Carabobo and Socororo). This is reflected in the presence of compounds with different levels of susceptibility to biodegradation and (d) evidence of an oil charge with oils generated by a source rock near the peak of the oil window with severe alteration (Lagunillas). In these cases, the alteration of the subsequent oil charges will depend on the ability of bacteria to biodegrade them. Consequently, the composition of reservoir crude oils and their physical properties are the result of the mix of oil charges and their subsequent biodegradation, as has been proposed for various oil basins (Wenger et al., 2002; Larter et al., 2003, 2006; Ross et al., 2010; Larter et al., 2012; Zhang et al., 2014).

4.7. V, Ni and S concentrations in crude oils and source rock, relationship with molecular parameters

Based on the V/Ni dependence on redox conditions (V vs Ni graph, Fig. 11), oils and source rocks can be grouped according to paleo-redox conditions using the Tyson and Pearson (1991) classification. They can also be classified according to source rock lithology. These results were compared with the saturated hydrocarbon biomarker source parameters determined in selected oils samples.

The graph in Fig. 11a and the biomarker indicators of organic matter type and sedimentation environment (Table 6, Figs. 6–8) show: (1) crude oils from Guafita and La Victoria with sulfur < 0.3% and V/Ni between 0.3 and 0.4, which suggests sedimentation under

suboxic–dysoxic conditions and a marine shale source rock. Pr/Ph > 1, C₃₅/C₃₄ ≥ 1, and C₂₄/C₂₃, C₂₂/C₂₁, C₂₆/C₂₅, C₃₁22R/C₃₀Hop ratios suggest suboxic–dysoxic conditions in marine shales or marls; (2) oils from Caípe, Silvestre, Sinco, Silván, Palmita, Hato, Mingo and Maporal with sulfur between 0.4% and 2.1% and V/Ni in the 1.1–3.5 range, which suggests anoxic–suboxic sedimentation conditions and a marine marl source rock. These oils have Pr/Ph ≈ 1, C₃₅/C₃₄ ≤ 1 and C₂₄/C₂₃, C₂₂/C₂₁, C₂₆/C₂₅, C₃₁22R/C₃₀Hop ratios that indicate anoxic–suboxic sedimentation conditions and a marine marl source rock; (3) oils from Junín, Ayacucho, Carabobo and Socororo, with sulfur between 0.8% and 5.7% and V/Ni between 1.3 and 5.5, from a source rock deposited in anoxic–suboxic conditions, which may be related to marine marls or carbonate source rocks from the Querecual Formation. These interpretations are supported by C₃₅/C₃₄ ≈ 1, C₂₄/C₂₃, C₂₂/C₂₁, C₂₆/C₂₅ and C₃₁22R/C₃₀Hop ratios, which suggest the generation of a marls or limestone source rock in an anoxic–suboxic environment; (4) oils from Los Manueles and Lagunillas, with a sulfur content between 0.4% and 1.1% and 2.3% and 3.4%, respectively, and V/Ni between 6.1 and 8.5, in a suboxic–dysoxic environment from marls or carbonate source rocks. Oils from Los Manueles have Pr/Ph = 1.2–2.5, which is related to a more oxygenated environment. Additionally, Los Manueles and Lagunillas have C₂₄/C₂₃, C₂₂/C₂₁, C₂₆/C₂₅ and C₃₁22R/C₃₀Hop ratios that suggest marls or carbonate source rocks and (5) oils from Mara, La Paz, Mara Oeste and Boscán, with varying sulfur content as the result of maturity or biodegradation. These oils have the highest V/Ni ratio (9.5–14.5), with euxinic sedimentation conditions and a carbonate source rock from the La Luna Formation. This is consistent with the data obtained from the biomarkers, in which Pr/Ph and C₃₅/C₃₄ suggest anoxic conditions, and the carbonate lithology of the source rock is supported

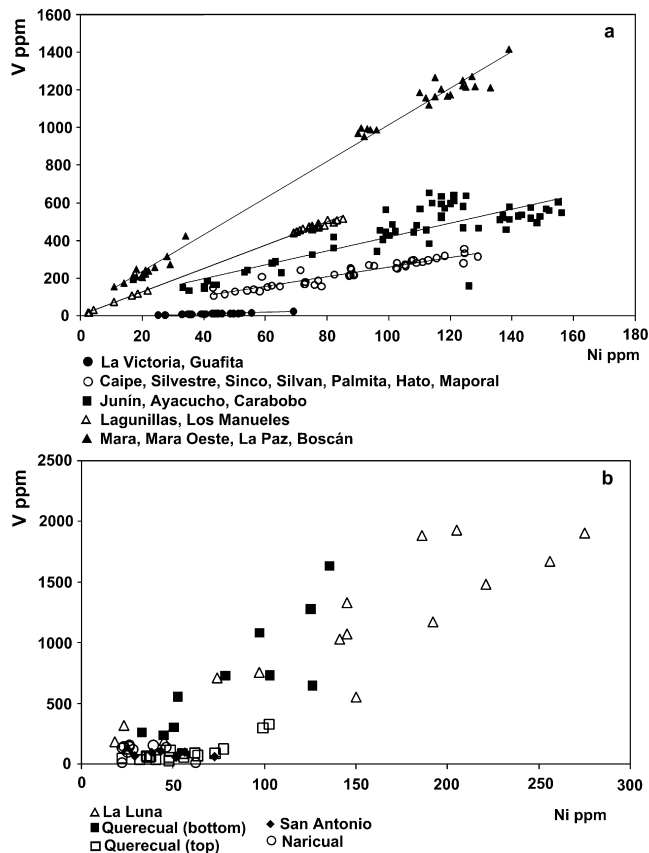


Fig. 11. Vanadium vs nickel concentrations in: (a) crude oils and (b) source rocks from Venezuelan oil basins.

by C₂₉ norhopane higher than C₃₀ hopane and C₂₄/C₂₃, C₂₂/C₂₁, C₂₆/C₂₅, C₃₁22R/C₃₀Hop ratios. Our classification based on S, V and Ni is similar to that of Barwise (1990), which determined oil classes based on V and Ni concentrations. It is also supported by the biomarker parameters.

These interpretations of V/Ni and V/(V + Ni) are independent of source rock maturity. Both the Querecual and San Antonio formations are post-mature source rocks, with $T_{\max} > 470$ °C, Mor/Hop ≤ 0.09 and Ts/(Ts + Tm) > 0.35 , whereas the La Luna and Narica formations have a maturity near the peak of the oil window, with $T_{\max} < 448$ °C, Mor/Hop from 0.06–0.141 and Ts/(Ts + Tm) < 0.35 (Tables 3 and 7, Fig. 9). Regardless of their maturity, the source rocks may have similar V/Ni ratios, since these depend mainly on the sedimentation environment, and the proportionality between both elements is maintained during oil generation.

5. Conclusions

The main source rocks from Venezuelan basins are the La Luna Formation (limestone) from the Maracaibo Basin, which originated in anoxic–euxinic environments, and the Querecual (limestone and marl) and San Antonio (shales) formations from the Eastern Basin, which originated in anoxic–suboxic environments. The results of our study of vanadium, nickel and sulfur along with Rock-Eval pyrolysis parameters and biomarkers support these interpretations.

The results obtained for the vanadium, nickel and sulfur concentrations of crude oils and source rocks from Venezuelan basins show variable sedimentation conditions (from suboxic–dysoxic to anoxic–suboxic) of source rocks with different lithology (shale, marl or carbonate), organic matter input (marine, terrigenous or mixture) and maturity (immature, mature or post-mature). These results support the data obtained from biomarker indicators of maturity, organic matter type and sedimentation environment.

However, in the case of crude oils from Lagunillas (mixed oils) and Los Manueles (terrigenous and mixed marine and terrigenous oils), the study of biomarkers and V/Ni or V/(V + Ni) ratios suggest differences in redox conditions when compared to other oils from the Maracaibo Basin. Similarly, crude oils from the Orinoco Oil Belt and Socororo field also suggest changes in paleo-redox conditions, which have been corroborated by comparing the V/Ni or V/(V + Ni) in the Querecual Formation, the source rock of these oils. Therefore, it seems necessary to identify changes in paleo-redox conditions in the La Luna Formation or in other potential source rocks (terrigenous organic matter) that may have contributed to the accumulation of hydrocarbons in the Maracaibo Basin. Moreover, the source rocks of crude oils from the Barinas sub-basin still need to be identified. All of this suggests that, although the main source rocks in Venezuelan basins are well established, there are still doubts concerning the lateral and vertical variations in organic and inorganic facies and paleo-oxygenation conditions. It is also possible that other source rocks have contributed to the accumulation of hydrocarbons in Venezuelan basins.

The composition of biodegraded crude oils is the result of the mix of oil charges and their subsequent biodegradation, which depends on the ability of bacteria present in the reservoir to biodegrade the incorporated oils.

Acknowledgements

This work was funded by the Consejo de Desarrollo Científico y Humanístico de la Universidad Central de Venezuela (CDCH-UCV) under research grant PG-03-8204-2011/2 and the Fondo Nacional de Ciencia, Tecnología e Innovación (FONACIT) under research grant G-2012002299. The authors are grateful for the critical input

of three anonymous reviewers who contributed to improving the original manuscript.

Associate Editor—Courtney Turich

References

- Alberdi, M., López, C., Galarraga, F., 1996. Genetic classification of crude oil families in the Eastern Venezuelan basin. *Boletín de la Sociedad Venezolana de Geólogos* 21, 7–21.
- Alberdi, M., López, L., 2000. Biomarker 18 α (H)-oleanane: a geochemical tool assesses Venezuelan petroleum systems. *Journal of South American Earth Science* 13, 751–760.
- Alberdi, M., Moldovan, J.M., Peters, K.E., Dahl, J.E., 2001. Stereoselective biodegradation of tricyclic terpanes in heavy oils from the Bolivar Coastal Fields, Venezuela. *Organic Geochemistry* 32, 181–191.
- Alberdi-Genolet, M., Tocco, R., 1999. Trace metals and organic geochemistry of the Machiques Member (Aptian–Albian) and La Luna Formation (Cenomanian–Campanian), Venezuela. *Chemical Geology* 160, 19–38.
- Barwise, A.J., 1990. Role of vanadium and nickel in petroleum classification. *Energy & Fuel* 4, 647–652.
- Behar, F., Beaumont, V., Pentead, H.L., 2001. Rock-eval 6 technology: performances and developments. *Oil & Gas Science and Technology – Revue de l'IFP* 56, 111–134.
- Branthaver, J.F., Filby, R.H., 1987. Application of metals complexes in petroleum to exploration geochemistry. In: Filby, R.H., Branthaver, J.F. (Eds.), *Metals Complexes in Fossil Fuels. Symposium Series*, vol. 344. American Chemical Society, pp. 84–99.
- Breit, G.N., Wanty, R.B., 1991. Vanadium accumulation in carbonaceous rocks: a review of geochemical controls during deposition and diagenesis. In: Branthaver, J.F., Filby, R.H. (Eds.), *Trace Metals in Petroleum Geochemistry*, Chemical Geology, vol. 91, pp. 83–97.
- Cassani, F., Eglinton, G., 1986. Organic geochemistry of Venezuelan extra-heavy oils: 1. Pyrolysis of asphaltenes: a technique for the correlation and maturity evaluation of crude oils. *Chemical Geology* 56, 167–183.
- Cassani, F., Eglinton, G., 1991. Organic geochemistry of Venezuelan extra-heavy crude oils. 2. Molecular assessment of biodegradation. *Chemical Geology* 91, 315–333.
- Connan, J., Bouroulec, J., Dessort, D., Albrecht, P., 1986. The microbial input in carbonate-anhydrite facies of a sabkha palaeoenvironment from Guatemala: a molecular approach. *Organic Geochemistry* 10, 2950.
- Curiale, J., 1985. Oil types and source rock-oil correlation on the North Slope, Alaska – a cooperative USGS-Industry study. In: Magoon, L.B., Claypool, G.E. (Eds.), *Alaska North Slope Oil-Rock Correlation Study: Analysis of North Slope Crude*, vol. 20. American Association of Petroleum Geologists Studies in Geology, pp. 203–231.
- Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature* 272, 216–222.
- Ellrich, J., Hirner, A., Stark, H., 1985. Distribution of trace elements in crude oils from southern Germany. *Chemical Geology* 48, 313–323.
- Filby, R., 1975. The nature of metals in petroleum. In: Yen, T.F. (Ed.), *The Role of Trace Elements in Petroleum*. Ann Arbor Science Publishers Inc., Ann Arbor, pp. 31–58.
- Filby, R.H., 1994. Origin and nature of trace elements species in crude oils, bitumens and kerogens: implications for correlation and other geochemical studies. In: Parnell, J. (Ed.), *Migration and Evolution of Fluids in Sedimentary Basins*, vol. 78. Geological Society, London, Special Publications, pp. 203–219.
- Gallango, O., Cassani, F., 1992. Biological marker maturity parameters of marine crude oils and rock extracts from the Maracaibo Basin, Venezuela. *Organic Geochemistry* 18, 215–224.
- González, C., Iturralde, J., Picard, X., 1980. *Geología de Venezuela y de sus Cuencas Petrolíferas*. Caracas, Ediciones Foninves, p. 1031.
- Greibrokk, T., Lundanes, E., Norli, H.R., Dyrstad, K., Olsen, S.D., 1994. Experimental simulation of oil migration-distribution effects on organic compound groups and on metal/metal ratios. *Chemical Geology* 116, 281–299.
- Hesse, P.R., 1971. *A Textbook of Soil Chemicals Analysis*. John Murray Publishers, London.
- Hirner, A.V., Xu, Z., 1991. Trace metals speciation in Julia Creek oil shale. In: Branthaver, J.F., Filby, R.H. (Eds.), *Trace Metals in Petroleum Geochemistry*, Chemical Geology, vol. 91, pp. 115–124.
- Hitchon, B., Filby, R.H., 1984. Use of trace elements for classification of crude oils into families-examples for Alberta, Canada. *American Association of Petroleum Geologists Bulletin* 68, 838–849.
- Hunt, J.M., 1996. *Petroleum Geochemistry and Geology*. W.H. Freeman, San Francisco.
- Jones, B., Manning, D.A.C., 1994. Comparison of geochemical indices used for the interpretation of paleoredox conditions in ancient mudstone. *Chemical Geology* 111, 111–129.
- Larter, S., Wilhelms, I., Head, I., Koopmans, M., Aplin, A., di Primio, R., Zwach, C., Erdmann, M., Telnaes, N., 2003. The controls on the composition of biodegraded oils in the deep subsurface. Part I – biodegradation rates in petroleum reservoirs. *Organic Geochemistry* 34, 601–613.

- Larter, S., Huang, H., Adams, J., Bennett, B., Jokanola, O., Oldenburg, T., Jones, M., Head, I., Riediger, C., Fowler, M., 2006. The controls on the composition of biodegraded oil in the deep surface: Part II Geological controls on subsurface biodegradation fluxes and constraints on reservoir-fluid property prediction. *Bulletin of the American Association of Petroleum Geologists* 90, 921938.
- Larter, S., Oldenburg, T., Marcano, N., Snowdon, L., Adams, J., Chanthramonti, K., Stopford, A., Huang, H., Song, F., Laflamme, C., Ranger, M., 2012. New Routes to Solutions of the WCSB Oil Charge Conundrum: γ -Ray Photons and Fourier Transform Mass Spectrometry. *Canadian Society of Petroleum Geologists Geoconvention*. 6 p (abstract).
- Lewan, M.D., 1984. Factors controlling the proportionality of vanadium and nickel in crude oils. *Geochimica et Cosmochimica Acta* 48, 2231–2238.
- Lewan, M.D., Maynard, J.B., 1982. Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geochimica et Cosmochimica Acta* 46, 2547–2560.
- Lo Mónaco, S., López, L., Labastida, E., 1999. Correlación de crudos de la subcuenca de Barinas. *Revista Latinoamericana de Geoquímica Orgánica* 5, 47–54.
- Lo Mónaco, S., López, L., Rojas, H., Lugo, P., García, D., Gastiel, J., 2007. Applications of electron microprobe analysis (EPMA) in the study of Venezuelan source rocks: La Luna and Querecual Formations. *Fuel* 86, 641–648.
- Lo Mónaco, S., López, L., Rojas, H., García, D., Premovic, P., Briceño, H., 2002. Distribution of major and trace elements in La Luna Formation, southwestern Venezuelan basin. *Organic Geochemistry* 33, 1593–1608.
- López, L., 1997. Comparación de evidencias geológicas y geoquímicas de migración primaria en rocas fuentes carbonáticas y lutíticas. *Revista Latinoamericana de Geoquímica Orgánica* 3, 1932.
- López, L., 2014. Study of the biodegradation levels of oils from the Orinoco Oil Belt (Junín area) using different biodegradation scales. *Organic Geochemistry* 66, 60–69.
- López, L., Lo Mónaco, S., 2004. Geochemical implications of trace elements and sulfur in the saturate, aromatic and resin fractions of crude oil from the Mara and Mara Oeste fields, Venezuela. *Fuel* 83, 365–374.
- López, L., Lo Mónaco, S., 2010. Geoquímica de crudos de la Faja Petrolífera del Orinoco. *Cuenca Oriental de Venezuela. Revista de la Facultad de Ingeniería-UCV* 25, 41–50.
- López, L., Pasquali, J., 1997. Primary migration within the Querecual Formation, Venezuela: geological and geochemical evidences. *Boletín de la Sociedad Venezolana de Geólogos* 22, 516.
- López, L., Lo Mónaco, S., Espinoza, A., Blanco, A., 1991. Distribución de S, V y Ni en crudos y asfaltenos de los campos Mara y Mara Oeste Cuenca del Lago de Maracaibo, Venezuela. *Interciencia* 16, 333–342.
- López, L., Lo Mónaco, S., Galarraga, F., Lira, A., Cruz, C., 1995. V/Ni ratio in maltene fractions of crude oils from West Venezuela Basin: Correlation studies. *Chemical Geology* 119, 255–262.
- López, L., Lo Mónaco, S., Richardson, M., 1998. Use of molecular parameters and trace elements in oil correlation studies, Barinas subbasin, Venezuela. *Organic Geochemistry* 29, 613–629.
- López, L., Lo Mónaco, S., Volkman, J.K., 2015. Evidence for mixed and biodegraded crude oils in the Socororo field, Eastern Venezuela Basin. *Organic Geochemistry* 82, 12–21.
- López, L., Quintero, K., Lugo, P., Lo Mónaco, S., 2011. Efecto de la inyección de vapor sobre la composición de crudos. *Revista de la Facultad de Ingeniería – UCV* 26, 83–95.
- Mackenzie, A.S., Patience, R.L., Maxwell, J.R., Vandenbroucke, M., Durand, B., 1980. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France. I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochimica et Cosmochimica Acta* 44, 17091721.
- Moldowan, J.M., Seifert, W., Gallegos, E.J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rocks. *American Association of Petroleum Geologists Bulletin* 69, 12551268.
- Moldowan, J.M., Huizinga, B.J., Dahl, J.E., Fago, F.J., Taylor, D.W., Hickey, L.J., 1994. The molecular fossil record of oleanane and its relationship to angiosperms. *Science* 265, 768771.
- Odermatt, J.R., Curiale, J.A., 1991. Organically bound metals and biomarkers in the Monterey Formation of the Santa Maria basin, California. In: Branthaver, J.F., Filby, R.H. (Eds.), *Trace Metals in Petroleum Geochemistry*, Chemical Geology, vol. 91, pp. 99–113.
- Peters, K.E., Moldowan, J.M., 1991. Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of homohopanes in petroleum. *Organic Geochemistry* 17, 4761.
- Peters, K.E., Moldowan, J.M., 1993. *The Biomarker Guide. Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Prentice Hall, New Jersey.
- Peters, K.E., Moldowan, J.M., Driscoll, A.R., Demaison, G.J., 1989. Origin of Beatrice oil by co-sourcing from Devonian and Middle Jurassic source rocks, Inner Moray Firth, United Kingdom. *American Association of Petroleum Geologist Bulletin* 73, 454471.
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The Biomarker Guide*. Cambridge University Press, Cambridge, UK.
- Quintero, K., Lo Mónaco-Carias, G., López, L., Lo Mónaco, S., Escobar, G., Peralba, M.C.R., Franco, N., Kalkreuth, W., 2012. Potential petroleum source rocks in a Tertiary sequence of the eastern Venezuelan basin. *Journal of South American Earth Science* 37, 256–265.
- Reynolds, R.C., 1963. Matrix corrections in trace element analysis by X-ray fluorescence: estimation of the mass absorption coefficient by Compton scattering. *American Mineralogist* 48, 11331141.
- Ross, A.S., Farrimond, P., Erdmann, M., Larter, S.R., 2010. Geochemical compositional gradients in a mixed oil reservoir indicative of ongoing biodegradation. *Organic Geochemistry* 41, 307320.
- Rullkötter, J., Spiro, B., Nissenbaum, A., 1985. Biological marker characteristics of oils and asphalts from carbonate source rocks in a rapidly subsiding graben, Dead Sea. *Israel. Geochimica et Cosmochimica Acta* 49, 13571370.
- Seifert, W.K., Moldowan, J.M., 1978. Applications of steranes, triterpanes and monoaromatics to the maturation of crude oils. *Geochimica et Cosmochimica Acta* 42, 7195.
- Seifert, W.K., Moldowan, J.M., 1980. The effect of thermal stress on source rock quality as measured by hopane stereochemistry. In: Douglas, A.G., Maxwell, J.R. (Eds.), *Advances in Organic Geochemistry 1979*. Pergamon Press, Oxford, pp. 229–237.
- Simoza, R.L., Carrion de La Rosa, N., Torres, J., López, C., 1985. Distribución de V, Ni, Zn, Mo, Ca, K, Fe y Cu en los crudos de la Cuenca Oriental de Venezuela. *Memorias VI Congreso Geológico Venezolano III*, 2087–2110.
- Talukdar, S.C., Marcano, F., 1994. Petroleum system of the Maracaibo basin, Venezuela. In: Magoon, L.B., Dow, W.G. (Eds.), *The Petroleum System-From Source Rock to Trap*, vol. 60. American Association of Petroleum Geologists Memoir, pp. 463–481.
- Talukdar, S., Gallango, O.S., Ruggiero, A., 1985. Formaciones La Luna y Querecual de Venezuela: Rocas Madres de Petróleo. *Memorias VI Congreso Geológico Venezolano VI*, 3606–3642.
- Talukdar, S., Gallango, O., Chin-Alien, M., 1986. Generation and migration of hydrocarbons in the Maracaibo basin: an integrated basin study. In: Leythaeuser, D., Rullkötter, J. (Eds.), *Advances in Organic Geochemistry 1985*. Pergamon Press, Oxford, pp. 261–279.
- Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence*. Springer-Verlag, New York.
- Tocco, R., Alberdi, M., Ruggiero, A., Jordan, N., 1994. Organic geochemistry of the Carapita Formation and terrestrial crude oils in the Maturin sub-basin, Eastern Venezuelan Basin. *Organic Geochemistry* 21, 11071119.
- Tocco, R., Parnaud, F., Gallango, O., Alberdi, M., Passalacqua, H., 1997. Geochemical modelling of the principal source rocks of the Barinas and Maracaibo basin, Western Venezuela. *Boletín de la Sociedad Venezolana de Geólogos* 22, 17–28.
- Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. *Chemical Geology* 232, 12–32.
- Tribovillard, N., Hatén, E., Overbuch, O., Barbecot, F., Bout-Roumazeilles, V., Trentesaux, A., 2015. Iron availability as a dominant control on the primary composition and diagenetic overprint of organic-matter-rich rocks. *Chemical Geology* 401, 67–82.
- Tyson, R.V., Pearson, T.H., 1991. Modern and ancient continental shelf anoxia: an overview. In: Tyson, R.V., Pearson, T.H. (Eds.), *Modern and Ancient Continental Shelf Anoxia*, vol. 58. Geological Society London Special Publications, pp. 1–26.
- Vandenbroucke, M., Largeau, C., 2007. Kerogen origin, evolution and structure. *Organic Geochemistry* 38, 719833.
- Wenger, L.M., Davis, C.L., Isaksen, G.H., 2002. Multiple controls on petroleum biodegradation and impact on oil quality. *SPE Reservoir Evaluation & Engineering* 5, 375383.
- Xu, G., Hannah, J.L., Bingen, B., Georgiev, S., Stein, H.J., 2012. Digestion methods for trace elements measurements in shales. *Chemical Geology* 324–325, 132147.
- Zhang, S., Huang, H., Su, J., Zhu, G., Wang, X., Larter, S., 2014. Geochemistry of Paleozoic marine oils from the Tarim Basin, NW China. Part 4: paleobiodegradation and oil charge mixing. *Organic Geochemistry* 67, 4157.
- Zumberge, J.E., 1984. Source rocks of the La Luna Formation (Upper Cretaceous) in the Middle Magdalena Valley, Colombia. In: Palacas, J.G. (Ed.), *Geochemistry of Source Rock Potential of Carbonate Rocks*. American Association of Petroleum Geologists, pp. 127–133.