Evidence for mixed and biodegraded crude oils in the Socororo field, Eastern Venezuela Basin

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ABSTRACT

This work presents a geochemical study of crude oils from the Socororo field (Socororo Major Area) in the Maturín Sub-basin of the Eastern Venezuelan Basin. The V + Ni total concentrations and V/(V + Ni) ratios suggest the presence of two oil groups. These oils are heavy aromatic–asphaltic and according to their sulfur content, API gravity and hydrocarbon compositions, fall into the same two groups established from the V and Ni proxies. Although the analyzed crude oils show evidence of biodegradation, it was possible to determine, based on various biomarkers parameters, that the oils originated from marine organic matter in a marine carbonate or marine marl source rock deposited under anoxic to suboxic conditions. The oils were generated near the peak of the oil window. Distributions of n-alkanes, isoprenoids, hopanes and steranes combined with a prominent unresolved complex mixture (UCM) indicate that the oils are biodegraded. Moreover, the presence of pristane and phytane, along with alteration of hopanes and steranes and the presence of 25-norhopanes, reveals that these oils are mixtures showing different levels of biodegradation. Sulfur content, V and Ni concentration and saturate, aromatic, resin and asphaltene (SARA) composition provide additional evidence for oil mixing. Such mixed oils originate from several episodes of charging and biodegradation in the reservoirs. The first charge was severely biodegraded and many biomarkers susceptible to degradation (n-alkanes, acyclic isoprenoids, terpanes, methyl hopanes, methyl steranes and steranes) were extensively altered or completely removed. The second oil charge was subjected to a lower degree of biodegradation and only the n-alkanes show significant biodegradation. Both oil charges seem to come from the same source rock, which was deposited under variable redox conditions. Moreover, due to their similar maturity, the generation and migration of these oils to reservoirs likely occurred close together in time.

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1. Introduction

One difficulty in the characterization of crude oils is the presence of oil mixtures in reservoirs, which can result from multiple oil charges from source rocks having different levels of maturity or representing different organic facies. Characterization is even more complex when the different oil charges have undergone different levels of biodegradation. In this case, the biomarker degradation sequences proposed in the literature are not always observed and compounds less resistant to biodegradation occur in oils that show evidence of alteration of more resistant compounds (e.g., Volkman et al., 1983a; Cassani and Eglinton, 1991; Dzou et al., 1999; Pomerantz et al., 2010; Ross et al., 2010; Larter et al., 2012; Zhang et al., 2014).

Microbial biodegradation of crude oil alters or removes various compounds depending on their molecular structures with some compounds more easily degraded than others. Different scales have been developed to assess the extent of oil biodegradation based on comparisons of the relative abundance of various hydrocarbon compound classes (e.g. n-alkanes, pristane, phytane, terpanes, steranes and aromatic steroids, methylnaphthalenes, phenanthrene, methylphenanthrenes, methyldibenzothiophenes) having different susceptibility to biodegradation (Volkman et al., 1983a,b; Volkman et al., 1984; Peters and Moldowan, 1993; Wenger et al., 2002; Larter et al., 2012). Additionally, aromatic compounds show different susceptibility to biodegradation depending on the number of aromatic rings and the position of the alkyl substituents (Volkman et al., 1984; Huang et al., 2004; Bennett and Larter, 2008). The biomarker biodegradation scales reflect the degradation sequence observed most frequently in oil reservoirs. In these scales the level of biodegradation is represented as a step-by-step or sequential process (Connan, 1984),

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but based on quantitative analysis of hydrocarbons from biodegraded oils, biodegradation is better considered as a quasi-stepwise process that results from alteration of some compound classes at quite different rates (Peters and Moldowan, 1991; Larter et al., 2003, 2006; Bennett and Larter, 2008). However, some compounds such as polycyclic aromatic hydrocarbons (PAH) and diasteranes may show no evidence of biodegradation until other more labile compounds are completely removed. Biodegradation decreases crude oil quality due to changes in properties, such vanadium and nickel concentrations, viscosity, API gravity, saturate, aromatic, resin and asphaltene (SARA) composition, isotopic composition and sulfur content (Connan, 1984; Wenger et al., 2002; Larter et al., 2003, 2006; Peters et al., 2005; Sun et al., 2005; Bennett et al., 2013).

One of the world's largest reserves of heavy and extra heavy biodegraded crude oil occurs in the Eastern Venezuelan Basin, which includes the widely studied Orinoco Oil Belt (Cassani and Eglinton, 1986; Audemard et al., 1987; Fiorillo, 1987; Vega and Rojas, 1987; Talukdar et al., 1988; Cassani and Eglinton, 1991; Alberdi et al., 1996; Pardo et al., 2007; López and Lo Mónaco, 2010; López, 2014). The Eastern Venezuelan Basin also contains other areas dominated by heavy crude oil, such as the Socororo Major Area in the Maturín Sub-basin, represented mainly by the Caricari, Cachicamo and Socororo fields (Ughi et al., 2010). The Socororo field is the subject of this study. Here, we describe a series of biomarker parameters measured in crude oils from different oil wells in the Socororo field, in order to provide insights into characteristics of the presumed source rocks (e.g., lithology, organic-matter input, redox depositional conditions and thermal maturity), as well as to establish the extent of biodegradation of each oil. The observed biomarker compositional trends fall outside the sequence of biodegradation commonly prescribed by the classical biodegradation schemes, indicating of oil mixtures from several episodes of charging and biodegradation in reservoirs.

2. Geological setting

The Socororo field (Fig. 1) is located in the Eastern Venezuelan Basin and belongs to the Socororo Major Area in the Maturín Sub-basin (Léxico Estratigráfico, 2014). This area is a monocline with northwest trending faults and regional dips 2–3° north. The sedimentary column, as penetrated by wells drilled in the Socororo Major Area, is represented by the Mesa, Las Piedras, Freites, Oficina and Merecure formations and Temblador and Carrizal groups. Heavy crude oils occur in shallow reservoirs in the Oficina (Miocene) and the Merecure (Oligocene) formations, which are the only commercial petroleum accumulations (Ughi et al., 2010).

The Merecure Formation is composed predominantly (> 50%) of sandstones, which are light gray to dark, massive, very poorly stratified, lenticular, hard, fine to coarse grained (even conglomeratic) and with crossbedding. These sandstones are separated by thin shale intervals, dark gray to black, carbonaceous, with some ferruginous claystones and occasional lignite. The Oficina Formation is composed of alternating gray or dark-gray shales interbedded with sandstones and siltstones. It also contains thin layers of lignite, lignitic shales, claystones with siderite spherules, glauconitic sandstones and thin limestone intervals (Léxico Estratigráfico, 2014).

3. Samples and methods

Eleven samples of crude oil (labeled 1 to 11) from the Socororo field were analyzed in this study. The analytical procedures included sulfur content, V and Ni concentrations, SARA (saturate, aromatic, resin and asphaltene) composition and biomarker analysis of the saturate and aromatic fractions.

3.1. Elemental composition

Trace elements (V and Ni) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Thermal Jarrel Ash ENVIRO II). Sulfur content was determined using a LECO SC-432 sulfur analyzer (López et al., 1998; Lo Mónaco et al., 2002; López and Lo Mónaco, 2004).

3.2. SARA composition

Crude oil samples were separated into asphaltene and maltene fractions applying the NF-T60.115 method (AFNOR, 1975). The
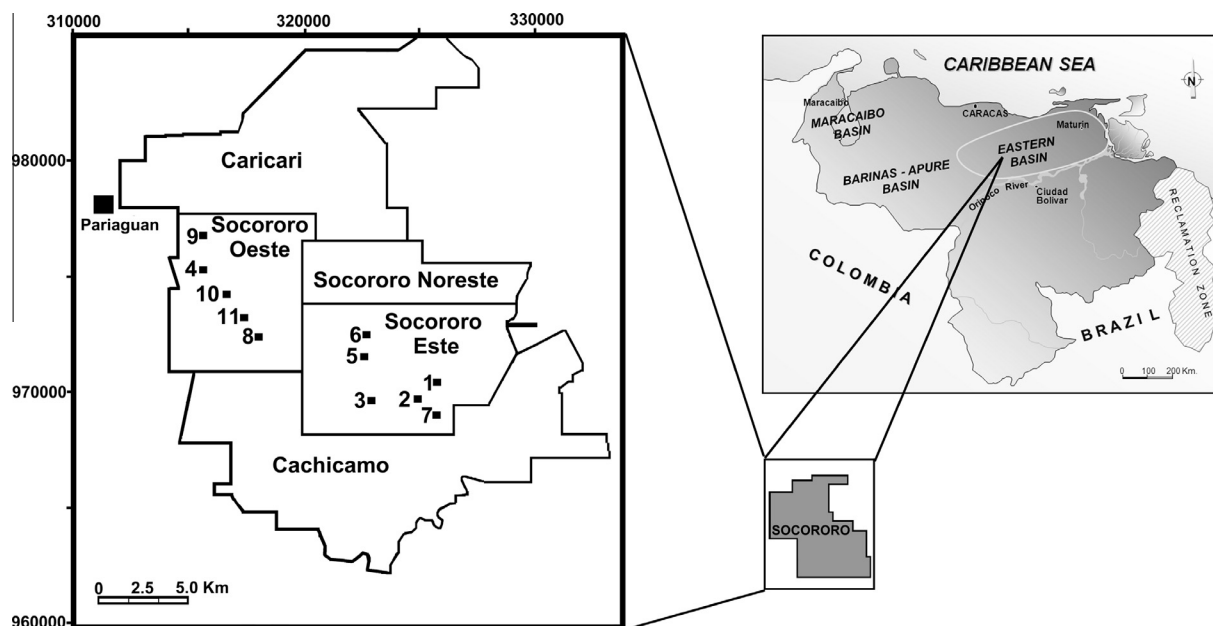

Fig. 1. Map of Venezuela showing the location of the Socororo field in the Eastern Venezuelan Basin.

maltene fraction was separated into its saturate, aromatic and resin fractions by means of adsorption chromatography using packed columns (20 cm long and 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 polar compounds (resins). Purification of the saturated and the aromatic hydrocarbon fractions was carried out twice by liquid chromatography using packed columns as described above.

3.3. Saturate and aromatic biomarkers

Gas chromatography (GC) of the saturated hydrocarbon fractions was carried out on a 6890N Agilent Technologies network gas chromatograph using a flame ionization detector (FID) and DB-1 fused capillary columns (60 m × 0.25 mm × 0.25 μm). Detailed analyses of the saturated and aromatic compounds were performed by gas chromatography-mass spectrometry (GC–MS) by coupling the gas chromatograph to a 5975 Agilent Technologies mass spectrometer operated in selected ion monitoring mode. The GC system was equipped with DB-1 or DB-5 fused silica capillary columns (60 m × 0.25 mm × 0.25 μm) to analyze the saturate and aromatic fractions, respectively. The monitored ions were m/z = 191, 177, 217, 218, 178 and 192 for terpanes, steranes, diasteranes, phenanthrene and methylphenanthrenes, respectively. Additionally, seven samples were analyzed in full scan mode to determine the distribution of diasteranes (m/z = 259), methylhopanes (m/z = 205) and methylsteranes (m/z = 231).

To verify the presence of acyclic isoprenoid alkanes, pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane), in the saturated hydrocarbon fractions, gas chromatograms and m/z = 113 fragmentograms were recorded, under the same conditions described above, using iso-octane solutions with different ratios (Pr/Ph = 0.5, 1.0, 2.0 and 4.0) prepared from CHIRON AS certified standards of pristane and phytane.

4. Results and discussion

4.1. V and Ni concentrations

All of the crude oils have a higher concentration of V than Ni (Table 1). This is characteristic of anoxic or euxinic source rocks containing limestone, marl or calcareous shale (Lewan and Maynard, 1982; Lewan, 1984). The oils can be divided into two groups according to their V + Ni total concentrations and V/Ni or V/(V + Ni) ratios: Group A (oils 1 to 6) has V + Ni in the range 168–208 ppm and average V/(V + Ni) = 0.789 ± 0.004 and Group B (oils 7 to 11) has V + Ni in the range 183–350 ppm and average V/(V + Ni) = 0.819 ± 0.001 (Fig. 2). These results suggest two
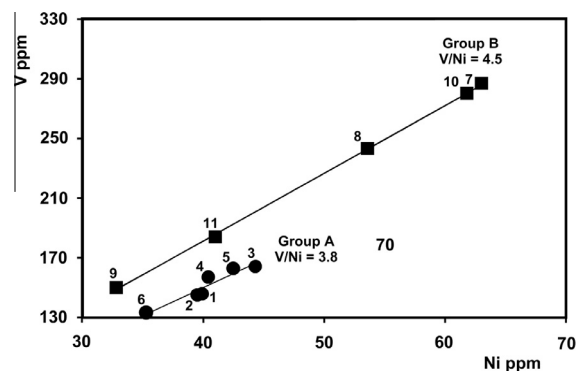

Fig. 2. Relationships between V and Ni concentrations for oil samples from the Socororo field.

distinct oil charges in the reservoirs. The separation of the analyzed crude oils into two distinct oil groups showing different compositional and physicochemical characteristics could result from: (a) mixing of oils from one source rock having variable redox during deposition, or (b) mixing of oils from multiple source rocks. The V/Ni ratio is commonly used as an indicator of paleoredox depositional conditions and for oil-oil correlations (Al-Shahristani and Al-Tyia, 1972; Curiale, 1985; Branthaver and Filby, 1987; Barwise, 1990; López et al., 1991, 1998; Frankenberger et al., 1994; Alberdi et al., 1996; López and Lo Mónaco, 2010; Xu et al., 2012).

The Querecual Formation is considered to be the main source rock for crude oils from the Eastern Venezuela Basin (Talukdar et al., 1985, 1988; Summa et al., 2003). Euxinic conditions existed during deposition of the lower part of the formation as reflected by high V/Ni (> 8) and V/(V + Ni) (average 0.88) ratios. Euxinic conditions decreased toward the top of the formation as reflected by lower values for V/Ni (< 1.7) and V/(V + Ni) (average 0.55). The sulfur contents range between 0.3% and 1.5%. Toward the San Antonio Formation V/Ni is less than 2.5 and V/(V + Ni) has an average value of 0.63 (Lugo et al., 2009). Thus, the variation of V/Ni ratios from the base to the top of the source rock is thought to reflect changes in redox conditions during sedimentation of Guayuta Group (Querecual and San Antonio formations).

In the Orinoco Oil Belt, changes in the V/Ni ratio have been attributed to variations in the redox conditions of sedimentation (Alberdi et al., 1996; López and Lo Mónaco, 2010). Based on the V/Ni ratio, Alberdi et al. (1996) separated the crude oils from the Orinoco Oil Belt into three families, two of which have high V/Ni ratios (A: V/Ni = 3.6 and B: V/Ni = 5.2). According to Alberdi et al. (1996), these two oil families originated from different facies of the source rock in the Upper Cretaceous Querecual and the San Antonio formations (Guayuta Group). The third oil family has a low V/Ni ratio (C: V/Ni = 0.7), indicating that the oils originated

Table 1
API gravity, sulfur (wt%), vanadium and nickel (ppm) and SARA (wt%) oil composition for oil samples from the Socororo field.

Sample	API	Sulfur %	V ppm	Ni ppm	V/Ni	V/(V + Ni)	Saturates %	Aromatics %	Resins %[a]	Asphaltenes %
1	17	2.04	146	40	3.7	0.785	34	35	17	14
2	17	2.02	145	40	3.7	0.784	33	37	18	12
3	16	2.44	164	44	3.7	0.789	37	32	17	14
4	16	2.15	157	40	3.9	0.797	29	36	22	13
5	17	2.11	163	43	3.8	0.791	30	36	21	14
6	16	2.10	133	35	3.8	0.792	28	39	19	14
7	12	3.45	287	63	4.6	0.820	17	37	30	16
8	13	2.96	243	54	4.5	0.818	26	35	25	14
9	11	3.09	150	33	4.5	0.820	17	38	30	15
10	14	2.51	280	62	4.5	0.819	24	36	25	16
11	14	2.85	184	41	4.5	0.818	23	35	30	12

[a] NSO compounds.

from an Upper Cretaceous or Paleogene–Neogene deltaic marine shale (Alberdi et al., 1996). In another set of crude oils from the Orinoco Oil Belt, López and Lo Mónaco (2010) also reported the presence of three oil families based on V/Ni ratios. Group I that includes oils from Ayacucho and Carabobo (V/Ni = 3.7 ± 0.1), group II which includes oils from Ayacucho and Junín (4.4 ± 0.2) and group III (5.2 ± 0.3) which includes oils located in Junín.

These results for oils from the Orinoco Oil Belt, together with the fact that the Guayuta Group represents the principal source rocks of the Eastern Venezuela Basin (Talukdar et al., 1985, 1988; Summa et al., 2003), implies that these crude oils were generated from one source rock deposited under varying redox conditions.

4.2. API gravity and sulfur content

The oil samples from the Socororo field are characterized by low API gravity (11–17° API), so they can be classified as heavy crude oils. Sulfur contents are in the range 2.0–3.5% (Table 1). Fig. 3 reveals that API gravity increases with decreasing sulfur content. This inverse correlation between oil API gravity and sulfur content is typically observed in altered crude oils (Peters and Moldowan, 1993; Hunt, 1996). Progressive biodegradation of crude oils increases the sulfur content (per unit weight of oil) and decreases the content of saturated and aromatic hydrocarbons, so the residual oil becomes enriched in NSO compounds (resins) and asphaltenes, resulting in a decrease in API gravity (Wenger et al., 2002; Larter et al., 2003, 2006). The established groups based on V + Ni concentration and V/(V + Ni) ratio have different API gravities and sulfur contents. Group A has lower sulfur contents (⩽ 2.4%) and API gravities in the range 16–17°, while Group B has higher sulfur contents (⩾ 2.5%) and API gravities between 11° and 14°.

4.3. SARA composition

The Socororo oil samples have saturated plus aromatic hydrocarbon concentrations of 54–70% of total oil and NSO compounds plus asphaltenes from 30–46% of total oil. According to the bulk SARA composition in Table 1, all of the analyzed oils can be classified as aromatic–asphaltic. Additionally, there are differences in SARA composition between the two oil groups based on V/(V + Ni). This difference can be seen in the ternary SARA composition diagram (Fig. 4). Note that those are the same groups previously established from V and Ni concentrations, V/(V + Ni) ratios, sulfur contents and API gravities.

4.4. Molecular composition

Fig. 5 shows examples of the distributions of n-alkanes and acyclic isoprenoids (GC-FID, m/z = 113, respectively), terpanes
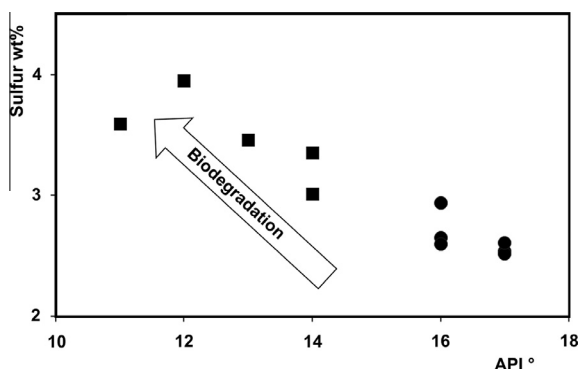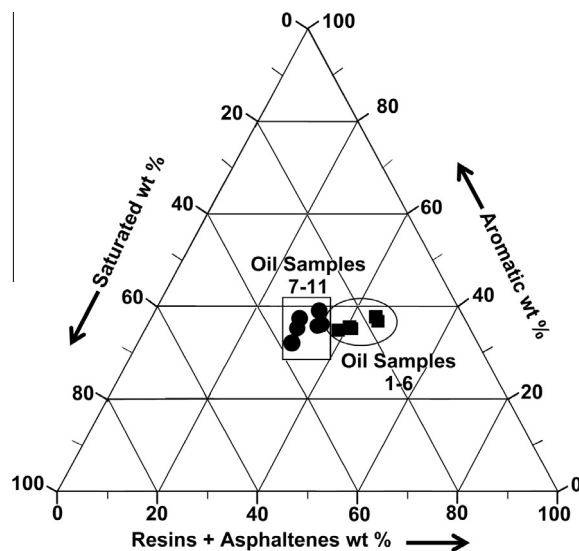
Fig. 4. Ternary diagram showing the bulk SARA (saturated, aromatic, resins and asphaltenes) composition of crude oil samples from the Socororo field.

and steranes for two oils (1 and 7) that are representative of the two groups. The n-alkane distributions are characterized by a dominant unresolved complex mixture (UCM) under a resolved peak envelope showing variations in the relative intensity of low (< n-C$_{25}$) versus high (> n-C$_{25}$) molecular weight n-alkanes. Additionally, the presence of acyclic isoprenoids (phytane and pristane), was corroborated in m/z 113 and 183 mass fragmentograms and compared with certified standards of these compounds.

In Fig. 6, the terpane distributions are characterized by abundant C$_{23}$ tricyclic terpanes, C$_{29}$ and C$_{30}$ pentacyclic terpanes and extended hopanes (C$_{31}$–C$_{35}$, S and R isomers). Fig. 6 also shows a comparison of hopane (m/z = 191) and 25-norhopane (m/z = 177) mass chromatograms, indicating the presence of 25-norhopanes at trace levels compared to hopanes. Note the presence of 28,30-dinorhopane (DNH) and its demethylated counterpart 25,28,30-trisnorhopane (TNH). 25-Norhopanes are found in many highly biodegraded oils (Seifert and Moldowan, 1979; Alexander et al., 1983; Volkman et al., 1983a,b; Noble et al., 1985; Peters and Moldowan, 1991; Peters et al., 1996; Dzou et al., 1999; Bennett et al., 2006; Wang et al., 2013) and have been previously observed in oils from Eastern Venezuelan Basin (Bost et al., 2001; Peters et al., 2005; López, 2014).

The steranes are characterized by a predominance of C$_{27}$ relative to C$_{29}$ regular steranes. In some oils, steranes are moderately biodegraded (Fig. 7) as shown by partial removal of 20R steranes (both ααα20R and αββ20R). The methylsteranes (m/z = 231) also show differences. Some oils are characterized by a normal distribution of these compounds, while others show the effects of biodegradation. The diasteranes (m/z 217 and 259), which are more resistant to biodegradation than steranes (e.g., Seifert and Moldowan, 1979; Volkman et al., 1983a), are present in all oils and show very similar distributions.

In summary, all oils show pristane, phytane, depletion of n-alkanes, traces of 25-norhopanes and in some cases, alteration of methylhopanes, steranes and methylsteranes. Table 2 presents a summary of biodegradation markers. Although the analyzed crude oils show evidence of biodegradation in the different oil charges, one can still make reasonable inferences about the source rock for the later charge, such as lithology, type of organic matter input, redox depositional conditions and thermal maturity, using a series of biomarker parameters.
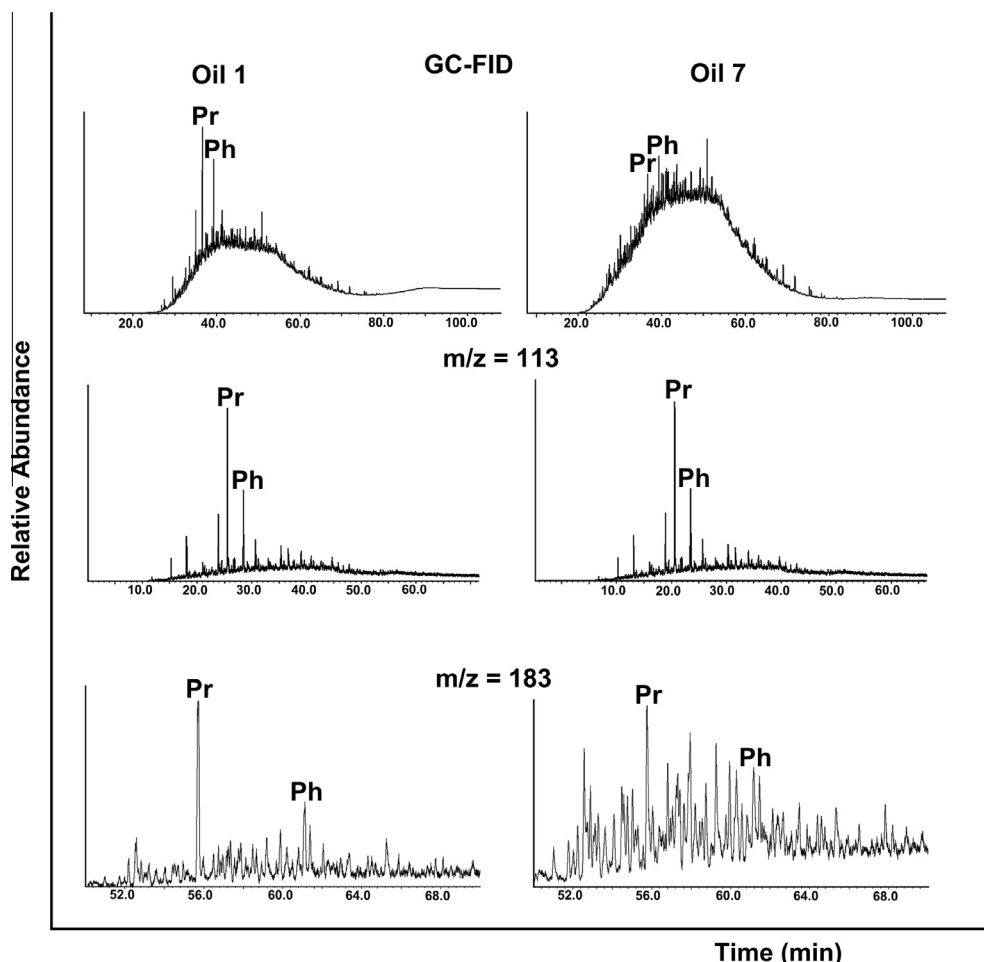
Fig. 3. Relationship between sulfur content and API gravity for oil samples from the Socororo field.

Fig. 5. Representative *n*-alkanes and acyclic isoprenoid alkane gas chromatograms (GC-FID) and mass fragmentograms (*m/z* = 113 and 183) for two selected oil samples.

4.5. Biomarkers: maturity

The 22S/(22S + 22R) ratio for the C_{32} 17α-hopanes is useful to assess source rock maturity (Seifert and Moldowan, 1980; Kolaczkowska et al., 1990). The C_{32} homohopane isomerization values fall in the range 0.57–0.64 (Table 3), indicating that the end-point has been reached (0.55–0.62) and the early phase of oil generation has been reached or surpassed (Peters et al., 2005). In the C_{31}–C_{35} 17α-hopanes, the 22R isomers are more susceptible to biodegradation (Peters and Moldowan, 1991; Peters et al., 1996). However, the values obtained for the 22S/(22S + 22R) ratios suggest that the 22R isomers have not been altered and can be used as indicators of thermal maturity for the analyzed oils.

The $T_s/(T_s + T_m)$ ratio is based on the lower thermal stability of 17α(H)-22,29,30-trisnorhopane (T_m) relative to that of 18α(H)-22,29,30-trisnorneohopane (T_s) (Seifert and Moldowan, 1978). The $T_s/(T_s + T_m)$ ratios for the samples are low (0.14–0.31, Table 3). According to Peters et al. (2005), oils from carbonate source rocks show unusually low $T_s/(T_s + T_m)$ ratios ($\leqslant$ 0.25) compared to those from shales representing anoxic environments [$T_s/(T_s + T_m)$ = 0.26–0.34]. The oils from Socororo field have $T_s/(T_s + T_m)$ values in the range 0.14–0.21, with only one sample having a $T_s/(T_s + T_m)$ > 0.26 (#4 = 0.31, Table 2). This indicates only small differences in the level of maturity among the oil samples from the Socororo field. The values for these ratios are typical of carbonate source rocks, as suggested by the other biomarkers (see Section 4.6).

The ratio Mor/Hop [C_{30}17β,21α(H)-moretane/C_{30}17α,21β(H)-hopane] decreases with increasing in maturity, with values around

0.8 typical of immature rocks, decreasing to < 0.15 at high maturity to a minimum of 0.05 (Mackenzie et al., 1980; Seifert and Moldowan, 1980). The Socororo oils have low Mor/Hop ratios (0.06–0.08; Table 3), suggesting that these oils were generated from source rock near the peak of the oil window.

Two C_{29} sterane isomerization ratios [C_{29}20S/(20S + 20R) and C_{29}αββ/(αββ + ααα)] were calculated for those samples where steranes were unaltered by biodegradation (Table 2). The values for these ratios (40.4–54.5%, 45.7–58.5%, respectively) indicate that the typical end point has not been reached (C_{29}20S: 52–55% = endpoint and C_{29}ββ: 67–71% = endpoint; Peters et al., 2005). These results also suggest that the crude oils were generated near the peak of the oil window.

Source rock maturity was also estimated using three methylphenanthrene indexes (PP-1, PP-1$_{modified}$ and PP-I), calculated using the peak areas of phenanthrene (P) and methylphenanthrene (MP) from *m/z* 178 and *m/z* 192 fragmentograms, respectively (Radke and Welte, 1983; Radke et al., 1983, 1986; Alexander et al., 1986; Radke, 1987; Cassani et al., 1988). The values of PP-1 (0.27–0.46), PP-1$_{modified}$ (0.63–1.09) and MPI-1 (0.72–1.54), plus maturity determined using the calculated vitrinite reflectance (Table 3) (Radke and Welte, 1983; Radke et al., 1986) derived from the PP-1$_{modified}$, (R_c = 0.78–1.05%) also indicate that the oils from the Socororo field were generated at the peak of the oil window. However, when using R_c for marine crude oils, a linear relationship between methylphenanthrene indexes and vitrinite reflectance is not always observed (Radke and Welte, 1983; Radke et al., 1986).
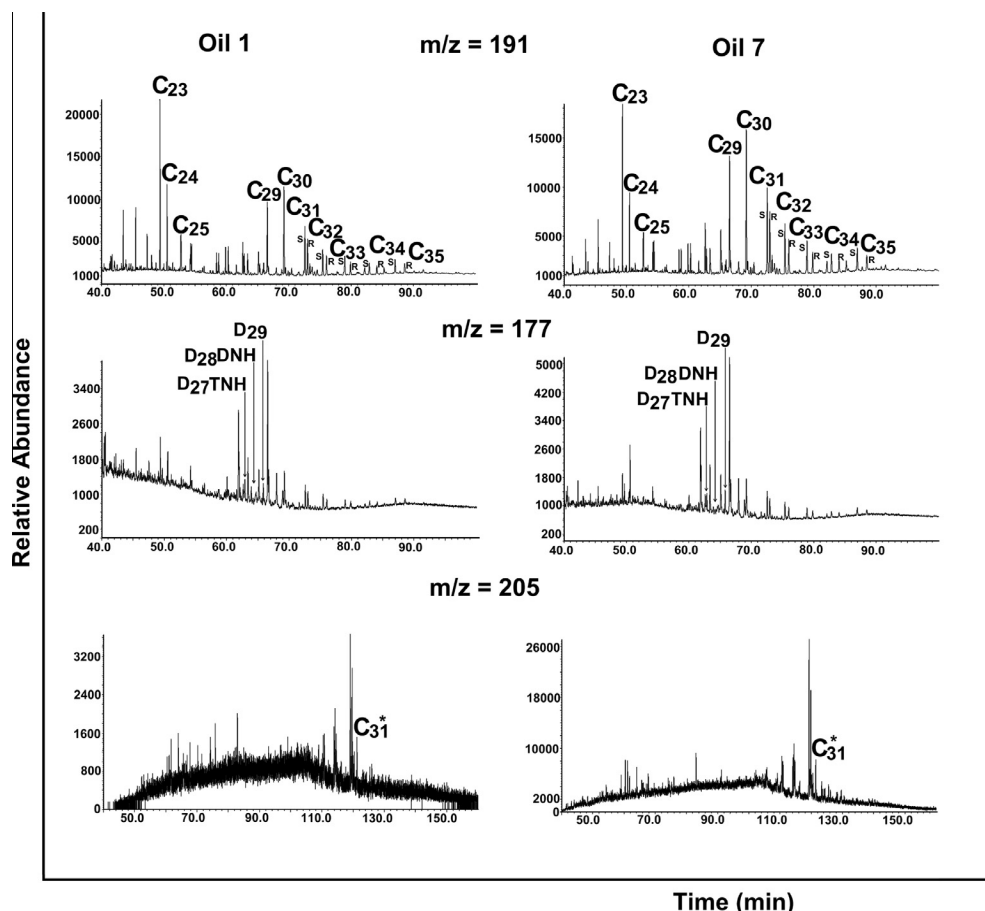
Fig. 6. Mass fragmentograms showing terpanes (m/z 191), 25-norhopanes (m/z = 177) and methylhopanes (m/z = 205) from four selected oil samples. TNH (D_{27}) = 25,28,30-trisnorhopane, DNH (D_{28}) = 28,30-dinorhopane, D_{29} = demethylated C_{30}-hopane, C_{31}^* = 17β,21α(H)-homohopane 22S + 22R.

4.6. Biomarkers: organic matter type and source rock

A dominant contribution of marine organic matter in the source rock for the second oil charge in the Socororo field samples inferred from the (1) abundant tricyclic terpanes (cheilanthanes), which maximize at C_{23}; (2) abundant C_{27} regular steranes relative to C_{29} steranes (Moldowan et al., 1985); and (3) presence of C_{30} sterane isomers: C30ααα20R, C30αββ20R and C30αββ20S (Peters and Moldowan, 1993). Similarities in the distributions of C_{27} to C_{29} regular steranes (Table 4) indicate that all of the oil samples originated from a source rock with similar organic facies; (4) presence of methylhopanes from a prokaryotic source (Peters et al., 2005); (5) absence of 18α(H)-oleanane and gammacerane, suggesting lack of input from angiosperms (Moldowan et al., 1994) and absence of water column stratification (Moldowan et al., 1985; Philp et al., 1989), respectively. Moreover, all samples show homohopane indices $C_{35}/C_{34} \geqslant 1$, which suggests anoxic-suboxic conditions during source rock deposition (Peters and Moldowan, 1991; Peters et al., 2005).

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 can be used to distinguish among oils derived from carbonate, marine shale, lacustrine, marl or carbonate source rocks (Peters et al., 2005). The calculated ratios in the two oil groups described previously based on other geochemical parameters are: Group A (oils 1 to 6) has C_{24}/C_{23} = 0.47–0.55, C_{22}/C_{21} = 1.4–2.5, C_{26}/C_{25} = 0.47–0.59 and C_{31}R/C_{30}Hop = 0.38–0.40 and Group B (oils 7 to 11) has C_{24}/C_{23} = 0.46–0.53, C_{22}/C_{21} = 1.6–2.4, C_{26}/C_{25} = 0.49–0.70 and C_{31}R/C_{30}Hop = 0.42–0.52 (Table 4). No significant differences between the ranges of

values for the calculated ratios are observed. 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 two oil groups for the C_{24}/C_{23}, C_{26}/C_{25} and C_{31}22R/C_{30}Hop ratios suggest that the Socororo oils originated from either a marine carbonate or a marine marl source rock. This is consistent with the lithology noted by Gómez et al. (2007) for the Querecual Formation (shales, limestones, marly limestones and marls), which is a possible source rock for these oils. The biomarker data thus suggest that the differences observed in V/(V + Ni) ratio may be attributed to mixing of oils from one source rock having variable redox during deposition. Although diasteranes are present (Fig. 7), their abundance is low, typical of carbonate source rocks (Rubinstein et al., 1975).

5. Evidence for crude oil mixtures with different degrees of biodegradation

Crude oil samples from the Socororo field are clearly biodegraded even though some contain some n-alkanes and acyclic isoprenoids (pristane and phytane) (Fig. 5). On the other hand, alteration of terpanes and steranes as well as the presence of 25-norhopanes, was observed in some samples those crude oils containing n-alkanes, pristane and phytane (Figs. 5 and 6). According to the PM biodegradation scale (Peters and Moldowan, 1993), oils showing little alteration of n-alkanes and presence of pristane and phytane have a biodegradation level in the range from 3 to 4.
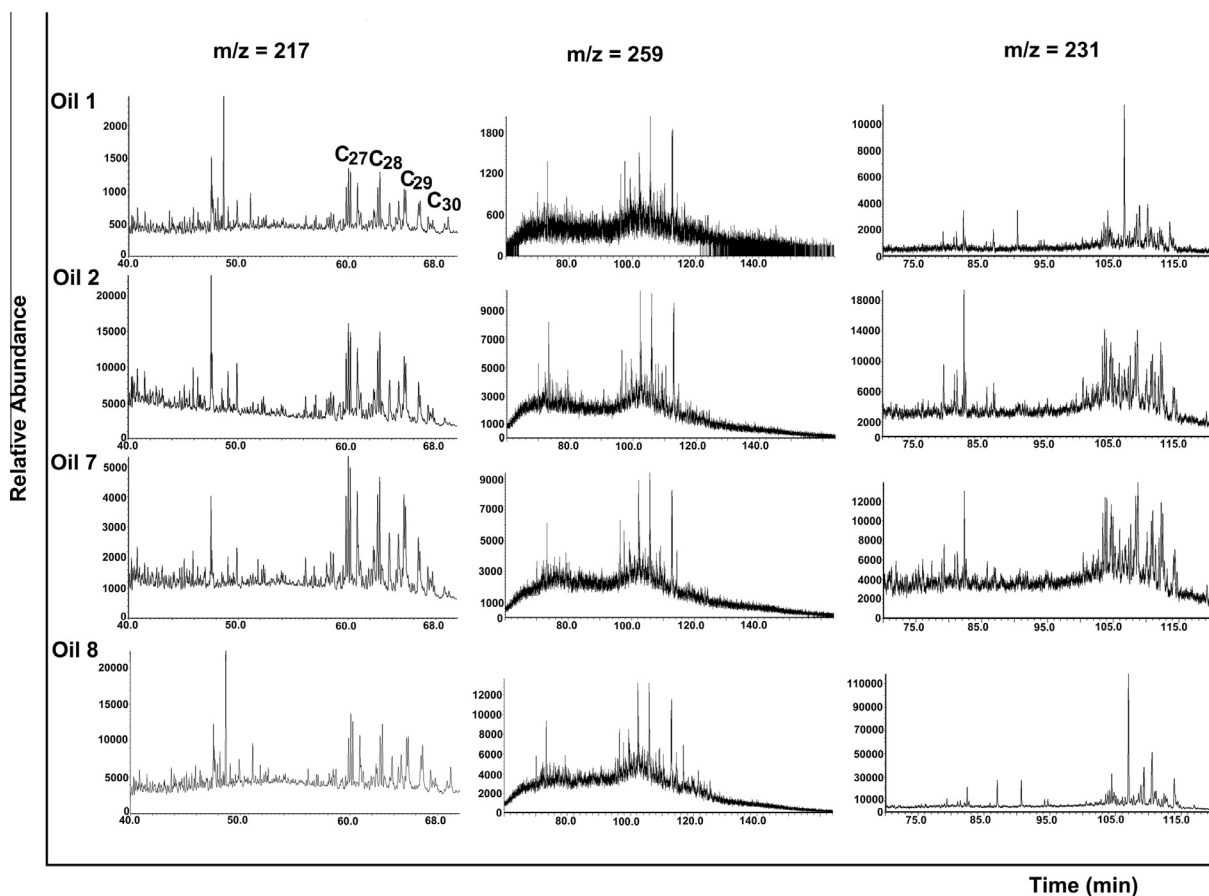
Fig. 7. Mass fragmentograms showing distributions of steranes ($m/z = 217$), diasteranes ($m/z = 259$) and methylsteranes ($m/z = 231$) in two selected oil samples. C$_{30}$ steranes: C30ααα20R, C30αββ20R and C30αββ20S.

Table 2
Biodegradation indicators in eleven crude oil samples from the Socororo field.

Sample	UCM[a]	Pr, Ph[b]	25-NH[c]	28,30-DNH[d]	25,28,30-TNH[e]	TNH/DNH[f]	Me-Hopanes[g]	20R Steranes[h]	Me-Steranes[i]
1	Present in all samples	Detected in all samples	Detected in trace levels compared to hopanes	Detected in all samples	Detected in all samples	17	Altered	Altered	Altered
2						11	Altered	Altered	Altered
3						4	Not altered	Not altered	Not altered
4						4	NA[j]	Altered	NA
5						8	Not altered	Altered	Not altered
6						7	NA	Not altered	NA
7						10	Not altered	Not altered	Altered
8						4	Not altered	Not altered	Not altered
9						NI[k]	NA	Not altered	NA
10						11	NA	Not altered	NA
11						13	Not altered	Not altered	Altered

[a] Unresolved complex mixture.
[b] Pr = pristane, Ph = phytane (in GC-FID, $m/z = 113$ and 183).
[c] 25-Norhopanes in homohopanes series.
[d] 28,30-Dinorhopane.
[e] 25,28,30-Trisnornopane.
[f] 25,28,30-TNH/28,30-DNH ratio (analyzed by single ion monitoring mode).
[g] methylhopanes – alteration of methylhopanes > C$_{31}$ (for samples analyzed in full scan mode).
[h] Partial removal of 20R steranes (both ααα20R and αββ20R).
[i] Alteration of 4α-methylsteranes (for samples analyzed in full scan mode). Diasteranes were detected in samples analyzed in full scan mode and using $m/z = 259$ mass fragmentograms.
[j] NA = not analyzed in full scan mode.
[k] NI = not identified in $m/z = 177$ mass fragmentograms.

Table 3
Saturated hydrocarbon biomarker maturity parameters and aromatic hydrocarbons ratios for oil samples from the Socororo field.

Sample	$C_{32}22S/C_{32}22(S+R)$[a]	$T_s/(T_s + T_m)$[b]	Mor/Hop[c]	$\%C_{29}20S$[d]	$\%C_{29}\alpha\beta\beta$[e]	PP-1[f]	PP-1$_{modified}$[g]	MPI-1[h]	R_c[i]
1	0.62	0.19	0.08	–[j]	–	0.39	0.65	1.24	0.79
2	0.60	0.15	0.08	–	–	0.34	0.67	1.23	0.80
3	0.59	0.14	0.08	42.6	55.5	0.30	0.64	1.23	0.78
4	0.57	0.31	0.08	–	–	0.30	0.63	1.20	0.78
5	0.58	0.14	0.07	–	–	0.27	0.65	1.30	0.79
6	0.59	U[k]	0.08	36.0	50.9	0.41	0.64	1.24	0.79
7	0.57	0.20	0.08	45.3	57.2	0.41	0.90	0.92	0.94
8	0.57	0.21	0.07	40.4	58.5	0.31	0.85	1.54	0.91
9	0.59	0.21	0.06	51.9	45.7	0.46	1.09	0.72	1.05
10	0.60	0.14	0.06	54.5	52.5	0.30	0.71	1.18	0.83
11	0.64	0.14	0.07	43.1	53.0	0.34	0.82	1.03	0.89

[a] $C_{32}22S/C_{32}(22S + 22R)$ = homohopane isomerization (Seifert and Moldowan, 1980; Kolaczkowska et al., 1990).
[b] $T_s/T_s + T_m$ = $C_{27}18\alpha$-trisnorneohopane/($C_{27}18\alpha$-trisnorneohopane + $C_{27}17\alpha$(H)-trisnorhopane) (Seifert and Moldowan, 1978).
[c] Mor/Hop = $C_{30}17\beta,21\alpha$(H)-moretane/$C_{30}17\alpha$(H),21β-hopane (Seifert and Moldowan, 1980).
[d] $\%C_{29}20S$ = $C_{29}20S/(C_{29}20S + C_{29}20R)$ steranes.
[e] $\%C_{29}\alpha\beta$ = $C_{29}\beta\beta/(C_{29}\beta\beta + C_{29}\alpha\alpha)$ steranes (Seifert and Moldowan, 1979; Mackenzie et al., 1980).
[f] PP-1 = 1MP/(2MP + 3MP) (Alexander et al., 1986) where MP = methylphenanthrene.
[g] PP-1$_{modified}$ = (1MP + 9MP)/(2MP + 3MP) (Cassani et al., 1988).
[h] MPI-1 = 1.89 * (2MP + 3MP)/(P + 1.26 * (1MP + 9MP)) (Cassani et al., 1988).
[i] R_c = (0.6 * PP-1$_{modified}$) + 0.4 (Radke and Welte, 1983).
[j] – = not measured.
[k] U = not identified in m/z = 191 mass chromatograms.

Table 4
Saturated hydrocarbon biomarker source parameters for oil samples from the Socororo field.

Sample	C_{24}/C_{23}[a]	C_{22}/C_{21}[a]	$C_{31}22R/C_{30}$Hop[b]	C_{26}/C_{25}[a]	C_{35}/C_{34}[c]	$\%C_{27}$[d]	$\%C_{28}$[d]	$\%C_{29}$[d]
1	0.48	1.4	0.38	0.59	0.98	36	26	38
2	0.48	1.6	0.39	0.47	1.14	45	29	25
3	0.55	1.6	0.47	0.56	0.92	37	26	37
4	0.52	1.6	0.43	0.56	0.95	40	28	33
5	0.47	2.5	0.39	0.59	1.10	41	29	31
6	0.54	2.1	0.40	0.54	1.00	41	26	33
7	0.49	1.7	0.43	0.62	0.89	38	28	34
8	0.52	1.6	0.44	0.49	0.92	38	28	34
9	0.47	2.1	0.46	0.70	1.00	39	30	31
10	0.46	2.4	0.42	0.61	1.37	39	26	35
11	0.53	1.5	0.52	0.56	1.21	40	26	34

[a] C_{24}/C_{23}, C_{22}/C_{21} and C_{26}/C_{25} = tricyclic terpane ratios.
[b] $C_{31}22R/C_{30}$Hop = 17α,21β-homohopane(22R)/$C_{30}17\alpha$,21β-hopane (Peters et al., 2005).
[c] C_{35}/C_{34} = homohopane index (Peters and Moldowan, 1991; Peters et al., 2005).
[d] Sterane proportions (Moldowan et al., 1994). $\%C_{27}$ = [$C_{27}/\Sigma(C_{27}$ to $C_{29})$] * 100; $\%C_{28}$: [$C_{28}/\Sigma(C_{27}$ to $C_{29})$] * 100; $\%C_{29}$: [$C_{29}/\Sigma(C_{27}$ to $C_{29})$] * 100.

Furthermore, the observed levels of alteration of terpanes and steranes and the formation of 25-norhopanes indicate biodegradation in the range from PM level 7 to 8. Therefore, these oil samples contain compounds with different susceptibility to degradation, indicating that they must be mixtures. Consequently, the assignment of a single biodegradation level to these crude oils based on biomarker compositional information is inappropriate (Peters and Moldowan, 1993; Wenger et al., 2002; Larter et al., 2003, 2006, 2012; Peters et al., 2005).

The crude oil samples from Socororo field have variable concentrations of saturated hydrocarbons (Table 1). Usually biodegradation decreases the amount of light fractions (saturated and aromatic hydrocarbons) and increases in the amount of heavy fractions (resins and asphaltenes). Oils from Group A are characterized by saturated hydrocarbon concentrations > 28% and NSO compounds and asphaltenes < 35%, whereas the opposite trend is observed in Group B, i.e., saturated hydrocarbons < 26% and NSO compounds and asphaltenes > 39% (Fig. 3). This compositional trend is attributed to mixing of oils having different levels of biodegradation.

Additional evidence for mixtures of oils is provided by opposite trends followed by some bulk physicochemical parameters, including API gravity, sulfur content and V and Ni concentrations. Increasing biodegradation increases sulfur contents and V and Ni concentrations, while lowering API gravities. However, the Group A oils have V + Ni contents in the range 168–208 ppm, lower sulfur contents (⩽ 2.4%) and API in the range 16–17°. In contrast, the Group B oils are characterized by V + Ni contents in the range 183–350 ppm, higher sulfur content (⩾ 2.5%) and API in the range 11–14°. These results also suggest that two major oil charges occurred in the reservoirs. During the first event, the crude oils were severely biodegraded and many susceptible biomarkers, such as *n*-alkanes, acyclic isoprenoids, terpanes, methyl hopanes, methyl steranes and steranes were altered and, in some cases, completely removed. The second oil charge was subjected to a lower degree of biodegradation, resulting in *n*-alkane alteration without the alteration of pristane, phytane, steranes, or terpanes. Because the crude oils have a similar maturity, the migration and accumulation of the two charges were close together in time. Note that the present depth of the wells in the Socororo field is 800–1500 m, with an average depth of 1200 m (Ughi et al., 2010). Additionally, the dynamics of reservoir charges in unconsolidated sands in oil fields from the southern part of the Eastern Venezuela Basin (Pardo et al., 2007) must have contributed to mixing of crude oils having different degrees of biodegradation.

6. Conclusions

According to V + Ni total concentration and V/(V + Ni) ratio, the crude oil samples from Socororo field can be divided into two groups. These samples are classified as heavy aromatic–asphaltic oils, based on sulfur content, API gravity and SARA composition. 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 hopane ratio indicate that the oils originated from a marine carbonate or marine marl source rock. The contribution of marine organic matter was corroborated by abundant tricyclic terpanes, C_{27} regular steranes, C_{30} steranes and absence of biomarkers for terrigenous organic matter such as triterpanes. Based on various biomarker maturity parameters, we infer that the crude oil samples from Socororo field were generated from a source rock near the peak of the oil window.

The biomarker distributions indicate that these oils represent mixtures that were biodegraded to different extents. The first charge of oil was subjected to severe biodegradation and many susceptible biomarkers (*n*-alkanes, acyclic isoprenoids, terpanes, methyl hopanes, methyl steranes and steranes) were extensively altered or completely removed. The second oil charge was subjected to a lower degree of biodegradation and, as a consequence, only the *n*-alkanes were biodegraded. Both oil charges likely originated from the same source rock, which was deposited under variable redox conditions based on inorganic proxy data. Moreover, due to the similar maturity of the oils, the generation and migration to reservoirs occurred close together in time.

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