

Classification of the asphalts and their source rock from the Dead Sea Basin (Israel): the asphaltene/kerogen vanadyl porphyrins

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The asphaltenes of the asphalts from the Dead Sea Basin were examined for the occurrence of vanadyl porphyrins. These examinations demonstrate that the asphalts fall into two broad class types: one which exhibits a relatively high vanadyl porphyrins content (> 300 ppm), and the other characterized with no vanadyl porphyrins (< 10 ppm). It is concluded that these asphalts belong to two distinct types and have separate origins. The kerogens isolated from the petroleum-source rock of the Dead Sea Basin were also analyzed. Two genetic types of kerogen appeared to exist: a marine one highly enriched with these pigments and a terrestrial one with no vanadyl porphyrins. For comparison, the asphaltenes of typical asphaltic crude oils from Western Venezuela and kerogen from their La Luna source rock were also examined. Previous detailed geochemical studies¹ indicated that the La Luna kerogen is derived from marine organic matter source. These materials have higher concentrations of vanadyl porphyrins than the Dead Sea asphaltenes and kerogens are enriched with these compounds. Our results strengthen the potential of vanadyl porphyrins of both petroleum asphaltenes and source-rock kerogen for use in genetic and correlation studies. © 1998 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

Previous geochemical studies of the asphalts from the Dead Sea (DS) Basin suggest a common origin from calcareous Senonian bituminous rock (SBR)^{2–9} for these bituminous materials. This conclusion is based on (a) the close association between these bituminous materials and (b) some geochemical similarities between the DS asphalts and the SBR bitumens/kerogens^{5,6}.

Spiro *et al.*⁷ have extensively studied organic material in SBR distributed throughout the DS Basin. On the basis of their detailed analysis, these authors recognized three genetic types of organic matter, namely marine, terrestrial and mixed marine and terrestrial organic matter in the basin. They concluded that organic matter in SBR at most sites is primarily derived from the marine algae, while material derived from land-plants dominates SBR in a few locations.

Rullkötter *et al.*¹⁰, in their study of the biological markers, provided evidence that the DS asphalts, conventional petroleum and asphaltic crudes originated from a

single type of source-SBR. According to these authors, the asphaltic crudes are alteration products derived from conventional-type crudes by secondary processes (water-washing, incipient degradation or physical losses of volatile components). Using steroid aromatisation¹⁰ and vanadyl porphyrin (VO²⁺-P) distribution¹¹ as the crucial maturity parameters under the given geological conditions in the DS Basin, these researchers concluded that the asphalts have to be classified as immature, whereas conventional and asphaltic crude oils are mature generation products. In addition, biomarker geochemistry indicates that substantial generation of conventional (mature) petroleum occurs in deeply (8000–10 000 m) buried SBR, whereas the DS asphalts either originated from a very immature and shallow SBR or represent early *in situ* generation¹⁰. However, an important question still remains, whether all the asphalts accumulated in the basin were essentially derived from the same group of source rocks or, if there also exists other group source rocks which contributed significantly to the asphalt generation in the basin.

One of the best ways to identify the source-rock of a reservoir petroleum and asphalt is to find geochemical

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Table 1 Geochemical data of the DS bituminous sediments: asphaltenes and kerogens (wt.%) of organic fractions

Sediment	Depth (m)	Asphaltenes	Kerogen
DS (floating asphalt) A	surface	67**	—
DS (floating asphalt) B	surface	48	8
Heimar (asphalt)	60–71	22***	< 1***
IPRG (asphalt)	60–62	65***	—
Ef'e (SBR)	surface	—	98*
Nebi Musa (SBR)	surface	7***	81***
Gurim 3 (heavy crude)	1560–1570	14 ^a	4
Massada (petroleum)	2100	2** ^b	—

*Organic fraction/petroleum containing no VO²⁺-P (< 10 ppm)**Organic fraction/petroleum containing VO²⁺-P (< 100 ppm)***Organic fraction/asphalt containing VO²⁺-P (< 300 ppm)^a Aizenshtat *et al.*⁴^b Aizenshtat and Sundararaman¹¹**Table 2** Geochemical data of asphaltic crude oils and source rock from Western Venezuela: asphaltenes and kerogens (wt.%) of organic fractions

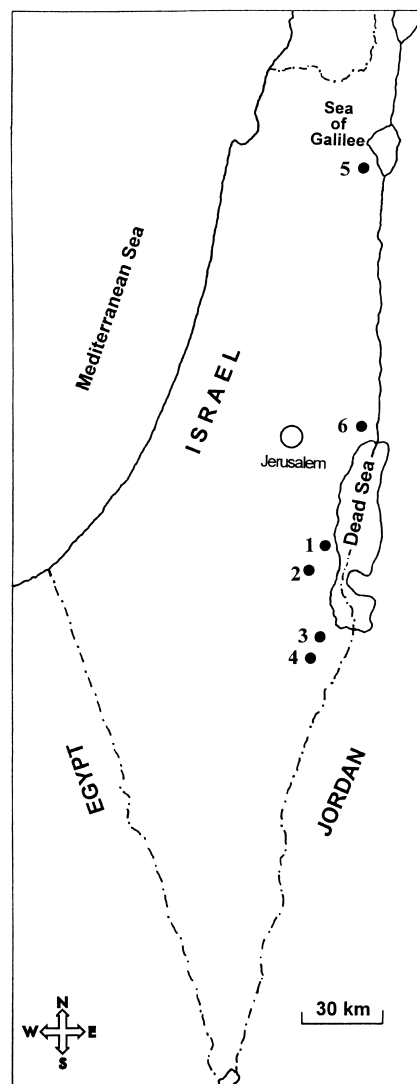
Organic fractions	Asphaltenes	Kerogen
La Luna QM-8	7	86
La Luna QM-10	8	75
La Luna QM-12	7	80
La Luna QM-14	7	86
Crude oil DM-119	19	—
Crude oil DM-120	16	—

(mainly compositional) similarities between kerogen of the source-rock and asphaltenes of the corresponding petroleum¹². The high VO²⁺-P petroleum, asphalts and bituminous rocks occur on all continents, in rocks of widely varied ages, at various depths, with various temperatures and pressure histories, and in reservoirs commonly interbedded closely with reservoirs of similar materials containing no VO²⁺-P. High VO²⁺-P content of the asphaltenes is a distinctive and readily detectable characteristics of many petroleum, asphalts and bituminous rocks¹³. Although long recognized in these materials, VO²⁺-P were not as widely used as other geochemical fingerprints for genetic and correlation studies. In fact, VO²⁺-P incorporated into the asphaltenes of both the petroleum and asphalts are inherited directly from the source-rock kerogen, and the abundance of these compounds in petroleum asphaltenes is a function of their high concentration in the source-rock kerogen existing at the time of petroleum generation¹⁴. Thus, VO²⁺-P associated with both petroleum asphaltenes and source-kerogens could be used in organic geochemical studies as both a genetic indicator and a correlation tool. The application of this hypothesis to the asphalts and kerogens from the DS area is the major focus of this communication. Namely, recent electron spin resonance (ESR) works in our laboratory has shown that most of asphaltenes of the DS asphalts^{15–17} contain a relatively high concentration of VO²⁺-P.

EXPERIMENTAL

Sample

The samples analyzed in this work are listed in Table 1 and their geographical locations shown in Figure 1. The present study focuses on the DS floating asphalts, the Heimar asphalt (sandstone cemented with asphalt) and the IPRG asphalt. The samples of floating asphalt were taken

**Figure 1** Geological map indicating DS sample locations: (1) Massada; (2) Gurim; (3) Heimar; (4) IPRG; (5) Ef'e; and, (6) Nebi Mussa

from large floating blocks that appeared in the northern (A) and southern (B) parts of the lake. According to Spiro *et al.*, the organic matter of the Nebi Mussa rock is typical of marine origin. Organic matter of the Ef'e rock is a type example of land-plant derived materials. For these reasons, we selected the kerogens isolated from these two rocks. The SBR samples were taken from the surface exposures, but the asphalt samples were taken from shallow prospecting and are from depths less than 75 m below the surface (Table 1). We also considered two typical DS crude oils: conventional petroleum (Massada) and heavy crude (Gurim). The asphalt samples were chosen to represent each mode of occurrence. The geological samples sets chosen are only representative of each broad class (terrestrial versus marine) and it is acknowledged that many other asphalt/petroleum samples of each class could have been included. However, such addition would not add to the general principles of behavior of VO²⁺-P concentration in each class.

One of the purposes of the present paper is to report on the extension of the foregoing study to the asphaltenes of typical Maracaibo asphaltic crude oils and the kerogens isolated from the La Luna source rocks (Table 2). Locations

of geological samples included in the present report are shown in Figure 2. Two oil samples (DM-119, DM-120) were obtained from two different West Mara oil fields. Four La Luna rock samples (QM-8, QM-10, QM-12, QM-14) (Table 2) were obtained from the Maraca site.

Extraction and separation

The DS asphalt was dissolved by refluxing (Soxhlet) for 48 h in benzene:methanol (6:1 v/v), was centrifuged (2 h) and the supernatant filtered (5 μ m pore filter). After solvent evaporation, the asphalt (10 g) was refluxed (Soxhlet) for 90 h in *n*-hexane to obtain the maltene fraction (after solvent evaporation). The remaining asphaltenes were washed several times with *n*-hexane until the wash solution was clear, then dried at 45°C. All fractions were weighed and examined by ESR spectrometry to determine their VO²⁺-P content (mainly in the asphaltene fraction) (Table 1).

Powdered bituminous rocks were treated with a boiling HCl (6 M) solution to remove most of the carbonates. The insoluble residue was demineralized further by a repeated treatment with a HCl/HF mixture 0.25 M and 22 M, respectively). This acid mixture removes silicates. The insoluble residue (organic fraction + insoluble inorganic minerals) was refluxed (Soxhlet) with *n*-hexane (maltene)

for 90 h and then with benzene (asphaltene) for 90 h. The asphaltene fraction was evaporated, dried with N₂ and weighed. Kerogen was separated from acid-resistant mineral grains in the final residue by the chloroform sink-float technique¹⁸.

Petroleum was agitated with a 20-fold excess of *n*-hexane at room temperature for 8 h, and then left for 24 h. Precipitated asphaltenes were filtered, washed with *n*-hexane to remove adsorbed compounds, dried with N₂, weighed and analyzed for their VO²⁺-P content by ESR.

Heating experiments

Powdered samples (100 mg) were sealed under vacuum in quartz tubes (4 mm o.d., 3 mm i.d.). Each tube was heated (electric furnace) at a single temperature between room temperature to 400°C for 1 day and with a temperature increment of 100°C. An identical procedure was employed for the air atmosphere heating experiments except that quartz tubes were opened.

Electron spin resonance

ESR measurements were performed on unheated/heated powdered samples in a quartz tubes (4 mm o.d., 3 mm i.d.).

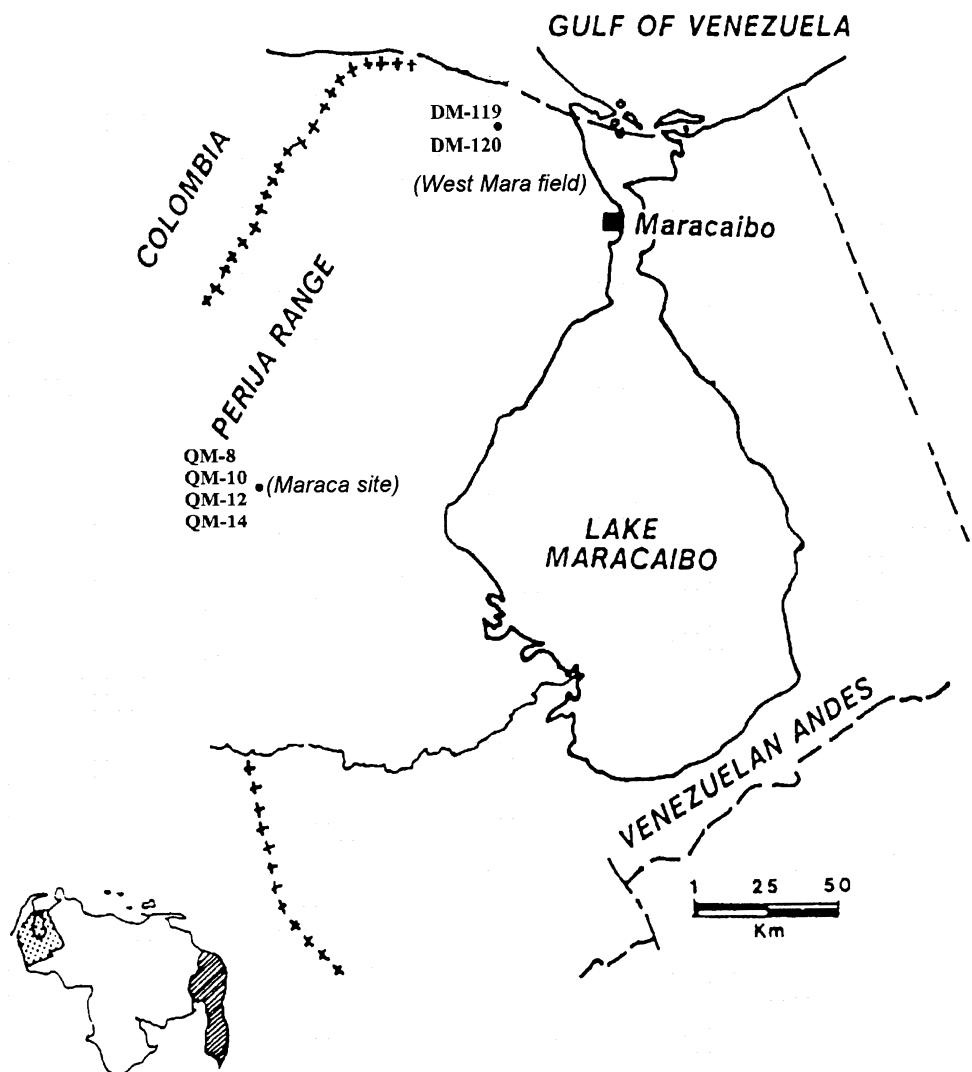


Figure 2 Geological map indicating Maracaibo sample locations: crude oils (West Mara field) and La Luna rocks (Maraca) (after Cabrera³²)

Table 3 Geochemical data of the DS bituminous sediments: inorganic and organic fractions (wt.%)

SBR	Carbonates	Silicates	Organic matter
Ef'e	73	6	21
Nebi Mussa	76	6	18

Spectra were run on a Bruker ER 200D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz interfaced to a PACOM computer. Signal intensities (proportional to the $\text{VO}^{2+}\text{-P}$ concentration) were calculated by double integration of the first derivative V hyperfine ($m = -5/2$) line using the PACOM system. Calculations of the $\text{VO}^{2+}\text{-P}$ distribution in asphaltene/kerogen were based upon comparisons with the total organic extract.

Emission spectrometry

A PGS-2 plane grating spectrograph (Carl Zeiss, Jena) was used with an attachment for photoelectric detection, an arc plasma excitation source, and a Bausch and Lomb diffraction grating as the monochromator¹⁹.

Atomic absorption spectrometry

A Perkin-Elmer model 4000 atomic absorption spectrometer was used with a Perkin-Elmer platinum hollow-cathode lamp and a nitrous oxide/acetylene burner head.

RESULTS AND DISCUSSION

ESR of vanadyl porphyrins

SBR is biomicritic limestone/marl in which the organic matter is generally homogeneously and finely dispersed⁷. Table 3 shows the composition of the SBR samples as determined by the fractionation procedure (described in Section 2). The major constituent is carbonate with lesser amounts of silicates; the total organic fraction constitutes 18–21% of the rock. Figure 3(a) shows a representative ESR spectrum of $\text{VO}^{2+}\text{-P}$ of asphaltene extracted from SBR at the Nebi Mussa locality. Similar spectra were recorded for the asphaltenes extracted from the DS asphalts enriched with $\text{VO}^{2+}\text{-P}$. Table 4 shows the distribution of $\text{VO}^{2+}\text{-P}$ among the asphaltenes of asphalts and the Bei Mussa kerogen determined by ESR. The $\text{VO}^{2+}\text{-P}$ concentration of this kerogen is comparable with that found in the asphaltenes of DS floating asphalt A (Table 4). In contrast to the asphaltenes of the asphalt A, ESR analysis of the asphaltenes extracted from the asphalt B shows no evidence for $\text{VO}^{2+}\text{-P}$ above the limit of detection of 10 ppm. The Ef'e kerogen showed, also, no evidence of $\text{VO}^{2+}\text{-P}$ at the detection limit.

Thermal stability of vanadyl porphyrins

The striking absence of $\text{VO}^{2+}\text{-P}$ in the asphaltenes of the asphalt B could be simply attributed to thermal decomposition of $\text{VO}^{2+}\text{-P}$ under geological conditions through natural heating. Very recently in our laboratory, a series of heating experiments in the absence of air combined with the ESR measurements have been carried out on the asphaltenes (abundant in $\text{VO}^{2+}\text{-P}$) isolated from the DS asphalts^{15–17}. The results of these studies demonstrated exceptional high thermal stability of $\text{VO}^{2+}\text{-P}$ of these materials indicating that the drastic temperatures ($> 400^\circ\text{C}$) are required for the destruction of their $\text{VO}^{2+}\text{-P}$. These temperatures are

Table 4 Geochemical data of the DS bituminous sediments: the normalized $\text{VO}^{2+}\text{-P}$ contents^a

	Floating asphalt A	Heimar	IPRG	Nebi Mussa
Asphaltenes	1.0	0.5	0.5	–
Kerogen	–	–	–	0.3

^a The $\text{VO}^{2+}\text{-P}$ content determined by ESR and normalized to the $\text{VO}^{2+}\text{-P}$ content of floating asphalt A (ca. 1000 ppm)

significantly higher than those (about 50–200°C) normally experienced even in deeply buried source rocks. Furthermore, geological evidence suggest that SBR at shallow sites (such as the Nebi Mussa and Ef'e rocks) has experienced a rather mild thermal history^{8,9}.

Vanadyl porphyrins and weathering: vanadyl-on-porphyrins

The essential condition for preservation of $\text{VO}^{2+}\text{-P}$ is a reducing environment at the place of deposition. Thus, the $\text{VO}^{2+}\text{-P}$ -bearing asphalts and the source-kerogens in such an environment tend to maintain the high level of $\text{VO}^{2+}\text{-P}$, but because of their instability these compounds in the shallow buried or outcrop rocks may become absent after an exposure to oxidizing conditions of weathering. Consequently, an alternative explanation could be that the absence of $\text{VO}^{2+}\text{-P}$ in the floating asphalt B is the result of the $\text{VO}^{2+}\text{-P}$ destruction during intense weathering. For this reason, in the second part of this study, asphaltenes of the DS floating asphalt A were heated at 250°C in the presence of air (O_2) for 20 days. The ESR spectrum of VO^{2+} compound(s) in this heated sample is given in Figure 3(b). This spectrum is similar to those reported for VO^{2+} ions incorporated into the structure of the Western Kentucky No. 9 coal (USA)²⁰. According to these authors, VO^{2+} ions within the structure of this coal are, probably, complexed with the coal oxygenated functional groups such as carboxylic/phenolic groups. For this reason, we suggest that their VO^{2+} compounds in air-heated DS materials (Figure 3(b)) are of non-porphyrin type ($\text{VO}^{2+}\text{-non-P}$). As no experimental evidence is found of $\text{VO}^{2+}\text{-non-P}$ in the asphaltenes of either the asphalt B or Ef'e kerogen, it seems reasonable to conclude that weathering is not responsible for the absence of $\text{VO}^{2+}\text{-P}$ in these materials.

One of the major processes that can affect petroleum or asphalts in reservoirs, especially shallow reservoirs, is biodegradation. One may argue that biodegradation may be a major factor in destroying for $\text{VO}^{2+}\text{-P}$ in the floating asphalt B. Available data, however, indicate that biodegradation has little effect on $\text{VO}^{2+}\text{-P}$ ^{21–25}. In addition, our experience shows that biodegraded oils from the Maracaibo Basin (Venezuela) contain a much higher $\text{VO}^{2+}\text{-P}$ content than non-biodegraded petroleum of similar source facies and maturity²⁶.

Classification of the source-rock kerogens and the asphalts

High $\text{VO}^{2+}\text{-P}$ content of petroleum and asphalts appears to be an original characteristics to the kind of kerogen of which the asphalt was derived. The abundance of $\text{VO}^{2+}\text{-P}$ of petroleum asphaltenes seems to characterize to a remarkable degree both asphaltenes and kerogen of marine source-rocks. This is as expected since for marine source-rocks, there is an abundant input of porphyrin-precursor chlorophylls to the organic matter derived from algae and/or bacteria where rich source-rocks are

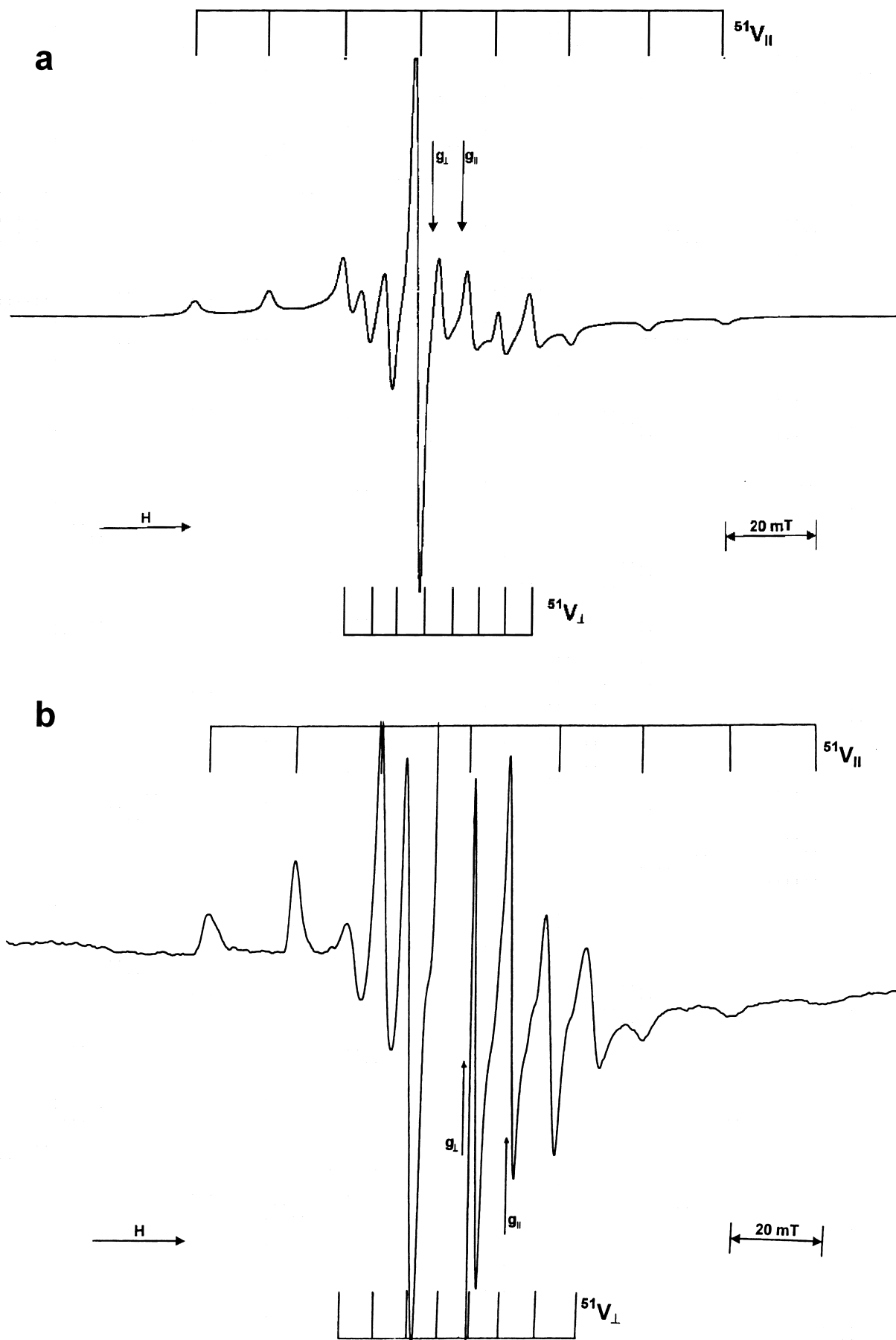


Figure 3 First-derivative room-temperature X-band anisotropic ESR spectra of: (a) $\text{VO}^{2+}\text{-P}$ of the Nebi Mussa asphaltene and (b) $\text{VO}^{2+}\text{-non-P}$ of DS asphaltene after their heating (after 6 days) at 250°C in the presence of air

Table 6 Geochemical data of asphaltic crude oils and source rock from Western Venezuela: the normalized VO²⁺-P contents ^a

	QM-8	QM-10	QM-12	QM-14	DM-119	DM-120
Asphaltenes	–	–	–	–	1.4	1.8
Kerogen	0.5	1.0	0.8	0.6	–	–

^a The VO²⁺-P content determined by ESR and normalized to the VO²⁺-P content of QM-10 (ca. 10 400 ± 1000 ppm)

Table 7 Geochemical data of asphaltic crude oils and source rock from Western Venezuela: the V and Ni contents (ppm) ^a and the Ni/V ratio

Rock/crude oil	Fraction	V	Ni	Ni/V
QM-8	kerogen	4000	350	0.09
QM-10	kerogen	4300	400	0.09
QM-12	kerogen	3600	290	0.08
QM-14	kerogen	4000	380	0.10
DM-119	asphaltenes	5500	400	0.07
DM-120	asphaltenes	4800	300	0.06

^a The vanadium content determined by both emission spectrometry and atomic absorption spectrometry

developed, and physiochemical conditions favor both VO²⁺ and its incorporation into porphyrins. For example, Kontorovich and Borisova²⁷ have studied, very recently, the average composition of 45 asphaltene samples of Jurassic sedimentary rocks from Western Siberia (Russia) having a terrestrial or marine origin. They demonstrated that asphaltenes of marine origin are characterized by the enriched presence of VO²⁺-P.

It appears reasonable to suggest that the high VO²⁺-P Nebi Mussa kerogen may reflect major contribution of marine organic matter (or of organic matter derived from marine algal/bacterial organisms) to the genesis of this material. This rationalization is compatible with the conclusion of Spiro *et al.*⁷. On the other hand, terrestrial Ef'e kerogen shows the absence of VO²⁺-P. This is as expected as discussed previously and may be a consequence of a relatively lower chlorophyll-porphyrins contribution to terrestrial kerogen and a insufficient preservation of any algal and/or bacterial derived chlorophyll-porphyrins under the more oxidizing conditions experienced by terrestrial biorganic matter.

The asphaltenes of the floating asphalt A, Heimar and IPRG asphalts are characterized by a high VO²⁺-P content (> 300 ppm). Hence, it appears reasonable to suggest that these high VO²⁺-P asphalts originated from a marine kerogen source rich in VO²⁺-P. On the other hand, the absence of VO²⁺-P in the floating asphalt B indicates that this material originated from kerogen containing no VO²⁺-P. However, the present work cannot identify the source of this asphalt. Thus, the DS asphalts are products of two distinctively SBR kerogens that, in turn, give rise to two distinctively different types of asphalts in terms of the presence and absence of VO²⁺-P.

Vanadium and nickel in the Dead Sea asphalts and kerogens

Enriched concentrations of vanadium (V) and nickel (Ni) have been noted in various geological materials including petroleum, asphalts and organic fractions of source rocks. How these metals entered these materials is still an open question, although it is generally believed that they entered at the time of their formation. Recent work by Barwise²⁸ has shown that for some petroleum classes, the absolute contraction of V and N and Ni/V ratio are both useful

petroleum classification parameters. According to the author, petroleum derived from marine source rocks are characterized by high absolute concentration of V and Ni and have a Ni/V ratio value of 1 or less. On the other hand, petroleum originated from terrestrial environments are characterized by a low metal content (< 50 ppm) and have higher Ni/V ratios (> 2), compared to petroleum generated from marine source rocks. They are potentially very useful parameters for the determination of the origin of organic matter present in petroleum, asphalts and source rocks and for oil/source correlation. It is for this reason that additional attention has been directed to these metals in the asphaltene and kerogens studied.

The trace metal data in Table 5 for the asphaltene of the DS asphalts show a clear-cut division of the DS asphalts in harmony with the above classification scheme proposed by Barwise²⁸. Namely, the absolute concentrations of metals dropped from high value (> 900 ppm) for the asphaltene of the asphalt A to very low value for the asphaltene of the asphalt B (2 ppm). In addition, the asphaltene of the asphalt A exhibit a low Ni/V ratio (0.4). Considerable support is given, therefore, to the foregoing classification of the DS asphalts based on their VO²⁺-P content.

In contrast to the asphalts, the contrast in metal contents (Table 5) of the studied kerogens is not striking and cannot serve to differentiate the foregoing class type of these materials.

Vanadyl porphyrins and the Dead Sea petroleum

The asphaltene of the Gurim asphaltic crude oil are characterized by the absence of VO²⁺-P and it seems reasonable to conclude that this petroleum is likely to be derived from the source-SBR kerogen with no VO²⁺-P. In contrast to the Gurim asphaltene, the asphaltene isolated from the Massada petroleum have a relatively high content of VO²⁺-P (> 100 ppm) which indicates that it originates from a marine source kerogen. Apparent explanation could be late catagenetic generation of the Massada petroleum from deeply buried SBR with kerogen abundant in VO²⁺-P. On the other hand, despite some organochemical differences (including the VO²⁺-P contents), geochemical and sedimentological characteristics suggest that the DS petroleum (e.g. the Massada/Gurim crude oils) originated in one formation. Alternatively, they originated in source

Table 5 Geochemical data of the DS bituminous sediments: the V and Ni contents (ppm) ^a and the Ni/V ratio

Rock/asphalt	Fraction	V	Ni	Ni/V
Floating asphalt A	asphaltene	675	250	0.4
Floating asphalt B	asphaltene	2	3	1.5
Heimar	asphaltene	215	110	0.5
IPRG	asphaltene	400	275	0.7
Ef'e	kerogen	45	225	5.0
Nebi Mussa	kerogen	95	110	1.2

^a The vanadium content determined by both emission spectrometry and atomic absorption spectrometry

sequence that contained very similar oil-prone kerogens with or without $\text{VO}^{2+}\text{-P}$.

Asphaltic crude oils in the Maracaibo Basin

Geochemical study of crude oils from the different reservoirs have identified three genetic types of crude oil in the Maracaibo Basin: a marine type essentially derived from marine La Luna source, a terrestrial type, and a third type derived from the mixing of the first two types¹. According to this study, marine (asphaltic) oils of low to moderate API gravity ($< 30\text{--}40$ API) are characterized by high V content (> 900 ppm). On the other hand, terrestrial oils are characterized by low V content (4 ppm). Very recently, López *et al.*²⁹ have detected traces of V and Ni in different fractions of some asphaltic petroleum from the Maracaibo Basin. These authors have shown that the metal ratio may be used as a correlation parameter in any of the petroleum fractions including asphaltenes. According to these authors, the asphaltic petroleum originated from the same source rock, the La Luna bituminous limestone.

$\text{VO}^{2+}\text{-P}$ content (> 3000 ppm) of the asphaltenes extracted from the Maracaibo asphaltic crude oils is much higher than that in the DS asphalt A (Table 6). These asphaltenes are also characterized by relatively large amounts of V (> 3500 ppm) and Ni (> 300 ppm) (Table 7). The ratio between the concentration of Ni and the concentration of V in the asphaltenes appears to remain within a fairly narrow range and less than 0.1 (Table 7). Two apparent conclusions could be advanced from these results.

Firstly, the petroleum from the West Mara fields do not have origins separate one from the other. This is in excellent agreement with established concept of the unification of these oil fields into a single one³⁰.

Secondly, within the Barwise's classification scheme these asphaltic petroleum are apparently derived from marine organic matter source lending support to similar conclusion reached by Talukdar *et al.*¹. Finally, the $\text{VO}^{2+}\text{-P}$ content, the V and Ni content as well as the Ni/V ratio of kerogen separated from the La Luna source rock as very similar to that of the Maracaibo asphaltic petroleum (Tables 6 and 7). The apparent conclusion is that the kerogen of marine La Luna rock is the principal source for asphaltic oils in the basin as proposed by Talukdar *et al.*¹. In general, to produce the vast quantities of petroleum containing asphaltenes enriched with $\text{VO}^{2+}\text{-P}$ in a prolific basin, the efficiency of kerogen abundant with $\text{VO}^{2+}\text{-P}$ is almost certainly a necessity.

Final remarks

From our continuing detailed study of $\text{VO}^{2+}\text{-P}$ of the kerogens of ancient carbonaceous sedimentary rocks throughout the world (PIP over 25 years) we conclude that: (1) only the kerogens derived from marine organic matter have high (> 100 ppm) $\text{VO}^{2+}\text{-P}$ content. The best illustrative example of this type of kerogen is that isolated from the famous Serpiano marl (Switzerland) on which Treibs³¹ based much of his earlier work, and (2) the kerogens originated from terrestrial organic source are characterized by the absence or almost complete absence (< 10 ppm) of $\text{VO}^{2+}\text{-P}$. The most illustrative cases are the kerogens separated from the well-studied lacustrine Green River (SA) and Messel (Germany) shales.

In addition, the conclusion towards which the evidence appears to lead is that high $\text{VO}^{2+}\text{-P}$ content of marine kerogens reflects the influence of a certain type of source algal/bacterial material which was particularly predominant

in near-shore anoxic marine deposits¹⁴, and was much less common or less abundant in terrestrial deposits. More work is needed to verify this contention.

CONCLUSIONS

The DS asphalts fall into two broad classes: those which contain asphaltenes with a relatively high $\text{VO}^{2+}\text{-P}$ content and those with the asphalts containing no $\text{VO}^{2+}\text{-P}$. It is reasoned that these asphalts belong to two distinct groups and have separate origins. On the other hand, two genetic types of the kerogens separated from SBR are identified: a marine type with a high abundance of $\text{VO}^{2+}\text{-P}$ and terrestrial type containing no $\text{VO}^{2+}\text{-P}$. In general, to a remarkable degree, the abundance of $\text{VO}^{2+}\text{-P}$ of the kerogen seems to typify ancient bituminous rocks of marine origin.

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