



Saturated hydrocarbons occluded inside asphaltene structures and their geochemical significance, as exemplified by two Venezuelan oils

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Abstract

Inside asphaltene aggregates in crude oils, the adsorbed hydrocarbons exist in the packed periphery while the occluded hydrocarbons exist inside the core of the asphaltene structures. Occluded hydrocarbons may be well protected from secondary alteration events in the reservoir due to the colloidal nature of asphaltenes, and can be representative of older oil than the reservoir oil, and so may be very useful for reservoir geochemical studies. In this work, two Venezuelan oils derived from the same source rock have been studied. The results indicate that the oxidative reagent $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ can release the occluded hydrocarbons from the asphaltene aggregates, making it possible to selectively study these compounds without interference from the moieties that are covalent-bonded to the asphaltene structures. In order to obtain the precise information from the occluded hydrocarbons, prior to the oxidation processes, acetone extraction of the asphaltenes has been applied to rule out interferences from the adsorbed compounds. Furthermore, pyrolysis of asphaltenes has been performed for comparison with the occluded saturated hydrocarbons.

From the oxidation products of asphaltenes from these two crude oils, the saturated hydrocarbons (from the occluded original oil) have very similar distributions, including terpanes and steranes, and almost the same biomarker parameters. These results are in accord with the fact that oil from the same source rock was occluded by both Ven1 and Ven2 asphaltenes. The geochemical information obtained from the occluded saturated hydrocarbons suggests that the source rock depositional setting for these two crude oil samples was an anoxic, hypersaline/evaporitic environment.

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1. Introduction

Many polyaromatic structural units exist within asphaltene structures, but also abundant in asphaltene structures are aliphatic moieties (homologous series of alkyl moieties up to C₄₀) which are covalent-bonded to the aromatic rings (Calemma et al., 1998; Strausz et al., 1999a,b; Bergmann et al., 2000). Because these structural units can be spatially bent or even curled, cages or vesicles can form inside the asphaltene aggregates (Acevedo et al., 1997; Schabron and Speight, 1998; Murgich et al., 1999; Mujica et al., 2000; Porte et al., 2003). Recently, asphaltene aggregates have been found to be highly porous and very tenuous (Rahmani et al., 2005). These structural features can enable oil asphaltenes to adsorb and occlude other organic HC species (Liao and Geng, 2002; Liao et al., 2005).

Asphaltenes display considerable polydispersity (Acevedo et al., 1997; Murgich and Strausz, 2001; Castillo et al., 2001; Buenrostro-Gonzalez et al., 2002; Strausz et al., 2002). Asphaltenes are considered as the soluble fraction of pseudo-kerogen consistent with a polydispersed nature. Constituents range from small species (MW below 1000) to macromolecules (MW > 10,000; Strausz et al., 2002). These aggregates may be made up of a well packed and insoluble asphaltene core, which is impervious even to polar solvent, and a loosely packed periphery which keeps the colloids in solution by allowing solvent penetration (Castillo et al., 2001). In the periphery of the asphaltene aggregates microporous structures exist, which can adsorb other organics such as resins (Murgich and Strausz, 2001; Leon et al., 2002). These adsorbed compounds may be exchanged with the bulk phase, while the occluded compounds can be adsorbed inside the asphaltene core. For example, Acevedo et al. (1997) have found the presence of radicals inside the asphaltene core, which suggests they were encapsulated within the core of asphaltenes. These occluded compounds are prevented from coming into contact with extraneous reagents, catalysts, microbes, or surface-derived formation water flowing through the deposit. Hence they could represent remnants of the original oil (Behar et al., 1984; Ekweozor, 1984, 1986; Peng et al., 1997, 1999). These preserved compounds are very useful for geochemical studies, such as oil-source rock and oil–oil correlations, and help follow the secondary evolution processes of reservoir oils (Pan et al., 2002; Russell et al., 2004).

Pyrolysis has been extensively applied in geochemical studies of asphaltenes, kerogen and source rocks. Slow pyrolysis can release hydrocarbons occluded within asphaltenes (Van Graas, 1986; Sofer, 1988; Jones et al., 1988; Wilhelms and Larter, 1993; Magnier and Huc, 1995). However, pyrolysis also produces aliphatic products by the cleavage of moieties covalent-bonded to the asphaltene structures and these would be difficult to distinguish from occluded oil. Ekweozor (1984, 1986) applied chemical reductive treatment to release occluded species, but also encountered the problem of mixing of occluded and cleaved hydrocarbons.

Fatty acids in high yields and high selectivity were obtained by H₂O₂ oxidation of low-rank coals (Miura et al., 1996; Mae et al., 1997). These reactions can be performed under mild conditions at room temperature and ambient pressure. The oxidation mechanism has been proposed as follows (Hayashi and Chiba, 1999): (1) the oxidation depolymerizes the coal by eliminating aromatic clusters; and (2) when a cluster is eliminated, the inter-cluster bridges are converted into peripheral chains with carboxyl groups at the ends. The structures of coal and asphaltenes are relatively similar, both having aromatic cyclic cores bridged by chain moieties. Hence, H₂O₂ has been chosen as the oxidation reagent in this work in order to obtain the occluded compounds from asphaltenes. What is more important is that H₂O₂ oxidation can release the occluded hydrocarbons from asphaltenes without interference from the cleaved hydrocarbons covalent-bonded to asphaltene molecules. The chains covalent-bonded to asphaltenes should be cleaved as polar compounds such as carboxylic acids under these oxidation conditions. Thus, from the oxidation products of asphaltenes, saturated hydrocarbons are not directly generated by bond cracking, but are thought to result from the occluded components inside asphaltene structures.

In this work, the occluded compounds inside the asphaltene core of two Venezuelan oil samples were released by H₂O₂/CH₃COOH treatment. Prior to the oxidation processes, acetone extraction of the asphaltenes was applied to rule out interference from the adsorbed compounds. Pyrolysis of asphaltenes has also been performed for comparison with the occluded hydrocarbons. The saturated hydrocarbons from the acetone extracts, the pyrolysis products and the oxidation products of asphaltenes have been studied by gas chromatography–mass

spectrometry (GC–MS), and their geochemical characteristics discussed.

2. Sample description

Two oil samples, Ven1 and Ven2, were collected from Venezuela. Previous work from Total Company (Total, CSTJF, Avenue Larribau, 64018 Pau

Cedex, France) indicated that these two oils were derived from the same source rock, containing Type II kerogens. Ven1 has been subjected to biodegradation, while Ven2 has not, resulting in very different saturated hydrocarbon distributions. In Ven1, the *n*-alkanes are absent, the regular steranes are only partly affected, while the pentacyclic terpanes, tricyclic terpanes and diasteranes unaffected. This is consistent with the biodegradation being moderate, possibly just grade 6 according to Peters and Moldowan (1993). Table 1 shows the SARA (Saturated hydrocarbons, Aromatic hydrocarbons, Resins, and Asphaltenes) composition of the crude oils, which were acquired using thin layer chromatography – flame ion detection (TLC-FID). Due

Table 1
Group composition (wt%) of the crude oils

Samples	Saturated hydrocarbons	Aromatic hydrocarbons	Resins	Asphaltenes
Ven1	14.3	41.4	34.8	10.5
Ven2	45.3	30.9	17.0	6.8

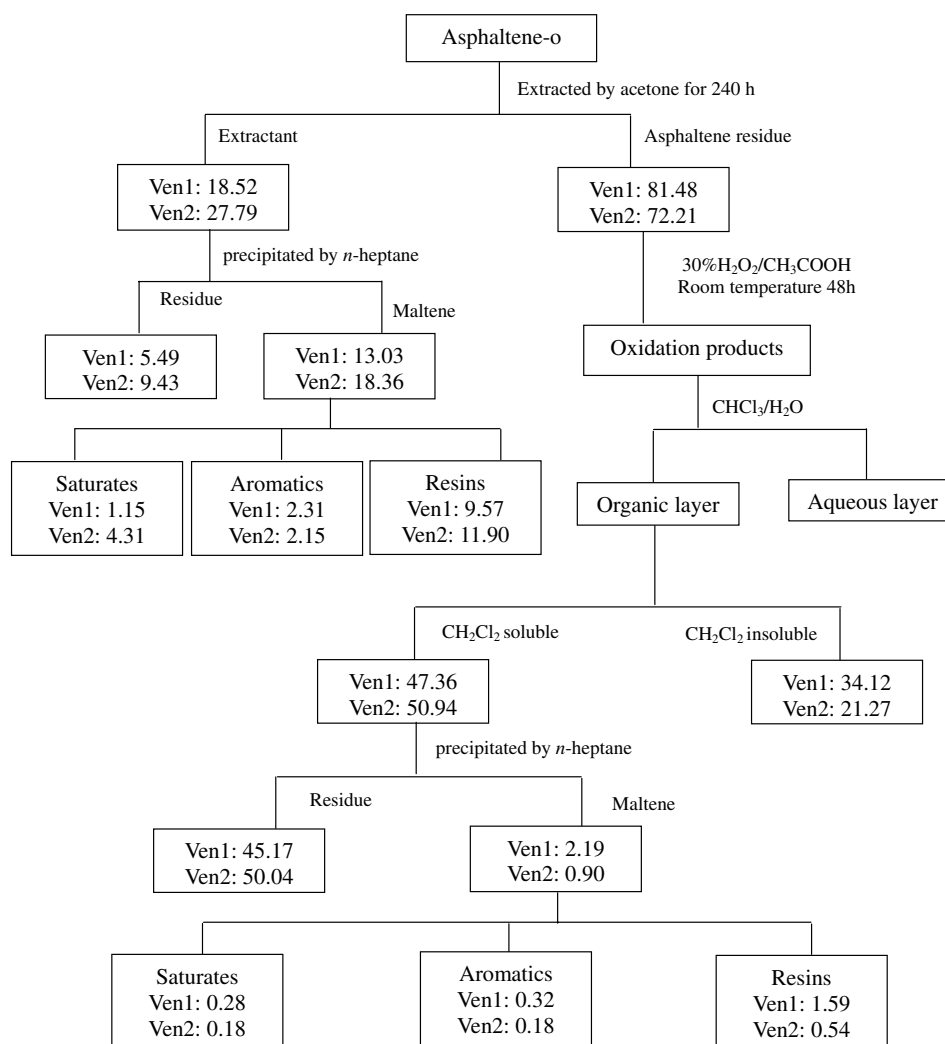


Fig. 1. Flow chart for the acetone extraction of *n*-heptane precipitated asphaltenes (Asphaltene-o) and the subsequent oxidation processes. All the numbers represent percentage yield values (wt%) based on the initial Asphaltene-o.

to biodegradation, Ven1 has a higher content of aromatic, resin and asphaltene fractions, and much lower amounts of saturated hydrocarbons.

3. Experimental

3.1. Preparation of asphaltenes

Asphaltenes were precipitated from the crude oils by *n*-heptane (Fluka HPLC grade). An aliquot (3 g) of oil was added to a 500 ml flat-bottomed flask. Toluene (6 ml, Aldrich HPLC grade) was added dropwise to the flask to make sure that the oil was dispersed and *n*-heptane (500 ml) was added, and the mixture stirred with a magnetic stirrer for about 12 h, and left overnight in the dark. The asphaltene deposit was isolated by centrifugation (3500 rpm for 5–8 min). After centrifugation and removal of the

supernatant, the asphaltenes were further washed (two times) in the PTFE centrifugation tube with *n*-heptane until the supernatant was almost colorless. The resulting asphaltene fraction (termed Asphaltene-o in this work; Fig. 1) was solid with a brittle appearance and metallic lustre.

3.2. Acetone extraction of Asphaltene-o

Acetone extraction of asphaltenes has been reported to separate asphaltenes into LMA (low molar mass asphaltenes) and HMA (high molar mass asphaltenes) fractions (Peng et al., 1997), and the adsorbed hydrocarbons can be removed from asphaltenes during this extraction process. In order to avoid interferences between adsorbed hydrocarbons and the occluded ones, the isolated asphaltenes (Asphaltene-o) were subjected to Soxhlet extraction

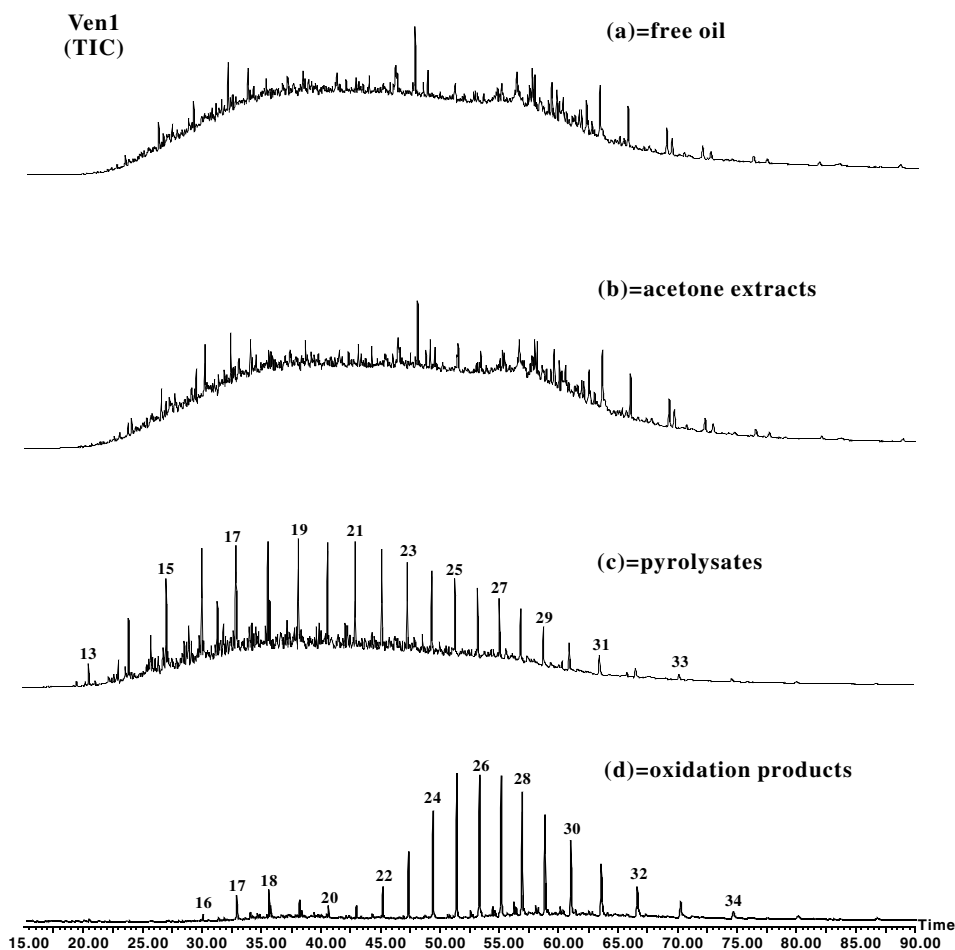


Fig. 2. Chromatograms of the saturated hydrocarbons from Ven1: (a) directly from the maltenes of crude oil Ven1, (b) from the acetone extracts of the corresponding asphaltenes, (c) from the pyrolysis products of the corresponding asphaltenes, and (d) from the oxidation products of the corresponding asphaltenes. The numbers in the figures represent the carbon number of *n*-alkanes.

with acetone for 10 days (240 h), and the extracts and residues were further fractionated according to the flow chart depicted in Fig. 1. The acetone extracts were separated by *n*-heptane into residue and the maltene fractions. The maltenes were further separated into saturates, aromatics and resins using SiO₂/Al₂O₃ column chromatography. The acetone-extracted asphaltenes (asphaltene residue in Fig. 1) were subsequently subjected to the oxidation as described below.

3.3. Oxidative reagent

The choice of the oxidative reagent has previously been discussed by Liao and Geng (2002). In summary, the strong interactions between asphaltene structures make them liable to self-aggregate even in a very dilute solution (Groenzin and Mullins, 1999; Bergmann et al., 2000). For effective degradation of asphaltenes, it is necessary to mitigate

these polar interactions. Protons can effectively interact with the polar parts of asphaltenes (Laux et al., 2000; Pan and Firoozabadi, 2000), leading to reduced overall polarity. Therefore, chemical degradation of the asphaltenes under acidic conditions is preferable.

The oxidative reagent used in this work is H₂O₂/CH₃COOH. H₂O₂ has a good oxidising ability, although it is prone to self-activity, and trace impurities may make it susceptible to decomposition or explosion. The acid CH₃COOH acts as a proton donor and a solvent for H₂O₂, stabilizing it so that the reaction readily proceeds.

3.4. Oxidation reaction (Fig. 1)

To extract the occluded components from the asphaltenes, about 200 mg of asphaltene residues (Fig. 1) were firstly transferred into a 250 ml flask using 20 ml toluene; then H₂O₂ (4 ml) and

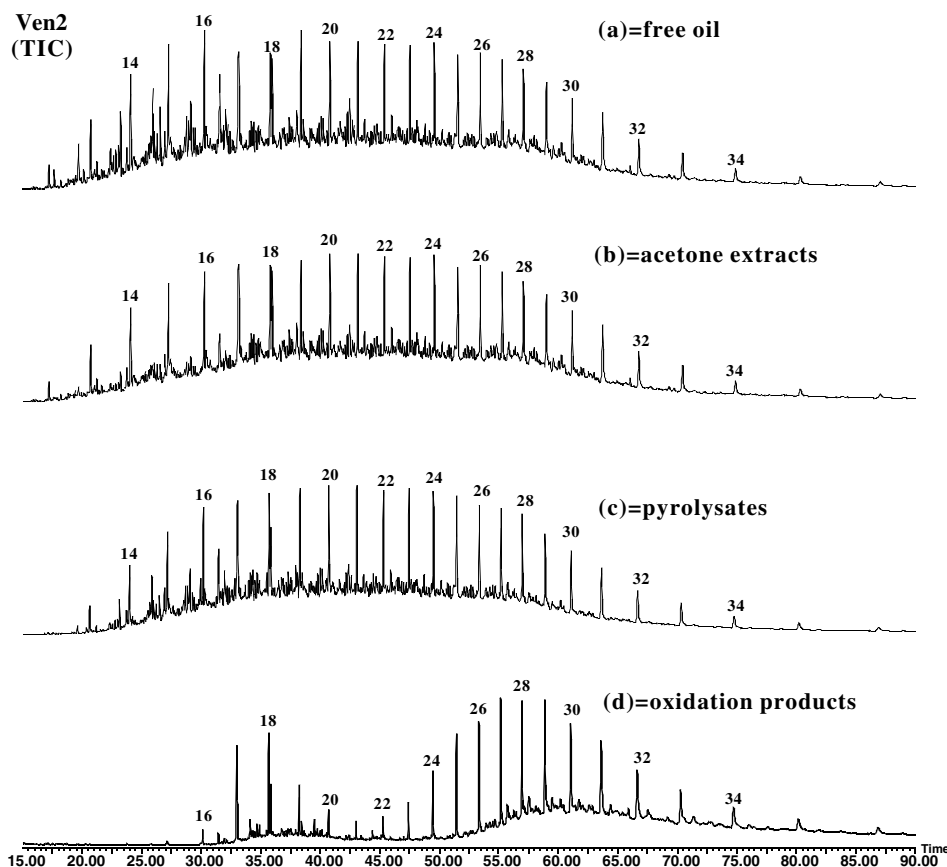


Fig. 3. Chromatograms of the saturated hydrocarbons from Ven2: (a) directly from the maltenes of crude oil Ven2, (b) from the acetone extracts of the corresponding asphaltenes, (c) from the pyrolysis products of the corresponding asphaltenes, and (d) from the oxidation products of the corresponding asphaltenes. The numbers in the figures represent the carbon number of *n*-alkanes.

CH_3COOH (15 ml) were mixed in a 50 ml beaker and slowly transferred into the flask containing the asphaltene residues, with stirring throughout. The reaction was carried out at ambient temperature (25 °C) with vigorous stirring for 48 h.

The reaction products were transferred into a 250 ml separating funnel using 50 ml toluene, and 40 ml of saturated aqueous NaCl was added. The organic layer was collected and dried using Na_2SO_4 . The organic phase was reduced to constant weight using a rotary evaporator. This organic phase can be further separated into CH_2Cl_2 soluble and CH_2Cl_2 insoluble fractions. The CH_2Cl_2 soluble fraction was precipitated by *n*-heptane into residues and maltenes, the latter fraction was then further separated into saturates, aromatics and resins using $\text{SiO}_2/\text{Al}_2\text{O}_3$ column chromatography, eluted by *n*-heptane, toluene and ethanol, respectively.

3.5. Pyrolysis of acetone-extracted asphaltene residues

Pyrolysis of asphaltenes has been extensively used over the past few decades (Van Graas, 1986; Sofer, 1988; Jones et al., 1988; Magnier and Huc, 1995), and has given valuable information to organic geochemists. This part of the experiment was aimed at comparing the hydrocarbons derived from pyrolysis and the oxidation products of asphaltenes, in order to make a proper interpretation of the oxidation-derived hydrocarbons.

Thus ~60 mg acetone-extracted asphaltenes were put into a glass tube (about 20 mm in diameter and 100 mm in height, with a narrower neck). This tube was then sealed under a flame, and air was extracted from the tube under a vacuum. This tube was then put into an oven for pyrolysis at 350 °C for 72 h.

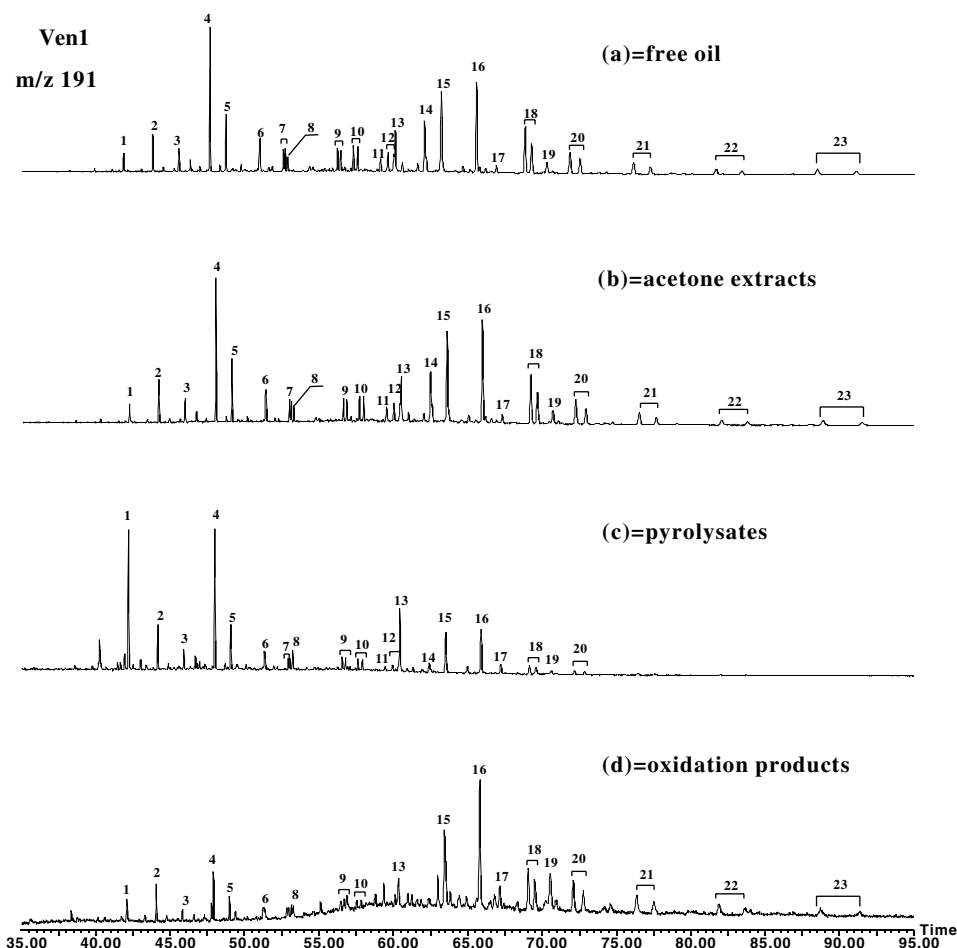


Fig. 4. *m/z* 191 mass chromatograms of the saturated hydrocarbons from Ven1: (a)–(d) as in Fig. 2. Peak identifications are given in Table 2.

After the asphaltene pyrolysis was over, the glass tube was taken out of the oven and broken open at the joint position of the narrow neck. The liquid pyrolysis products were collected using 40 ml CH_2Cl_2 , which were further separated into saturated hydrocarbons, aromatics and resins using $\text{SiO}_2/\text{Al}_2\text{O}_3$ column chromatography, eluted by *n*-heptane, toluene and ethanol, respectively.

3.6. GC–MS

Full scan GC–MS was performed using a Platform II MS detector combined with an HP6890 GC analyzer. The GC was fitted with a split/splitless injector and a CP-8CB Sil MS column ($60\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$) was used. Helium was used as the carrier gas (1.2 ml/min). The oven temperature was initially set at $80\text{ }^\circ\text{C}$ for 4 min, and was

programmed to $290\text{ }^\circ\text{C}$ at $4\text{ }^\circ\text{C}/\text{min}$, and then was held isothermally for 45 min. The MS was operated with an ionization energy of 70 eV, a source temperature of $155\text{ }^\circ\text{C}$, an electron multiplier voltage of 1765 V, and a mass range of 19–500 amu.

4. Results and discussion

4.1. Compositions of Asphaltene-o

In Fig. 1, the percentage yield (wt%) values of all fractions are expressed as a concentration in terms of the initial Asphaltene-o material. From the acetone soluble extract, the *n*-heptane insoluble fraction has been referred to as the LMA (low molar mass asphaltenes) compounds by Peng et al. (1997), and more aptly as the HSA (Higher Soluble Asphaltenes) fraction by Liao et al. (2005). More

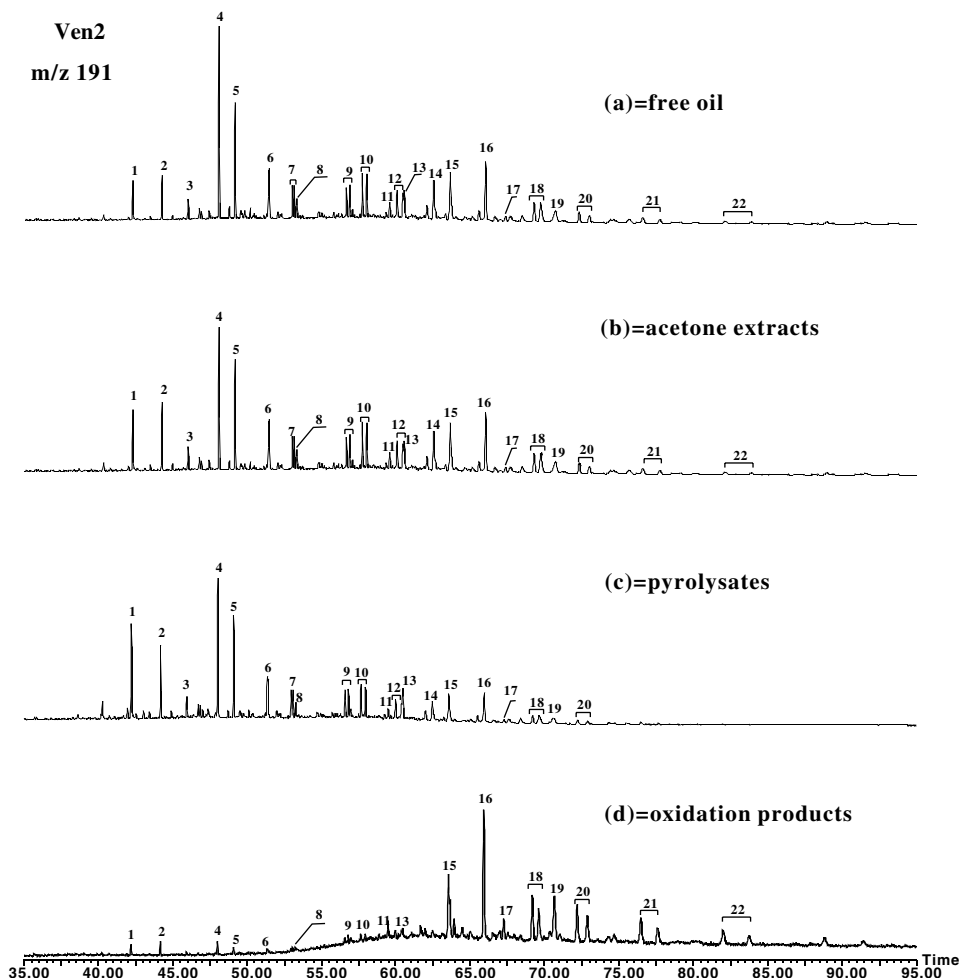


Fig. 5. m/z 191 mass chromatograms of the saturated hydrocarbons from Ven2: (a)–(d) as in Fig. 3. Peak identifications are given in Table 2.

acetone extract was obtained for Ven2 (27.8%) compared to Ven1 (18.5%) asphaltenes. This is due to structural differences because of biodegradation of Ven1. Likewise, the maltenes of the extracts reveal there are many more saturated hydrocarbons for Ven2 sample (4.31 cf. 1.15% of Ven1). This is also due to the biodegradation-induced loss of saturated hydrocarbons from Ven1. There is potentially a significant proportion of hydrocarbons adsorbed/co-precipitated inside Ven2 asphaltenes. These results indicated some exchanges should have taken place between the adsorbed hydrocarbons and those compounds from the bulk crude oils.

Oxidation of the acetone-extracted asphaltene residues yielded both CH₂Cl₂ soluble and insoluble fractions. *n*-Heptane was added to the CH₂Cl₂ soluble fraction, and a further precipitate and soluble fraction obtained. The maltenes were further separated and a saturated hydrocarbon fraction was acquired (the saturated hydrocarbons were the focus of this work, because this method is not valid to study the other fractions occluded inside asphaltenes, since the functionalized compounds, e.g., compounds bearing oxygen derived from the oxidation process could be introduced into these fractions). In our work, these saturated hydrocarbons were thought to represent occluded compounds inside the asphaltene structures, which have been little affected by the secondary evolution processes occurring in oil reservoirs. The occluded saturated hydrocarbons should represent the original kerogen-derived oils, and therefore can act as an important sample from which to obtain relevant geochemical information for oil correlation studies.

4.2. GC–MS results for saturated hydrocarbons

Figs. 2 and 3 are the chromatograms of saturated hydrocarbons for the Ven1 and Ven2 samples, among which (a), (b), (c) and (d) are of the crude oil maltenes, the acetone extracts, the pyrolysis products and the oxidation products of the corresponding asphaltenes, respectively. In the Ven1 crude oil (Fig. 2(a)), *n*-alkanes and acyclic isoprenoids are absent due to biodegradation, while some terpane compounds have been detected. Saturated hydrocarbons from the acetone extracts, thought to represent the adsorbed compounds inside asphaltenes, show similar distribution features. This indicates that exchange between the adsorbed compounds and the bulk crude oils have taken place

during geological time. However, saturated hydrocarbons from the pyrolysis products of asphaltenes have a different distribution (Fig. 2(c)), including having *n*-alkanes being dominant. Lastly the occluded saturated hydrocarbons (Fig. 2(d)) inside asphaltene structures represented by the oxidation products show a slightly bimodal feature, distinctly different from the other three chromatograms. In order to obtain precise information from the occluded hydrocarbons, interferences from the adsorbed ones should be ruled out. The occluded

Table 2
Identification of terpanes and steranes in Figs. 4–7

Peak	Identification
<i>Terpanes (m/z 191)</i>	
1	C ₂₀ tricyclic terpane
2	C ₂₁ tricyclic terpane
3	C ₂₂ tricyclic terpane
4	C ₂₃ tricyclic terpane
5	C ₂₄ tricyclic terpane
6	C ₂₅ tricyclic terpane
7	C ₂₆ tricyclic terpane
8	C ₂₄ tetracyclic terpane
9	C ₂₈ tricyclic terpane
10	C ₂₉ tricyclic terpane
11	C ₂₇ 18 α (H)-22,29,30-trisnorneohopane – Ts
12	C ₃₀ tricyclic terpane
13	C ₂₇ 17 α (H)-22,29,30-trisnorneohopane – Tm
14	C ₂₈ 17 α (H),21 β (H)-28,30-bisnorhopane
15	C ₂₉ 17 α (H),21 β (H)-30-norhopane
16	C ₃₀ 17 α (H),21 β (H)-hopane
17	C ₃₀ 17 β (H),21 α (H)-hopane (C ₃₀ moretane)
18	C ₃₁ 17 α (H),21 β (H)-hopanes
19	<i>Gammacerane</i>
20	C ₃₂ 17 α (H),21 β (H)-hopanes
21	C ₃₃ 17 α (H),21 β (H)-hopanes
22	C ₃₄ 17 α (H),21 β (H)-hopanes
23	C ₃₅ 17 α (H),21 β (H)-hopanes
<i>Steranes (m/z 217)</i>	
1	C ₂₁ sterane
2	C ₂₂ sterane
3	C ₂₇ 13 β (H),17 α (H)-diacholestane (20S)
4	C ₂₇ 13 β (H),17 α (H)-diacholestane (20R)
5	C ₂₈ diasterane
6	C ₂₇ 5 α (H),14 α (H),17 α (H)-cholestane (20S)
7	C ₂₇ 5 α (H),14 β (H),17 β (H)-cholestane (20R)
8	C ₂₇ 5 α (H),14 β (H),17 β (H)-cholestane (20S)
9	C ₂₇ 5 α (H),14 α (H),17 α (H)-cholestane (20R)
10	C ₂₈ 24-methyl-5 α (H),14 α (H),17 α (H)-cholestane (20S)
11	C ₂₈ 24-methyl-5 α (H),14 β (H),17 β (H)-cholestane (20R)
12	C ₂₈ 24-methyl-5 α (H),14 β (H),17 β (H)-cholestane (20S)
13	C ₂₈ 24-methyl-5 α (H),14 α (H),17 α (H)-cholestane (20R)
14	C ₂₉ 24-ethyl-5 α (H),14 α (H),17 α (H)-cholestane (20S)
15	C ₂₉ 24-ethyl-5 α (H),14 β (H),17 β (H)-cholestane (20R)
16	C ₂₉ 24-ethyl-5 α (H),14 β (H),17 β (H)-cholestane (20S)
17	C ₂₉ 24-ethyl-5 α (H),14 α (H),17 α (H)-cholestane (20R)
18	C ₃₀ steranes

hydrocarbons also show a different profile to the pyrolysates, so are not thought to derive from the asphaltene macromolecular structures, but rather represent a distinct organic moiety occluded inside asphaltenes.

The *n*-alkanes represent the dominant compounds of Ven2 oil (Fig. 3(a) and (b)) which have not been biodegraded. The similar distributional features between Fig. 3(a) and (b) strengthen the point that the bulk oil has been adsorbed onto the asphaltene surface. There are also abundant *n*-alkanes, particularly paraffins (cf. Fig. 3 and 2(c)). This is in accord with the fact that Ven1 oil has been biodegraded while Ven2 has not. Similarly, the oxidation process yielded distinctly different saturated hydrocarbon distributions from the other three data sets. The oxidation data of Ven1 and Ven2 are similar. This is because Ven1 and Ven2 oils were

derived from the same source rocks, and occluded the same original oils.

4.3. Terpanes and steranes

Terpane compounds are shown in Figs. 4 and 5 for the Ven1 and Ven2 samples, with (a–d) from the same fractions as those in Figs. 2 and 3, and with peak identifications given in Table 2. The Ven1 oil has very similar terpane distributions in the maltenes and acetone extracts fractions (Fig. 4(a) and (b)). The same is true for sample Ven2 (Fig. 5). The occluded saturated hydrocarbons (Fig. 4 and 5(d)), pentacyclic terpanes are most abundant, while the tricyclic series are much less abundant in comparison with the other chromatograms in Figs. 4 and 5. This is in accord with the occluded hydrocarbons having been little affected

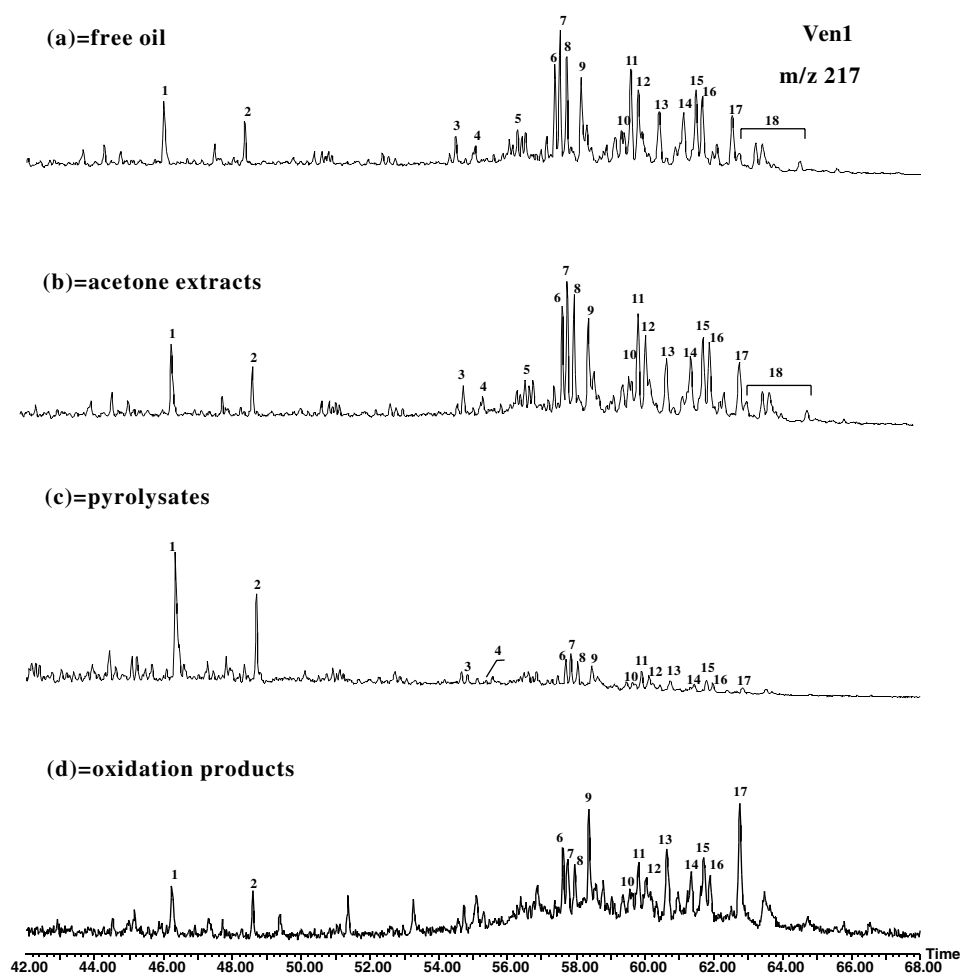


Fig. 6. *m/z* 217 mass chromatograms of the saturated hydrocarbons from Ven1: (a)–(d) as in Fig. 2. Peak identifications are given in Table 2.

by post-alteration processes in oil reservoirs, whilst the others may have been subjected to secondary alteration processes such as maturation and biodegradation. The same distribution features in Figs. 4 and 5(d) are consistent with generation of first oil from the same source rock, which has then been preserved inside the asphaltene structures as the occluded compounds.

28,30-Bisnorhopane (BNH; peak 14) has been found in the maltenes, acetone extracts and pyrolysates (Figs. 4 and 5(a)–(c)) but is absent in the occluded hydrocarbons (Figs. 4 and 5(d)). It has been reported that BNH is not generated from kerogen but is passed from the original free bitumen in the source rock to the oil (Peters et al., 2005, and references therein). Asphaltenes are derived from kerogen, and can be taken as the soluble fraction

of kerogen in crude oils (Tissot and Welte, 1984), but here BNH is not found in the occluded hydrocarbons inside the asphaltene structures. These results suggest that occlusion must occur before asphaltenes were detached from the kerogen, and in crude oils these occluded compounds cannot be exchanged with the bulk phase. This is consistent with the very similar hydrocarbon compositions that have been observed from the occluded compounds inside the asphaltenes isolated from Ven1 and Ven2 oils, despite their different post-alteration in the oil reservoirs, because they were derived from the same set of kerogens. Likewise, sterane distributions in Figs. 6 and 7 have almost the same distribution features in (a) and (b), due to exchange between the adsorbed compounds and the crude oil maltenes.

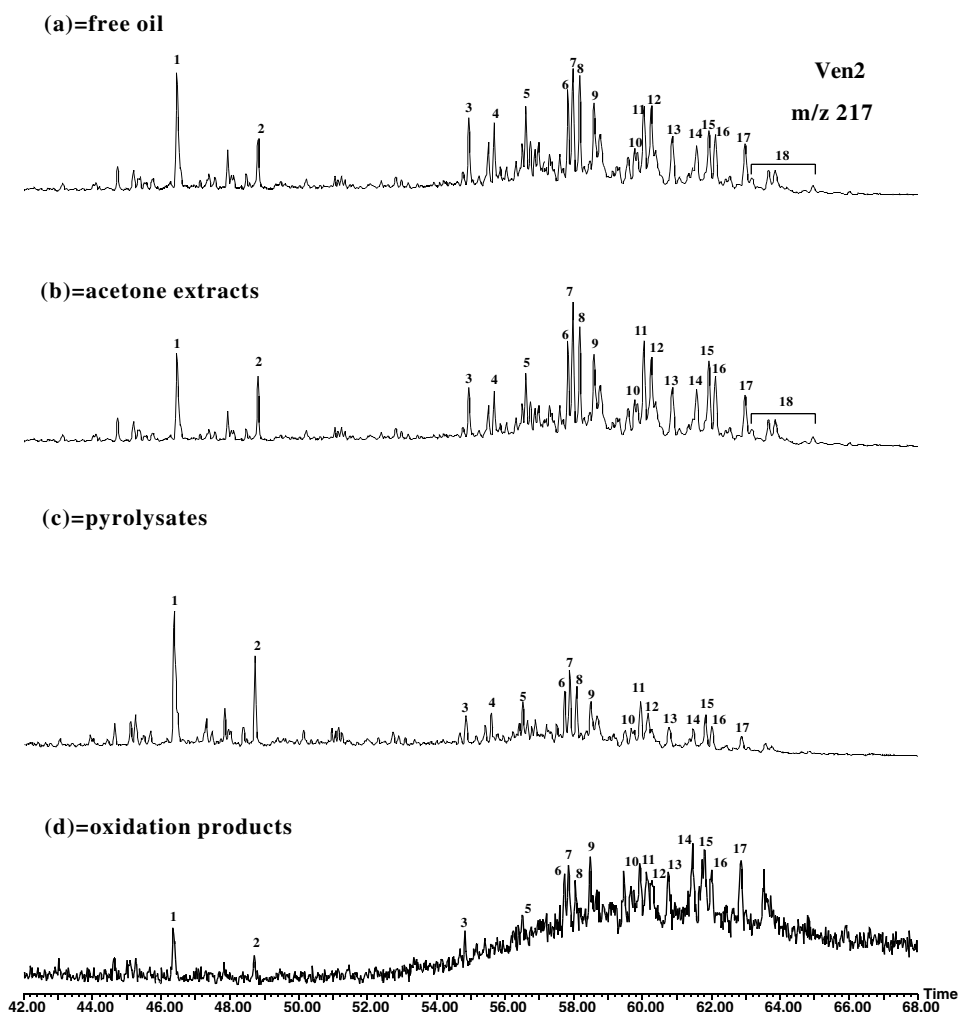


Fig. 7. m/z 217 mass chromatograms of the saturated hydrocarbons from Ven2: (a)–(d) as in Fig. 3. Peak identifications are given in Table 2.

Table 3
Biomarker parameters for terpanes and steranes

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>Ven1</i>														
Ven1-a	0.90	0.090	10.03	3.75	0.092	0.98	0.20	0.59	0.48	0.13	1.34	0.51	0.52	0.51
Ven1-b	0.79	0.093	8.52	3.52	0.096	0.95	0.20	0.58	0.49	0.13	1.28	0.51	0.49	0.50
Ven1-c	1.73	0.25	6.91	0.70	0.24	0.94	0.12	0.51	0.95	0.20	3.10	0.51	0.55	0.55
Ven1-d	0.19	0.052	3.66	0.50	0.20	0.75	0.42	0.57	0.27	0.24	0.61	0.41	0.28	0.44
<i>Ven2</i>														
Ven2-a	1.52	0.24	9.32	1.45	0.094	0.94	0.49	0.42	0.64	0.25	1.52	0.55	0.52	0.57
Ven2-b	1.44	0.18	8.17	1.06	0.097	0.83	0.51	0.40	0.63	0.24	1.41	0.56	0.52	0.54
Ven2-c	2.54	0.29	8.82	0.67	0.12	0.96	0.46	0.35	0.88	0.28	2.21	0.54	0.47	0.59
Ven2-d	0.059	0.010	7.06	0.49	0.18	0.61	0.53	0.55	0.28	0.25	0.55	0.43	0.30	0.45

(1) C_{23} tricyclic/ $C_{30}\alpha\beta$ terpanes = peak 4/peak 16 in m/z 191 mass chromatograms. (2) C_{24} tetracyclic/ $C_{30}\alpha\beta$ terpanes = peak 8/peak 16 in m/z 191 mass chromatograms. (3) C_{23} tricyclic/ C_{24} tetracyclic terpanes = peak 4/peak 8 in m/z 191 mass chromatograms. (4) Ts/Tm = peak 11/peak 13 in m/z 191 mass chromatograms. (5) $C_{30}\beta\alpha/C_{30}\alpha\beta$ terpanes = peak 17/peak 16 in m/z 191 mass chromatograms. (6) $C_{29}\alpha\beta/C_{30}\alpha\beta$ terpanes = peak 15/peak 16 in m/z 191 mass chromatograms. (7) Gammacerane/ $C_{30}\alpha\beta$ terpanes = peak 19/peak 16 in m/z 191 mass chromatograms. (8) $C_{31-22S}/(22S + 22R)$ homohopanes = peak 18-1/(peak 18-1 + peak 18-2) in m/z 191 mass chromatograms. (9) $C_{21}/(C_{21} + C_{29})$ steranes = peak 1/(peak 1 + peak 17) in m/z 217 mass chromatograms. (10) C_{27} diasteranes/ C_{27} steranes = (peak 3 + peak 4)/(peak 6 + ... + peak 9) in m/z 217 mass chromatograms. (11) C_{27}/C_{29} steranes = peak 9/peak 17 in m/z 217 mass chromatograms. (12) $C_{27}\alpha\beta\beta/(C_{27}\alpha\beta\beta + C_{27}\alpha\alpha\alpha)$ steranes = (peak 7 + peak 8)/(peak 6 + ... + peak 9) in m/z 217 mass chromatograms. (13) $C_{29-20S}/(20S + 20R)$ = peak 14/(peak 14 + peak 17) in m/z 217 mass chromatograms. (14) $C_{29}\alpha\beta\beta/(C_{29}\alpha\beta\beta + C_{29}\alpha\alpha\alpha)$ steranes = (peak 15 + peak 16)/(peak 14 + ... + peak 17) in m/z 217 mass chromatograms.

Ven1(2)-a: Saturated hydrocarbons directly from the maltenes of crude oils. Ven1(2)-b: Saturated hydrocarbons from the acetone extractants of the corresponding asphaltenes. Ven1(2)-c: Saturated hydrocarbons from the pyrolysis products of the corresponding asphaltenes. Ven1(2)-d: Saturated hydrocarbons from the oxidation products of the corresponding asphaltenes.

From the biomarker parameters for the terpanes and steranes (Table 3), for both the Ven1 and Ven2 samples the ratio of C_{23} tricyclic/ $C_{30}\alpha\beta$ terpanes (1) decreases from a to b to d, but with Ven1(2)-c being much more abundant than the other fractions. Similar trends have also been found for parameters such as C_{24} tetracyclic/ $C_{30}\alpha\beta$ terpanes (2), $C_{21}/(C_{21} + C_{29})$ steranes (9) and C_{27}/C_{29} steranes (11). These parameters are influenced by the maturation and/or biodegradation status of these fractions (Peters et al., 2005). The occluded hydrocarbons (d) have the lowest maturation level and have not been significantly altered by biodegradation (also the parameter $C_{29-20S}/(20S + 20R)$ steranes (13) in Table 3).

In Table 3, maturity parameters such as Ts/Tm (4), $C_{30}\beta\alpha/C_{30}\alpha\beta$ terpanes (5) and the sterane isomers $C_{29-20S}/(20S + 20R)$ (13) generally indicate that the maturity levels decrease from a to b to c to d. These results are consistent with the general observations that the adsorbed and more so occluded hydrocarbons should have a lower maturity level compared to those of the crude oil maltenes (Peng et al., 1997; Pan et al., 2002; Liao et al., 2005). Compared to Ven2-a, b, the much higher Ts/Tm (4) ratio for Ven1-a, b may be ascribed to its biodegradation (Peters et al., 2005).

However, the same maturity level trends can not be found in the parameter $C_{31-22S}/(22S + 22R)$ homohopanes (8), especially for the relatively high values for Ven1(2)-d, but this may be accounted for by the hypersaline environments of the source rocks (Peters et al., 2005).

The occluded hydrocarbons of Ven1 and Ven2 generally show similar biomarker values (Table 3). These results are in accord with the fact that the two oils studied in this work were derived from the same source rocks, thus yielding asphaltene-occluded hydrocarbons of similar compositions. The asphaltene-occluded saturated hydrocarbons (Ven1(2)-d in Table 3) were characterized by a relatively high abundance of C_{24} tetracyclic terpane, abundant pregnanes and homopregnanes, abundant gammacerane, and a relatively low concentration of diasteranes. Based on data in Peters et al. (2005), these results are consistent with the source rock of these two oils being deposited in an anoxic, hypersaline/evaporitic environment.

5. Conclusions

The saturated hydrocarbons adsorbed by asphaltene structures derive from crude oil maltenes, whereas the occluded hydrocarbons may represent

the original oil derived from kerogens retained inside asphaltenes over geological time.

Using a $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ oxidative system, the occluded hydrocarbons (the *original oil*) can be released from the asphaltenes, making it possible to directly study these compounds without interference from other moieties that are covalent-bonded to the asphaltene molecular structures. This method is economical, simple to carry out, and especially applicable to the study of biodegraded crude oils, from which it is difficult to obtain molecular information. In order to obtain precise geochemical information from the occluded compounds inside asphaltene structures, potential interference from the adsorbed hydrocarbons should be eliminated (e.g., by acetone extraction) before using the oxidative reagent to release the occluded oil.

The saturated hydrocarbons of the oil occluded inside the Ven1 and Ven2 asphaltenes showed very similar distributions. This indicated almost the same terpane and sterane distributions and values for associated biomarker parameters. All these results are consistent with the interpretation that the Ven1 and Ven2 oils were derived from the same source rock and occluded the same type of original oils. The geochemical information obtained from the occluded saturated hydrocarbons inside the asphaltenes suggests that the source rock of these two oils was deposited in an anoxic, hypersaline/evaporitic environment.

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