

## Laboratory pyrolysis of asphaltene/kerogen vanadyl porphyrins

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The thermal stability of vanadyl ( $\text{VO}^{2+}$ ) porphyrins (P) incorporated into the asphaltene/kerogen structures of the Dead Sea (DS) asphalt "float", the La Luna Mara (LLM) limestone and the Serpiano (Se) marl was studied by electron spin resonance (ESR). Comparative studies were also made of synthetic alkyl  $\text{VO}^{2+}$ -P: (C<sub>32</sub>) deoxophylloerythroetioporphyrin (DPEP). According to these studies, alkyl  $\text{VO}^{2+}$ -P predominate by far within the asphaltene/kerogen framework. These P are stable up to 400 °C during laboratory heating and at this temperature their content sharply decreases. At 500 °C and 600 °C, the asphaltene/kerogen  $\text{VO}^{2+}$ -P content follows a similar pattern to that at 400 °C, except that at 600 °C it was reduced to a non-detectable point in less than 12 h. In addition, it is implied that a high proportion (ca. 60% of original asphaltene/kerogen alkyl  $\text{VO}^{2+}$ -P) is transformed during this pyrolysis into relatively stable (at temperature  $\geq 400$  °C) multiaryl  $\text{VO}^{2+}$ -P incorporated into the asphaltene/kerogen matrix.

*Key words:* Asphaltene, kerogen, vanadyl porphyrins, thermal stability

The discovery of  $\text{VO}^{2+}$ -P in petroleum, shales, coals and bitumens by Treibs<sup>1</sup> is marked as the beginning of modern organic geochemistry. Treibs<sup>2</sup> showed that the major components were alkyl P,  $\text{VO}^{2+}$ -DPEP and -ETIO as shown in Figs. 1a and b, respectively. These compounds are mainly derived from chlorophylls and bacteriochlorophylls.<sup>3</sup> The  $\text{VO}^{2+}$ -P in ancient shales can be arbitrarily divided according to their physicochemical properties into the following two groups: extractable alkyl  $\text{VO}^{2+}$ -P with (a) relatively low molecular weight and (b) relatively high molecular weight.<sup>3</sup>

Premović *et al.*<sup>4</sup> determined the distribution of vanadium (V) and  $\text{VO}^{2+}$ -P in various fractions of LLM and Se marl by employing a variety of geochemical and spectroscopic techniques and the existence of  $\text{VO}^{2+}$ -P in kerogen fractions was shown using ESR spectrometry. It has been suggested that they are incorporated into the kerogen structures through aliphatic bonds.<sup>5</sup> Bitumen fractions of these rocks are also characterized by a high concentration of  $\text{VO}^{2+}$ -P (mostly the DPEP type).<sup>4</sup>

The asphalts in the DS Basin occur in different forms. The most dramatic occurrence is that of huge floating blocks of asphalt on the surface of the lake. Aizenshtat *et al.*<sup>6</sup> analyzed metallo- and free base P (1000-1500 ppm) isolated from this material by ultraviolet (UV)-visible (VIS) spectrophotometry and mass spectrometry. According to these authors the major metal P ( $\geq 95\%$ ) are  $\text{VO}^{2+}$ -P and mostly of the DPEP type.

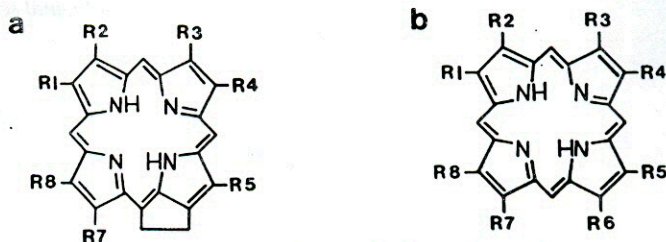


Fig. 1. Generalized structures of (a) DPEP and (b) ETIO porphyrins ( $R_{1-8} = \text{H}$  or alkyl substituents).

In this report the thermal stability of  $\text{VO}^{2+}$ -P incorporated into the organic structures of DS asphalt, LLM and Se rocks has been investigated with the object of gaining further insight into the organic geochemistry of  $\text{VO}^{2+}$ -P during kerogen forming/cracking processes. For this reason, we have conducted laboratory heating experiments to follow the fate of  $\text{VO}^{2+}$ -P using ESR. A series of heating experiments was carried out on the asphaltene fractions of DS asphalt, LLM and Se rocks as well as LLM and Se kerogens. Comparative studies were also conducted with synthetic  $\text{VO}^{2+}$ -DPEP.

#### EXPERIMENTAL

**Samples.** The sample of DS asphalt was taken from a large floating block which appeared in the northern part of the lake. The sample has a high purity ( $\geq 99.9\%$  organic matter) with an atomic hydrogen (H)/carbon (C) ratio of 1.3.

LLM limestone and Se marl have approximately 11% and 36% organic matter by weight, respectively. A remarkable characteristic of these shaly rocks is the high  $\text{VO}^{2+}$ -P content, mostly of the DPEP-type.<sup>4</sup>

Supplementary information for the DS asphalt<sup>7</sup> and the LLM and Se rocks<sup>4,8</sup> can be found in the corresponding literature.

$\text{VO}^{2+}$ -DPEP is synthesized by the method of preparation described by Baker *et al.*<sup>9</sup>

**Separation and extraction.** The DS asphalt "float" was separated into two components: methanol soluble (polar fraction) + methanol insoluble, *n*-pentane soluble (resin) and *n*-pentane insoluble (asphaltene), Table I. The sample was refluxed (Soxhlet) for 48 h in benzene : methanol (6:1 v/v), whereupon it dissolved completely. The solution was then centrifuged (2 h) and the supernatant filtered ( $5 \mu\text{m}$  pore filter). After solvent evaporation, the asphalt (10 g) was dissolved in 20 mL of benzene and the solution was poured into a 250 mL polyethylene bottle; 200 mL *n*-pentane was added and the bottle shaken for 4 h at room temperature to precipitate the asphaltene. The solution was centrifuged and the asphaltene was washed several times with the *n*-pentane/benzene mixture (20:1 v/v) until the wash solution was clear. The asphaltene was then dried at 45 °C to remove the solvent. The precipitation was repeated and the resulting precipitate combined with the bulk of the asphaltene. The (polar + resin) fractions were recovered by evaporation of the *n*-pentane/benzene solution. The (polar + resin) and asphaltene fractions were weighted and their proportions determined. All fractions were examined by ESR to determine their  $\text{VO}^{2+}$ -P content (mainly in the asphaltene fraction), Table I.

Bituminous rocks were crushed and extracted with benzene : methanol (6:1 v/v). Removal of the carbonates and silicates was carried out by HCl/HF, and the pyrite was removed by  $\text{LiAlH}_4$ .<sup>10</sup> The residue was extracted again with benzene : methanol (6:1 v/v) and the isolated kerogen examined by X-ray diffraction.

The fractionation procedure for the sediment bitumens was similar to that used for DS asphalt. The  $\text{VO}^{2+}$ -P distribution in three organic components (polar fraction + resin, asphaltene and kerogen) was determined by ESR and UV-VIS (except kerogen) analyses.

**Electron spin resonance (ESR).** ESR measurements were performed on unheated and heated samples in an ESR quartz tube (4 mm o.d.). Spectra were run on a Bruker ER 200 D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz interfaced to an ASPECT 2000 computer. Signal intensities (proportional to the  $\text{VO}^{2+}$ -P concentration) were calculated by double integration of the first

derivative V hyperfine ( $m = -3/2$ ) line using the ASPECT system. Calculations of the  $VO^{2+}$ -P distribution in various fractions were based upon comparisons with the total organic extract.

TABLE I. Compositions of organic fractions [%] and the  $VO^{2+}$ -P distribution [%] in various organic fractions of LLM and Se sediments and DS asphalts.

	Whole organic fraction (%)	Bitumen		Kerogen
		Resin + methanol soluble (%)	Asphaltene (%)	(%)
LLM				
Organic matter	100	35	14	51
$VO^{2+}$ -P	100	11	27	62
Se				
Organic matter	100	11	3	86
$VO^{2+}$ -P	100	1	5	94
DS				
Organic matter	100	39	61	-
$VO^{2+}$ -P	100	18	82	-

*Heating experiment.* Samples (100 mg) were sealed under vacuum in quartz tubes (4 mm o.d. and 3 mm i.d.) after flushing with nitrogen. Each tube was heated (electric furnace) at a single temperature between room temperature to 600 °C for a specified time in the range of 1 to 20 days and with a specified temperature increment in the range of 100 °C.

## RESULTS AND DISCUSSION

### *Pyrolysis of the asphaltene/kerogen $VO^{2+}$ -P*

Table I contains the distribution of  $VO^{2+}$ -P among organic components separated from DS asphalt, and LLM and Se sediments: (polar fraction + resin), asphaltene and kerogen (LLM and Se). Results show that the asphaltenes from the asphalt contain the highest concentration of  $VO^{2+}$ -P, though the kerogen fraction of the sediments accounts for the major part of  $VO^{2+}$ -P. The kerogen  $VO^{2+}$ -P are, in

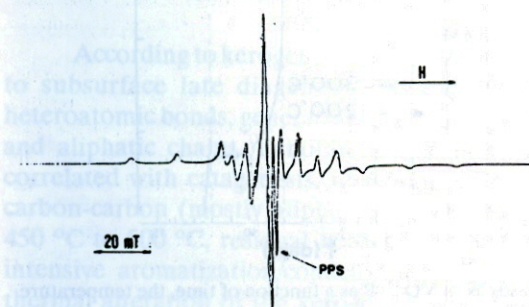


Fig. 2. First derivative room temperature, X-band ESR spectrum of the kerogen  $VO^{2+}$ -P. H is the magnetic field.

fact, the most characteristic property of these rocks.<sup>4</sup> Figure 2 is a typical ESR spectrum of  $\text{VO}^{2+}$ -P incorporated into the kerogen matrix of Se marl. LLM kerogen and DS asphaltene spectra (not shown) were basically identical.

Shown in Fig. 3a is the change in relative ESR signal intensity ( $N$ , normalized to the signal intensity of the unheated DS asphaltene sample) of DS asphaltene  $\text{VO}^{2+}$ -P as a function of pyrolysis temperature and time. As this intensity is directly proportional to the  $\text{VO}^{2+}$ -P concentration, it can be deduced that the  $\text{VO}^{2+}$ -P content changes dramatically over the temperature range studied. Up to about 300 °C, no change (within experimental error) occurs but at about 400 °C this content decreases sharply and then remains relatively constant with further increases in time. At 500 °C and 600 °C, the  $\text{VO}^{2+}$ -P content change per temperature or time unit was similar to that at 400 °C, except that at 600 °C it was reduced in less than 12 h to a non-detectable

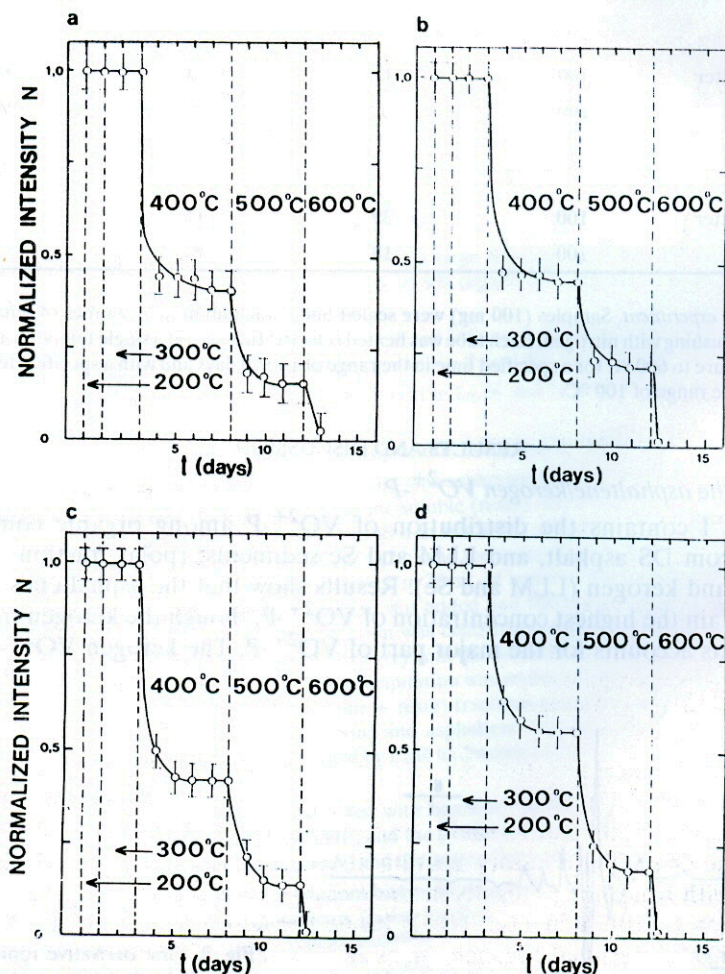


Fig. 3. Decrease in normalized ESR signal intensity  $N$  of  $\text{VO}^{2+}$ -P as a function of time, the temperature changes being (increment: 100 °C) from 100 °C to 600 °C during laboratory pyrolysis: (a) DS asphaltene and (b) asphalt; and (c) LLM and (d) Se asphaltenes.

point. The limit of ESR detection was about 20 ppm for  $\text{VO}^{2+}\text{-P}$ . The temperature effects on  $\text{VO}^{2+}\text{-P}$  of DS asphalt are shown in Fig. 3b. As might be expected, the thermal changes in the DS asphaltene (Fig. 3a)  $\text{VO}^{2+}\text{-P}$  (99% of total  $\text{VO}^{2+}\text{-P}$ , Table I) are similar to that of the asphalt (Fig. 3b). We also found that  $\text{VO}^{2+}\text{-P}$  kinetic patterns for LLM (Fig. 3c) and Se (Fig. 3d) asphaltenes resemble (within experimental error) those for DS asphaltene (Fig. 3a) and asphalt (Fig. 3b).

The most appealing characteristics of the LLM and Se kerogen samples are their high  $\text{VO}^{2+}\text{-P}$  content (up to 4700 ppm).<sup>4</sup> The pyrolytic behavior of LLM and Se kerogen  $\text{VO}^{2+}\text{-P}$  (Fig. 4) is qualitatively similar to that of DS (Fig. 3a), LLM (Fig. 3c) and Se (Fig. 3d) asphaltene  $\text{VO}^{2+}\text{-P}$ , although they differ quantitatively. No difference (within experimental error) was observed between the two kerogens throughout the entire temperature region (Fig. 4).

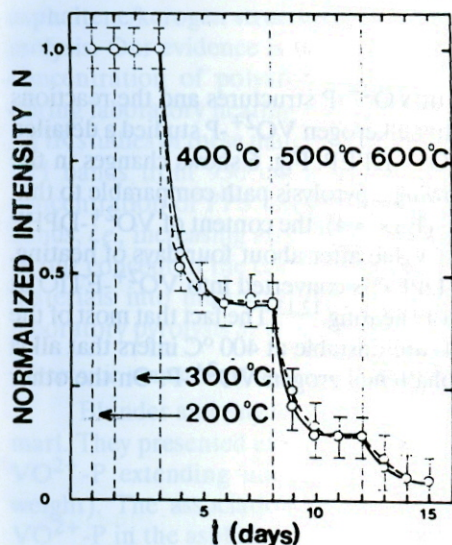


Fig. 4. Decrease in normalized ESR signal intensity  $N$  of  $\text{VO}^{2+}\text{-P}$  as a function of time, the temperature changes being (increment: 100 °C) from 100 °C to 600 °C during laboratory pyrolysis: the LLM (—) and Se (-----) kerogens.

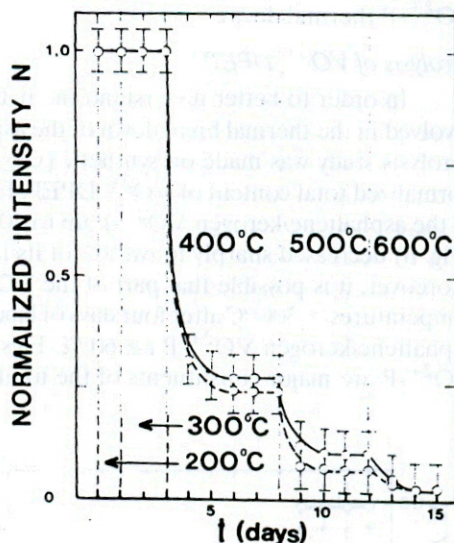


Fig. 5. Decrease in normalized ESR signal intensity  $N$  of the kerogen  $\text{VO}^{2+}\text{-P}$  as a function of time, the temperature changes being (increment: 100 °C) from 100 °C to 600 °C during laboratory pyrolysis: carbonate free-samples of LLM limestone (—) and Se marl (-----).

According to kerogen studies,<sup>11</sup> laboratory heating to *ca.* 350 °C, which conforms to subsurface late diagenesis in sedimentary basins, results in the rupture of heteroatomic bonds, generating small structural units containing one to several nuclei and aliphatic chains. Laboratory heating at *ca.* 350 °C to 500 °C, which may be correlated with catagenesis, results in the cleavage of various bond types including carbon-carbon (mostly aliphatic) bonds inside the kerogen framework. Beyond *ca.* 450 °C to 500 °C, residual kerogen encounters its major structural rearrangement: intensive aromatization/condensation. Thus, we may conclude that with artificial thermal alteration of the kerogens between *ca.* 400 °C to 500 °C, the  $\text{VO}^{2+}\text{-P}$  con-

centration decrease is associated with bond cleavages within kerogen and its aromatization and, hence, the elimination of functional groups.

It might be argued that the reactions within isolated kerogen and sediment differ because of variations in their contents of inorganic matter, and that pyrolytic degradation of  $\text{VO}^{2+}$ -P in isolated kerogen cannot be used to corroborate this degradation for both sediments and isolated kerogens. It is likely that catalytic activity of clay minerals, their abundance, or otherwise, could be important in controlling the thermal decomposition of the kerogen  $\text{VO}^{2+}$ -P under laboratory as well natural conditions. For these reasons we have pyrolysed kerogens in carbonate-free sediment samples employing similar heating/time procedures as that for its isolated kerogens. However, we found that the  $\text{VO}^{2+}$ -P kinetic patterns for the carbonate-free samples (Fig. 5) are similar (within experimental error) to those for isolated kerogens (Fig. 4). This result suggests that clay mineral components of the rocks studied have little/no effect on kerogen  $\text{VO}^{2+}$ -P thermal decay.

#### Pyrolysis of $\text{VO}^{2+}$ -DPEP

In order to better understand the nature of  $\text{VO}^{2+}$ -P structures and the reactions involved in the thermal breakdown of the asphaltene/kerogen  $\text{VO}^{2+}$ -P studied a detailed pyrolysis study was made on synthetic ( $\text{C}_{32}$ ),  $\text{VO}^{2+}$ -DPEP. Fig. 6 shows changes in the normalized total content of  $\text{VO}^{2+}$ -DPEP. Following a pyrolysis path comparable to that of the asphaltene/kerogen  $\text{VO}^{2+}$ -P up to  $400^\circ\text{C}$  (Figs. 3/4), the content of  $\text{VO}^{2+}$ -DPEP (Fig. 6) decreased sharply to ca. 5% of its initial value after about four days of heating. Moreover, it is possible that part of the  $\text{VO}^{2+}$ -DPEP is converted into  $\text{VO}^{2+}$ -ETIO at temperatures  $\geq 300^\circ\text{C}$  after four days of laboratory heating.<sup>12,13</sup> The fact that most of the asphaltene/kerogen  $\text{VO}^{2+}$ -P ( $\geq 60\%$ , Figs. 3/4) are unstable at  $400^\circ\text{C}$  infers that alkyl  $\text{VO}^{2+}$ -P are major constituents of the total asphaltene/kerogen  $\text{VO}^{2+}$ -P. On the other

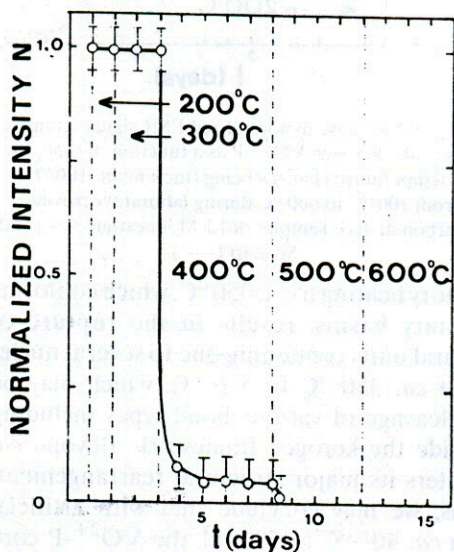


Fig. 6. Decrease in normalized ESR signal intensity of  $\text{VO}^{2+}$ -DPEP concentrate as a function of time, the temperature changes being (increment:  $100^\circ\text{C}$ ) from  $100^\circ\text{C}$  to  $600^\circ\text{C}$  during laboratory pyrolysis.

hand, we tentatively conclude that the asphaltene/kerogen  $\text{VO}^{2+}\text{-P}$ , which are thermally resistant at temperatures  $> 400^\circ\text{C}$ , are substituted by aromatic moieties or else they are fused to polyaromatic ring structures.

The high proportion of presumed multiaryl  $\text{VO}^{2+}\text{-P}$  may arise either through (1) natural aromatization/polyaromatization of the initial alkyl  $\text{VO}^{2+}\text{-P}$  during diagenetic/catagenetic processes or (2) artificial aromatization/polyaromatization during laboratory heating. Rho *et al.*<sup>14</sup> in their study of extractable  $\text{VO}^{2+}\text{-P}$  in the Nonesuch shale reported the predominance of high molecular weight aryl  $\text{VO}^{2+}\text{-P}$ . These authors concluded that in view of the high degree of thermodynamic stability of these  $\text{VO}^{2+}\text{-P}$ , the preferential survival of the multiaryl  $\text{VO}^{2+}\text{-P}$  through geologic time can be expected. In addition, Yen<sup>15</sup> pointed out the prevalence of  $\text{VO}^{2+}\text{-P}$  of higher aromaticity, including  $\text{VO}^{2+}\text{-P}$  in asphaltenes.

It is more likely that the conversion of alkyl  $\text{VO}^{2+}\text{-P}$  (incorporated into the asphaltene/kerogen structures) into multiaryl  $\text{VO}^{2+}\text{-P}$  occurs during laboratory thermolysis. Our evidence is based on the fact that we observed a sharp increase in the concentration of polyaromatic paramagnetic structures (PPS), detected by ESR, during laboratory heating at  $400^\circ\text{C}$  of the asphaltene/kerogen materials. Very recent FTIR studies of these materials heated at  $400^\circ\text{C}$  showed a definite increase in aromatic CH bands from  $930\text{ cm}^{-1}$  to  $700\text{ cm}^{-1}$ . Obviously, the observed increase in the concentration of PPS has probably the same origin as the increase in aromatic CH bands, *i.e.*, increasing aromatization/polyaromatization. These findings give credence to our concept of the conversion of the original alkyl  $\text{VO}^{2+}\text{-P}$  of asphaltene/kerogen materials into multiaryl  $\text{VO}^{2+}\text{-P}$  through aromatization/polyaromatization during laboratory pyrolysis at temperatures  $\leq 400^\circ\text{C}$ .

#### *Electronic structure of the asphaltene/kerogen $\text{VO}^{2+}\text{-P}$*

Blunder and Snyder<sup>16</sup> have studied the  $\text{VO}^{2+}\text{-P}$  of high molecular weight in Se marl. They presented evidence for the existence of a homologous series of asphaltene  $\text{VO}^{2+}\text{-P}$  extending into the high molecular weight region (*ca.* 20,000 molecular weight). The association of the typical alkyl  $\text{VO}^{2+}\text{-P}$  electronic spectra with the  $\text{VO}^{2+}\text{-P}$  in the asphaltenes studied, indicates that the  $\text{VO}^{2+}\text{-P}$  ring system preserves its basic electronic structure in such large molecular systems as asphaltenes. Moreover, ESR special parameters for the asphaltene/kerogen  $\text{VO}^{2+}\text{-P}$  are not different from those of alkyl  $\text{VO}^{2+}\text{-P}$ . This supports the above electronic identity concept but also suggests that the incorporation of alkyl  $\text{VO}^{2+}\text{-P}$  into the asphaltene/kerogen structures does not affect such fine detail of the electronic structure as the distribution of unpaired d-electron density of  $\text{VO}^{2+}$  in the  $\text{VO}^{2+}$  conjugated ring system. Blumer and Snyder<sup>16</sup> also pointed out that this 20,000 asphaltene  $\text{VO}^{2+}\text{-P}$  fraction represents only a minor part of the total asphaltene  $\text{VO}^{2+}\text{-P}$  and reasoned that  $\text{VO}^{2+}\text{-P}$  in the high molecular weight fraction of Se asphaltene is mainly associated with much larger polymer systems (*ca.* 30,000 to 50,000 molecular weight).

#### *Origin of asphaltene/kerogen and their $\text{VO}^{2+}\text{-P}$*

Our results infer that kerogens and asphaltenes contain similar compositional macromolecular structures and consequently these structures (such as those containing  $\text{VO}^{2+}\text{-P}$ ) should follow a similar evolution path during either natural or laboratory

heating. This kind of correspondence is expected if one assumes that there is a mutual interrelationship between asphaltenes and kerogens and that asphaltenes represent fragments of the kerogen structures.

In organic and petroleum geochemistry it is generally accepted that the formation of kerogen is the result of a series of consecutive/random repolymerization and polycondensation reactions of a very small fraction of the bio(degradation) products of extant biomaterials.<sup>11</sup> According to this concept, at an earlier stage of diagenesis, alkyl  $\text{VO}^{2+}$ -P units were already incorporated into the asphaltene/kerogen precursor structures by unknown mechanisms. An alternative concept for the formation of kerogen, or parts thereof, has been suggested.<sup>17</sup> Based on this concept, asphaltenes/kerogens can be envisaged as being chiefly composed of selectively preserved and/or partly modified, resistant biomacromolecules. Thus, according to the second view, asphaltene/kerogen  $\text{VO}^{2+}$ -P are associated with macromolecular structures which were highly resistant to (bio)chemical degradation.

#### CONCLUSIONS

From the data presented in this work the following conclusions can be reached:

1) The content of the asphaltene/kerogen  $\text{VO}^{2+}$ -P decreases rapidly during laboratory pyrolysis at temperatures  $\geq 400$  °C. These changes follow a stepwise kinetic pattern.

2) Most of the asphaltene/kerogen  $\text{VO}^{2+}$ -P are alkyl-type and they are incorporated into the asphaltene/kerogen structures. A part of these alkyl  $\text{VO}^{2+}$  are converted into more stable  $\text{VO}^{2+}$ -P during laboratory heating at temperature  $< 400$  °C.

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#### ИЗВОД

#### ЛАБОРАТОРИЈСКА ПИРОЛИЗА АСФАЛТЕНСКИХ/КЕРОГЕНСКИХ ВАНАДИЛ ПОРФИРИНА

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Електронспинском резонанцом (ESR) испитивана је термална стабилност ванадил ( $\text{VO}^{2+}$ ) порфирина (P) уграђених у асфалтенске/керогенске структуре "пливајућег" асфалта из Мртвог мора (DS), Ја Луна Мара (LLM) кречњака и Серпиано (Se) битуминозног лапорца. Упоредна проучавања су урађена на синтетичком алкил  $\text{VO}^{2+}$ -P (C32) деоксофилоеритроетиопорфирину (DPEP). Добивени резултати показују да су алкил  $\text{VO}^{2+}$ -P преобладајући у асфалтенским/керогенским структурама. У току лабораторијске пироллизе сви P су стабилни све до 400 °C, а онда на овој температури њихов садржај нагло опада. На 500 °C и 600 °C, садржај асфалтенских/керогенских  $\text{VO}^{2+}$ -P следи сличан кинетички пут оним на 400 °C, изузев што је на 600 °C њихов садржај смањен на недетективни ниво за мање од 12 h. Додатно, нађено је да је велики део (око 60% почетних асфалтенских/керогенских алкил  $\text{VO}^{2+}$ -P) претворено, у току пироллизе, у релативно стабилне (на температурама  $\geq 400$  °C) мултиарил  $\text{VO}^{2+}$ -P уграђене у асфалтенске/керогенске матриксе.

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## REFERENCES

1. A. Treibs, *Ann. Chem.* **509** (1934) 103
2. A. Treibs, *Angew. Chem.* **49** (1936) 682
3. E. W. Baker, J. W. Louda, in *Biological Markers in the Sedimentary Record*, R. B. Johns, Ed., Elsevier, 1986, p. 121
4. P. I. Premović, M. S. Pavlović, N. Z. Pavlović, *Geochim. Cosmochim. Acta* **50** (1986) 1923
5. A. S. Mackenzie, J. M. E. Quirke, J. R. Maxwell, in *Advances in Organic Geochemistry*, 1979, A. G. Douglas and J. R. Maxwell, Eds., Pergamon, 1980, p. 239
6. U. Aizenshtat, D. Dinur, A. Nissenbaum, *Chem. Geol.* **24** (1979) 161
7. A. Nissenbaum, *AAPG. Bull.* **62** (1978) 837
8. P. I. Premović, in *Geochemistry and Mineral Formation of the Earth Surface*, R. Rodriguez Clemente and Y. Tardy, Eds., C.S.I.C., Madrid, 1987, p. 431
9. E. L. Baker, A. H. Corwin, E. Klesper, P. E. Wei, *J. Org. Chem.* **33** (1968) 3144
10. D. L. Lawlor, J. I. Fester, W. E. Robinson, *Fuel* **42** (1963) 239
11. B. P. Tissot, D. H. Welte, *Petroleum Formation and Occurrence*, Springer-Verlag, 1984, p. 583
12. B. M. Didyk, Y. I. A. Alturki, T. Pillinger, G. Eglinton, *Nature* **256** (1975) 563
13. A. J. G. Barwise, I. Roberts, *Org. Geochem.* **6** (1984) 167
14. J. H. Rho, A. J. Bauman, H. B. Boettger, T. F. Yen, *Space Life Sci.* **4** (1973) 69
15. T. F. Yen, in *The Role of Trace Metals in Petroleum*, T. F. Yen, Ed., Ann Arbor Science, 1975, p.1
16. M. Blumer, W. D. Shyder, *Chem. Geol.* **2** (1967) 35
17. E. W. Tegelaar, J. W. de Leeuw, S. Derenne, C. Largeau, *Geochim. Cosmochim. Acta* **53** (1989) 3013.