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 presence of vanadyl porphyrins. These examinaitons demonstrated that the asphalts fall into two broad class types, one having a relatively high vanadyl prophyrins content (>300 ppm) and the other characterized by no vanadyl porphyrins (<10 ppm). It is concluded that these asphalts belong to two genetic 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 studies[1] indicated that La Luna kerogen is derived from marine organic matter source. These materials have higher concentrations of vanadyl porphyrins than the Dead Sea asphaltenes and the 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.

Key words: asphalt, vanadyl porphyrins, kerogen, petroleum.

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 the 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 in the basin, namely marine, terrestrial and mixed marine and terrestrial organic matter. They concluded that the

organic matter in the SBR at most sites is primarily derived from marine algae, while material derived from land-plants dominates in the SBR at a few locations.

Rullkötter *et al.,*[10] in a study of biological markers, provided evidence that the DS asphalts, conventional petroleums and asphaltic crudes originated from a single type of source-SBR. According to these authors, the asphaltic crudes are altered products derived from conventional-type crudes by secondary processes (water-washing, incipient degradation or physical loss of volatile components). Using steroid aromatisation[10] and the vanadyl porphyrins (VO^{2+}-P) distribution[11] as the crucial maturity parameters under the geological conditions given in the DS Basin, these researchers concluded that the asphalts have to be classified as immature, whereas the conventional and asphaltic crude oils are mature generation products. In addition, biomarker geochemistry indicates that substantial generation of conventional (mature) petroleums occurs in deeply (8,000 to 10,000 m) buried SBR, whereas the DS asphalts either originated from very immature and shallow SBR or represent early *in situ* generation.[10] However, an important question still remains, whether all the asphalts accumulated in the basin are essentially of the same genetic type and were derived from the same group of source rocks or if other groups of source rocks exist which contributed significantly to the asphalt generation in the basin.

One of the best ways to identify the source-rock of reservoired petroleum and asphalt is to find geochemical (mainly compositional) similarities between the kerogen of the source-rock and the asphaltenes of the corresponding petroleum.[12] High VO^{2+}-P petroleums, 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 VO^{2+}-P. A high VO^{2+}-P content of asphaltenes is a distinctive and readily detectable characteristics of many petroleums, asphalts and bituminous rocks.[13] Although long recognized in these materials, VO^{2+}-P have not been as widely used as other geochemical fingerprints for genetic and correlation studies. In fact, the VO^{2+}-P incorporated into the asphaltenes of both petroleums 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 generation.[14] Thus, VO^{2+}-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 VO^{2+}-P.

EXPERIMENTAL

Sample

The samples analyzed in this work are listed in Table Ia and their geographical locations shown in Fig. 1. The present study focuses on: the DS floating asphalts, the Heimar asphalt (sandstone

TABLE I. Geochemical data of the DS bituminous sediments

(a) Asphaletenes and kerogens [wt %] of organic fractions

Organic fractions	Depth [m]	Asphaltenes	Kerogen
DS (floating asphalt) A	surface	67[***]	–
DS (floating asphalt) B	surface	48	
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	14.0[a]	4
Massada (petroleum)	2100	2[**b]	–

[*]Organic fraction/petroleum containing no VO^{2+}-P (<10 ppm)
[**]Organic fraction/petroleum containing VO^{2+}-P (>100 ppm)
[***]Organic fraction/asphalt containing VO^{2+}-P (>300 ppm)
[a]Aizenshtat et al.[4]
[b]Aizenshtat and Sundararaman[11]

(b) Inorganic and organic fractions [wt %]

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

(c) The normalized VO^{2+}-P contents[*]

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

[*]The VO^{2+}-P content determined by ESR and normalized to the VO^{2+}-P content of the floating asphalt A (ca. 1000 ppm)

(d) The V and Ni contents [ppm][*] and the Ni/V ratio

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

[*]The vanadium content determined by both emission spectrometry and AAS

cemented with asphalt) and the IPRG asphalt. The samples of floating asphalt were taking from large floating blocks that appeared in the northern (A) and the southern (B) parts of the lake. According to Spiro et al.,[7] the organic matter of the Nebi Mussa rock is typical of marine origin. Organic matter of
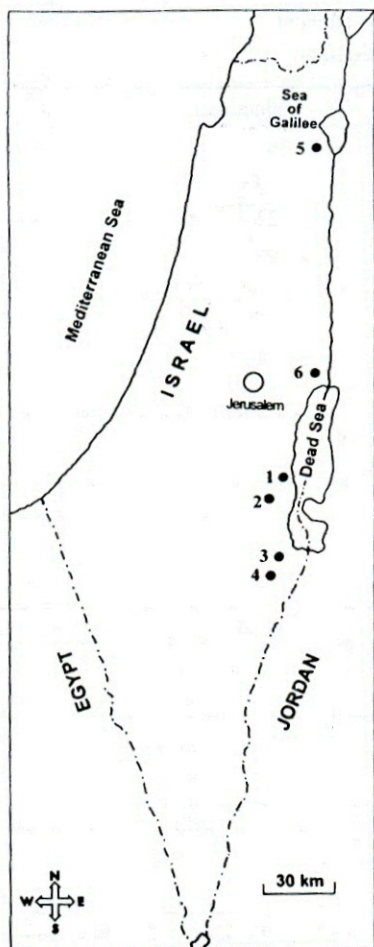
Fig. 1. Geological map indicating the DS sample locations: (1) Massada; (2) Gurim; (3) Heimar; (4) IPRG; (5) Ef'e; and, (6) Nebi Mussa.

the Ef'e rock is a typical example of land-plant derived material. For these reasons, we selected the kerogens isolated from these two rocks. The SBR samples were taken from surface exposures, but the asphalt samples were taken from shallow prospecting and are from depths of less than 75 m below the surface (Table Ia). 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 chosen geological samples sets are only representative of each broad class (terrestrial *vs.* marine) and it is acknowledged that many other asphalt/petroleum samples of each class could have been included. However, such addition would not have added to the general principles of the behavior of the VO^{2+}-P concentration in each class.

One of the purposes of the present paper is to report on the extension of the foregoing study of the asphaltenes of typical Maracaibo asphaltic crude oilsand kerogens isolated from La Luna source rocks (Table IIa). The locations of the geological samples included in the present report are shown in Fig. 2. Two oil samples (DM-119, 120) were obtained from two different West Mara oil fields. Four La Luna rock samples (QM-8, 10, 12, 14) (Table IIa) were obtained from the St. Rosa location and two from the Maraca site.

TABLE II. Geochemical data of the asphaltic crude oils and source rock from Western Venezuela
(a) 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	–

(b) The normalized VO^{2+}-P contents[*]

	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	–	–

[*]The VO^{2+}-P content determined by ESR and normalized to the VO^{2+}-P content of QM-10(*ca.* 10,400 ± 1000 ppm)

(c) The V and Ni contents [ppm][*] 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

[*]The vanadium content determiened by both emission spectrometry and AAS.

Extraction and separation

The DS asphalt was dissolved by refluxing (Soxhlet) for 48 h in benzene: methanol (6:1 v/v), centrifuged (2 h) and the supernatant filtered (5 μm 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 electrion spin resorance (ESR) spectroscopy to determine their VO^{2+}-P content (mainly in the asphaltene fraction) (Table Ia).

The powdered bituminous rocks were treated with a boiling HCl (6M) 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 N_2 and weighed. Kerogen was separated from the acid-resistant mineral grains in the final residue by the chloroform sink-float technique.[18]

The petroleum was agitated with a twenty-fold excess of *n*-hexane at room temperature for 8 h, and then left for 24 h. The precipitated asphaltenes were filtered, washed with *n*-hexane to remove adsorbed compounds, dried with N_2, weighed and analyzed for their VO^{2+}-P content by ESR spectroscopy.
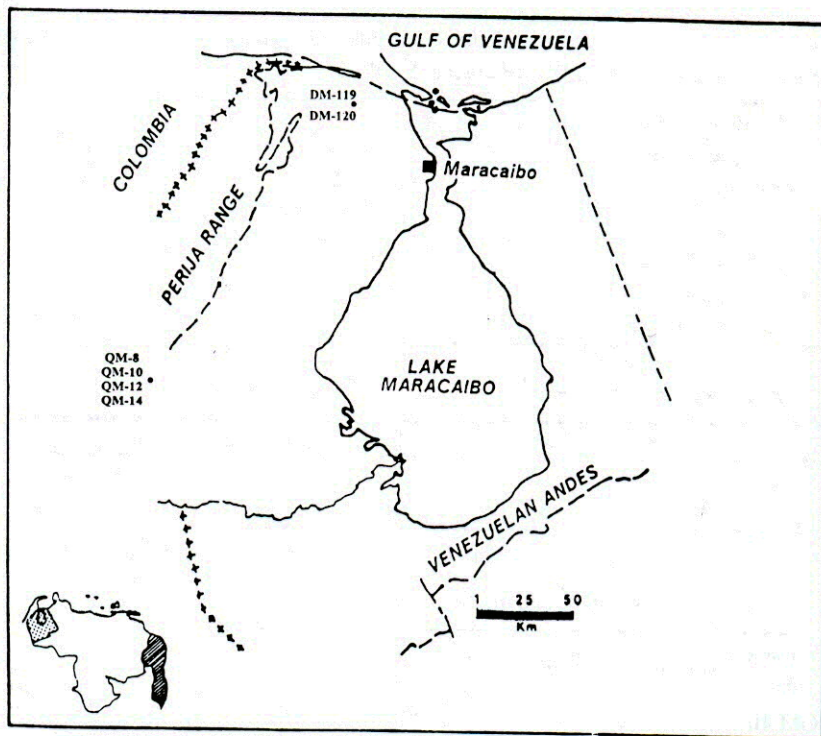
Fig. 2. Geological map indicating the Maracaibo sample locations: Crude oils (West Mara field) and La Luna rocks (Maraca).

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 with temperature increments of 100 °C. An identical procedure was employed for the air atmosphere heating experiments except that the quartz tubes were not sealed.

Elecron spin resonance

ESR measurements were performed on the unheated/heated powdered samples in a quartz tube (4 mm o.d., 3 mm i.d.). The spectra were recorded on a Bruker ER 200D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz interfaced to a PACOM computer. The signal intensities (proportional to the VO^{2+}-P concentration) were calculated by double integration of the first derivative V hyperfine ($m = -5/2$) line using the PACOM system. The calculations of the VO^{2+}-P distribution in the asphaltene/kerogen were based on 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 monochromator.[19]

Atomic Absorption Spectrometry (AAS)

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 dispersed.[7] The composition of the SBR samples, as determined by the described fractionation procedure, are given in Table Ib. The major constituent is carbonate with lesser amounts of silicates; the total organic fraction constitutes $18 - 21$ % of the rock.

A representative ESR spectrum of the VO^{2+}-P of the asphaltene extracted from the SBR at the Nebi Musa locality is shown in Fig. 3a. Similar spectra were recorded for the asphaltenes extracted from the DS asphalts enriched with VO^{2+}-P. The ESR determined distribution of the VO^{2+}-P among the asphaltenes of the asphalts and the Nebi Mussa kerogen are given in Table Ic. The VO^{2+}-P concentration of this kerogen is comparable with that found in the asphaltenes of the DS floating asphalt A (Table Ic). In contrast to the asphaltenes of asphalt A, ESR analysis of the asphaltenes extracted from asphalt B shows no evidence for VO^{2+}-P above the detection limit of 10 ppm. The Ef'e kerogen also showed no evidence of VO^{2+}-P above the detection limit.

Thermal stability of the vanadyl porphyrins

The striking absence of VO^{2+}-P in the asphaltenes of asphalt B could be simply attributed to thermal decomposition of the VO^{2+}-P under geological conditions through natural heating. Very recently in our laboratory, a series of heating experiments in the absence of air, combined with ESR measurements have been carried out on the asphaltenes (abundant in VO^{2+}-P) isolated from the DS asphalts.[15-17] The results of these studies demonstrated the exceptional high thermal stability of the VO^{2+}-P of these materials, indicating that drastic temperature (>400 °C) are required for the destruction of their VO^{2+}-P. These temperatures are significantly higher than those (about $50 - 200$ °C) normally experienced even in deeply buried source rocks. Furthermore, geological evidence suggests that the 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-non-porphyrins

The essential conditions for the preservation of VO^{2+}-P is a reducing environment at the place of deposition. Thus, the VO^{2+}-P-bearing asphalts and the source-kerogens in such an environment tend to maintain a high level of VO^{2+}-P but, because of their instability, these compounds in the shallow buried or outcrop rocks may become absent after exposure to oxidizing conditions of weathering. Consequently, an alternative explanation could be that the absence of VO^{2+}-P in the floating asphalt B is a result of VO^{2+}-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 the VO^{2+} compound(s) in this heated sample is given in Fig. 3b. This spectrum
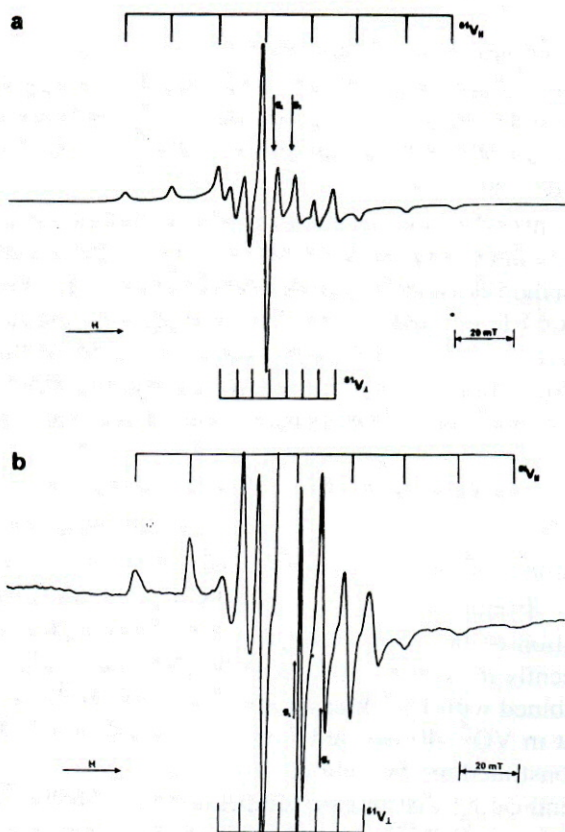
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Fig. 3. First derivative room temperature X-band anisotropic ESR spectra of (a) VO^{2+}-P of the Nebi Mussa asphaltene and (b) VO^{2+}-non-P of DS asphaltene after heating for 6 days at 250 °C in the presence of air.

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, the VO^{2+} ions within the structure of this coal are, probably, complexed with oxygenated functional groups of the coal, such as carboxylic/phenolic groups. For this reason, we suggest that their VO^{2+} compounds in air-heated DS materials (Fig. 3b) are of a non-porphyrin type (VO^{2+}-non-P). As no experimental evidence was found for VO^{2+}-non-P in the asphaltenes of either asphalt B or Ef'e kerogen, it seems reasonable to conclude that weathering was not responsible for the absence of VO^{2+}-P in these materials.

One of the major processes that can effect petroleums or asphalts in reservoirs, especially shallow reservoirs, is biodegradation. One may argue that biodegradation may be a major factor in the destruction of VO^{2+}-P in the floating asphalt B. Available data, however, indicate that biodegradation has little effect on VO^{2+}-P.[21-25] In addition, our experience shows that biodegraded oils from the Maracaibo Basin

(Venezuela) contain a much higher VO^{2+}-P content than non-biodegraded petroleums of similar source facies and maturity.[26]

Classification of the source-rocks kerogens and the asphalts

A high VO^{2+}-P content of petroleums and asphalts appears to be an original characteristics related to the genetic environment or to the kind of kerogen from which the asphalt was derived. An abundance of VO^{2+}-P in petroleum asphaltenes seems to characterize, to a remarkable degree, both asphaltenes and kerogen of marine source rocks. This is to be expected since marine source rocks had an abundant input of the porphyrin-precursor chlorophyls, derived from algae and/or bacteria, to the organic matter where rich source rocks were developed, and physicochemical conditions favored both VO^{2+} and its incorporation into porphyrins. For example, Kontorovich and Borisova[27] studied, very recently, the average composition of 45 asphaltene samples of Jurassic sedimentary rocks from Western Siberia (Russia) having either a terrestrial or marine origin. They demonstrated that the asphaltenes of marine origin are characterized by an enriched presence of VO^{2+}-P.

It appears reasonable to suggest that the high VO^{2+}-P content of Nebi Mussa kerogen may reflect a 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 VO^{2+}-P. This is as expected, as discussed previously, and may be a consequence of the relatively low chlorophyll-porphyrins contribution to terrestrial kerogen and an insufficient preservation of any algal and/or bacterial derived chlorophyll-porphyrins under the more oxidizing conditions experienced by terrestrial bio-organic matter.

The asphaltenes of the floating asphalt A, Heimar and IPRG asphalts are characterized by high VO^{2+}-P contents (>300 ppm). Hence, it appears reasonable to suggest that these high VO^{2+}-P asphalts originated from a marine kerogen source rich in VO^{2+}-P. On the other hand, the absence of VO^{2+}-P in the floating asphalt B indicates that this material originated from kerogen containing no VO^{2+}-P. The present work cannot identify the source of this asphalt. Thus, the DS asphalts are the products of two distinctly different SBR kerogens that, in turn, give rise to two distinctly different types of asphalts in terms of the presence and absence of VO^{2+}-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 petroleums, 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 Barwise[28] has shown that for some petroleum classes, the absolute concentration of V and Ni and the Ni/V ratio are both useful petroleum classification parameters. According to the author, petroleums derived from marine source rocks are characterized by high absolute concentrations of V and Ni and have a Ni/V ratio of 1 or less. On the

other hand, petroleums originating from terrestrial environments are characterized by a low metal content (<50 ppm) and a higher Ni/V ratio (>2), compared to petroleums generated from marine source rocks. They are potentially very useful parameters for the determination of the origin of the organic matter present in petroleum, asphalts and source rocks and for oil/source correlations. It is for this reason that additional attention was directed to these metals in the asphaltenes and kerogens studied.

The trace metal data in Table Id for the asphaltenes of the DS asphalts show a clear-cut division of the DS asphalts, in harmony with the above classification scheme proposed by Barwise.[28] Namely, the absolute concentrations of the metals dropped from a high value (>900 ppm) for the apshaltenes of apshalt A to a very low value for the asphaltenes of asphalt B (2 ppm). In addition, the asphaltenes of asphalt A exhibited a low Ni/V ratio (0.4). Considerable support is therefore given to the foregoing classification of the DS asphalts based on their VO^{2+}-P content.

In contrast to the asphalts, the difference in the metal contents (Table Id) 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 petroleums

The asphaltenes of the Gurim asphaltic crude oil are characterized by the absence of VO^{2+}-P and it seems reasonable to conclude that this petroleum is likely to be derived from a source-SBR kerogen with no VO^{2+}-P. In contrast to the Gurim asphaltenes, the asphaltenes isolated from the Massada petroleum have a relatively high content of VO^{2+}-P (>100 ppm) which indicates that it originates from a marine source kerogen. An apparent explanation could be the late catagenetic generation of the Massada petroleum from deeply buried SBR with kerogen abundant in VO^{2+}-P. Based on organic geochemical and sedimentological characteristics, it is proposed that the DS petroleums are likely to be of similar organic matter source. If this is true then the drastic differences in the VO^{2+}-P content between the conventional Massada and the Gurim asphaltic crude oils (Table Ia) could be due to the mixing (in-migration) of the conventional petroleum with the SBR bitumen enriched with VO^{2+}-P. Namely, as the conventional petroleum travels gradually updip, it may dissolve a portion of the bitumens (enhanced with VO^{2+}-P) which are indigenous to the SBR strata through which it passes. Since only the same members of the same formation are involved, these conventional petroleums would all be very similar except in the VO^{2+}-P content. It is conceivable, of course, that some small fraction of VO^{2+}-P is entirely obscured by the predominating non-indigenous VO^{2+}-P. A similar interpretation was presented by Premović[26] for "non-indigenous" VO^{2+}-P associated with petroleums of Western Venezuela. The Massada crude oil, however, exhibits a marked difference in the VO^{2+}-P distribution compared to the DS asphaltic bitumens,[11] suggesting that the VO^{2+}-P in this petroleum are indigenous.

Asphaltic crude oils in the Maracaibo Basin

A geochemical study of the crude oils from different reservoirs identified three genetic types of crude oil in the Maracaibo Basin: a marine type essentially derived

from the marine La Luna source, a terrestrial type, and a third type derived from the mixing of the first two types.[1] According to this study the marine (asphaltic) oils of low to moderate API gravity (<30–40 API) are characterized by a high V content (>900 ppm). On the other hand the terrestrial oils are characterized by a low V content (4 ppm). Very recently, López et al.[29] detected traces of V and Ni in different fractions of some asphaltic petroleums from the Maracaibo Basin. These authors showed that the metal ratio may be used as a genetic indicator in any of the petroleum fractions including the asphaltenes. According to these authors, the asphaltic petroleums originated from the same source rock, the La Luna bituminous limestone.

The VO^{2+}-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 IIb). These asphaltenes are also characterized by relatively large amounts of V (>3500 ppm) and Ni (>300 ppm) (Table IIc). The ratio between the concentration of Ni and the concentration of V in the asphaltenes appears to remain within a fairly narrow range and is less than 0.1 (Table IIc). Two apparent conclusions can be advanced from these results. Firstly, the petroleums from the West Mara fields have a common origin. This is in excellent agreement with established concept of the unification of these oil fields into a single one.[30] Secondly, within the Barwise classification scheme, these asphaltic petroleums are apparently derived from a marine organic matter source, lending suport to a similar conclusion reached by Talukdar et al.[1] Finally, the VO^{2+}-P content, the V and Ni contents, as well as the Ni/V ratio of the kerogen separated from the La Luna source rock are very similar to that of the Maracaibo asphaltic petroleums (Tables IIb and IIc). The apparent conclusion is that the kerogen of the marine La Luna rock is the principal source for the asphaltic oils in the basin, as proposed by Talukdar et al.[1]

Final remarks

From our continuing detailed study of VO^{2+}-P of the kerogens of ancient carbonaceous sedimentary rocks throughout the world (PIP over 25 years) we conclude that: 1) only kerogens derived from marine organic matter have a high (>100 ppm) VO^{2+}-P content. The best illustrative example of this type of kerogen is that isolated from the famous Serpiano marl (Switzerland) on which Treibs[31] based much of his earlier work, and 2) kerogens originating from a terrestrial organic source are characterized by the absence, or almost complete absence (<10 ppm) of VO^{2+}-P. The most illustrative cases are the kerogens separated from the well-studied lacustrine Green River (USA) and Messel (Germany) shales.

In addition, a conclusion towards which the evidence appears to lead is that the high VO^{2+}-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 deposits,[14] and was much less common or less abundant in terrestrial deposits. More work is needed to verify this contention.

CONCLUSIONS

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

ИЗВОД

КЛАСИФИКАЦИЈА АСФАЛТА И ЊИХОВИХ ИЗВОРНИХ СТЕНА ИЗ БАСЕНА МРТВОГ МОРА (ИЗРАЕЛ): ВАНАДИЛ ПОРФИРИНИ АСФАЛТЕНА/КЕРОГЕНА

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Испитивано је присуство ванадил порфирина у асфалтенима изолованих из асфалта басена Мртвог мора. Истраживања су показала да асфалти припадају двема широким типским класама, једна која показује релативно висок садржај ванадил порфирина (>300 ppm) и друга која се карактерише одсуством ванадил порфирина (< 10 ppm). Закључено је да ови асфалти могу да се класификују у два генетска типа који имају различито генетско порекло. Керогени изоловани из изворних стена нафте из басена Мртвог мора такође су били испитивани. Изгледа да постоје два генетска типа керогена: морски са високим садржајем ових пигмената и копнени који се одликује одсуством ванадил порфирина. За упоређење, асфалтени типичних асфалтних нафти из западне Венецуеле и кероген издвојен из њихових изворних стена Ла Луна формације су такође испитивани. Претходне детаљне геохемијске студије[1] показују да је овај кероген изведен од морске органске материје. Ови материјали имају више концентрације ванадил порфирина него асфалтени и керогени Мртвог мора који су обогаћени овим једињењима. Ови резултати указују на потенцијал коришћења ванадил порфирина у нафтним асфалтенима и изворним керогенима за генетска и корелациона проучавања.

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