

# Electron spin resonance study of the kerogen/asphaltene vanadyl porphyrins: air oxidation

P.I. Premović<sup>a,\*</sup>, I.R. Tonsa<sup>a</sup>, M.T. Pajović<sup>b</sup>, L. Lopez<sup>c</sup>, S.L. Monaco<sup>c</sup>,  
D.M. Đorđević<sup>a</sup>, M.S. Pavlović<sup>d</sup>

<sup>a</sup>Laboratory for Geochemistry and Cosmochemistry, Department of Chemistry, Faculty of Science, University of Niš, P.O. Box 91, 18 000 Niš, Yugoslavia

<sup>b</sup>The Institute for Geological Explorations of Montenegro, 81 000 Podgorica, Yugoslavia

<sup>c</sup>Instituto de Ciencias de la Tierra, Facultad de Ciencias, Universidad Central de Venezuela, Aptdo. 3895, Caracas, 1010-A Venezuela

<sup>d</sup>Institute of Nuclear Sciences Vinca, P.O. Box 522, 11001 Belgrade, Yugoslavia

Received 4 June 2000; revised 1 September 2000; accepted 7 September 2000

## Abstract

Thermal behavior of vanadyl porphyrins was studied by electron spin resonance during heating of the kerogens isolated from the La Luna (Venezuela), Maganik (Montenegro) and Serpiano (Switzerland) bituminous rocks at 150 and 250°C for 1 to 20 days in the presence of air. During the thermal treatment of the kerogens the vanadyl porphyrins' resonance signals decrease monotonically and become quite small after six days of heating. Concomitantly, new vanadyl signals appear, and, at longer heating times, dominate the spectrum. It is suggested that the secondary vanadyl species must have been formed from vanadyl porphyrins. Similar conversion of vanadyl porphyrins are observed under the same experimental conditions for the asphaltenes extracted from the La Luna and Serpiano rocks, and the floating asphalt from the Dead Sea (Israel). A comparison of the spin-Hamiltonian parameters for vanadyl porphyrins and vanadyl compounds obtained during pyrolysis of the kerogens/asphaltenes suggests that these are of non-porphyrin type. For comparison, a study was conducted on the Western Kentucky No. 9 coal enriched with vanadium (up to 800 ppm) from six mines. All coal samples show only the presence of predominant vanadyl-non-porphyrin compounds similar to those generated through laboratory heating of the kerogens/asphaltenes in air. In addition, some samples also contain a minor amount of vanadyl porphyrins. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Vanadyl porphyrins; Kerogen; Electron spin resonance

## 1. Introduction

The discovery of the electron spin resonance (ESR) signals of vanadyl porphyrins ( $\text{VO}^{2+}\text{-P}$ ) in petroleum and asphaltenes by O'Reilly [1] prompted researchers to apply the technique for the detection of  $\text{VO}^{2+}\text{-P}$  in various carbonaceous geological materials with or without recourse to extraction [2]. Hocking and Premović [3] for the first time used this technique to study  $\text{VO}^{2+}\text{-P}$  in the coal/coal-like inclusions of Athabasca tar sand. We applied ESR to estimate the distribution of  $\text{VO}^{2+}\text{-P}$  in the bitumen and kerogen fractions of ancient shaly-type sediments: La Luna (LL) limestone and Serpiano marl [4,5] and very recently in Maganik (Ma) limestone [6]. Finally, Nissenbaum et al. [7] detected floating asphalt by ESR  $\text{VO}^{2+}\text{-P}$  in the Dead Sea (DS).

The purpose of the present report was to carry out an ESR

investigation of  $\text{VO}^{2+}\text{-P}$  associated with the kerogens/asphaltenes isolated from LL, Ma and Se rocks before and after laboratory pyrolysis at 250°C in the presence of air. In addition,  $\text{VO}^{2+}\text{-P}$  in asphaltenes extracted from DS asphalt float as well as solid bitumens (imponite/grahamite) from Oklahoma (USA) were also examined. It was expected that these studies might yield additional information about the thermal stability of  $\text{VO}^{2+}\text{-P}$  associated with kerogens/asphaltenes in the presence of air  $\text{O}_2$  [8–10].

## 2. Experimental

### 2.1. Sample

LL [5,11], Ma [6] and Se [12] rocks have apparently experienced a fairly low temperature history. The most intriguing characteristics of the kerogens isolated from the LL, Ma and Se materials is their high  $\text{VO}^{2+}\text{-P}$  content: 4700 ppm (LL), <1000 ppm (Ma) and 2500 ppm (Se) [5,6,13]. Methanol-soluble fractions of the bitumens of

\* Corresponding author. Fax: +381-18-46-460.

E-mail address: fprem@filfak.ni.ac.yu (P.I. Premović).

these rocks are characterized by a high concentration of alkyl VO<sup>2+</sup>-P: mostly of deoxophylloerythroetioporphyrins (DPEP) type [5,8,9].

The most spectacular occurrences of bitumen in the DS Basin (Israel) are the huge floating blocks of asphalt on the surface of the Dead Sea. The samples of DS asphalt float (studied in this communication) of extreme purity (99.9% of extractable organic matter) are rich in both vanadium (V) (up to 1500 ppm) and VO<sup>2+</sup>-P (up to 1000 ppm) [13,14].

Asphaltite (grahamite) and asphaltic pyrobitumen (imponite) deposits are found in a number of localities in the Ouachita Mountains (Oklahoma); the best known occurrences are in the Page and Windingstair locations, in southern Le Flore County [15]. Grahamite is partly soluble in common organic solvents and imponite is almost insoluble [16].

The Western Kentucky (Springfield) No. 9 coal of the Carbonale Formation (Middle Pennsylvanian) in the Western Kentucky coalfield of the Illinois Basin is the most abundant coal there. Very recently, Premović et al. [17] applied ESR spectroscopy to probe the chemical and structural environment of VO<sup>2+</sup> in the coal/shale samples from the Providence Mine (Union County) of this coalfield enriched with V (>1000 ppm). According to these authors, the coal VO<sup>2+</sup> exists as VO<sup>2+</sup>-non-porphyrins (VO<sup>2+</sup>-non-P) in which VO<sup>2+</sup> is bound to oxygen ligand donor atoms with no evidence for VO<sup>2+</sup> as VO<sup>2+</sup>-P. The coal samples used in the present study came from the top ≤20 cm of the Western Kentucky seam at three mines (Providence, Millport and Nebo) containing up to 800 ppm of V. Parts of the seam are exceptionally high in V, up to 1800 ppm [17]. In fact, the abundant V and VO<sup>2+</sup>-non-P of these coal samples are the most characteristic features of this coal.

### 2.2. Sample preparation and pyrolysis

The geological samples were ground to a fine powder (200–400 mesh) with a ball mill and Soxhlet extracted exhaustively with benzene/methanol azeotrope to remove soluble organic material (bitumen). The bitumen fraction 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 bitumen (10 g) was refluxed (Soxhlet) for 90 h in methanol to obtain the methanol soluble fraction (after solvent evaporation). The remaining (resin + asphaltene) fraction was refluxed (Soxhlet) in *n*-hexane for 90 h to yield the resin fraction. The remaining asphaltenes were washed several times with *n*-hexane until the wash solution was clear, then dried at 45°C.

The extracted LL/Ma/Se rocks were treated with 20% hydrochloric acid (HCl) to remove carbonates. After filtration and washing, the remaining minerals were acid leached by digestion for 72 h at room temperature using 1:1 (v/v) mixture of concentrated hydrofluoric acid (HF) (48%) and HCl (20%). The mixture was filtered and the residue washed

repeatedly with boiling distilled water to pH 7. After drying, the kerogen concentrate was again exhaustively extracted with benzene/methanol azeotrope until the solvent siphoning to the flask was clear. The kerogen was dried at 80°C and stored in a desiccator. An identical procedure was employed to obtain the coal insoluble organic fraction. The kerogens/asphaltenes were then heated at temperatures ≤250°C in air for periods of time between one and 20 days.

### 2.3. Electron spin resonance

ESR measurements were performed on finely ground powders of the kerogen/asphaltene samples, which were transferred to an ESR quartz tube. Spectra were recorded on a Bruker ER-200 series ESR spectrometer with either a Bruker ER-044 X-band bridge or a Bruker ER-053 Q-band bridge, using standard 100 kHz field modulation. X-band measurements were made at 9.3 GHz utilizing a rectangular TE cavity, and those at Q-band using a cylindrical TE cavity. Magnetic field calibration was performed with the DPPH standard ( $g = 2.0037 \pm 0.0005$ ) [18]. Frequency was measured using a Hewlett–Packard frequency meter.

## 3. Results and discussion

### 3.1. VO<sup>2+</sup> and pyrolysis of kerogens/asphaltenes: nature and origin of VO<sup>2+</sup>-non-porphyrins

A typical ESR spectrum of VO<sup>2+</sup>-P of the Ma kerogen before heating is shown in Fig. 1(a). The Ma kerogen was pyrolyzed at 250°C in the presence of air for 5 days. The X-band anisotropic ESR spectrum of VO<sup>2+</sup> compounds in the pyrolyzed sample of the Ma kerogen is shown in Fig. 1(b). A similar spectrum was recorded for LL/Se kerogen/asphaltene and the LL/DS asphaltenes after the heat treatment described above, as well for the methanol-soluble fractions of the bitumens of the LL/Ma/Se rocks containing mostly VO<sup>2+</sup>-DPEP. The VO<sup>2+</sup>-P content of the Ma asphaltenes could not be estimated, however, due to the small amount of the asphaltene samples extracted.

ESR measurements at 34 GHz have the potential to resolve resonancies that might be obscured at 9 GHz and are more sensitive to the  $g$  anisotropy. Moreover, 34 GHz measurements are more sensitive to details of the VO<sup>2+</sup> sites such as the presence of symmetry lower than axial. For this reason, we recorded, also, a Q-band anisotropic spectrum of VO<sup>2+</sup>-species of heated Ma kerogen (see Fig. 1(d)). Within experimental error (<1 mT) this spectrum is axial. In this case all the spin-Hamiltonian parameters can be derived from this ESR spectrum using the axially symmetric spin-Hamiltonian

$$H = \beta_0 [g_{\parallel} H_Z S_Z + g_{\perp} (H_X S_X + H_Y S_Y) + A_{\parallel} (S_Z I_Z) + A_{\perp} (S_X I_X + S_Y I_Y)]$$

where  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  are the parallel ( $z$ ) and perpendicular

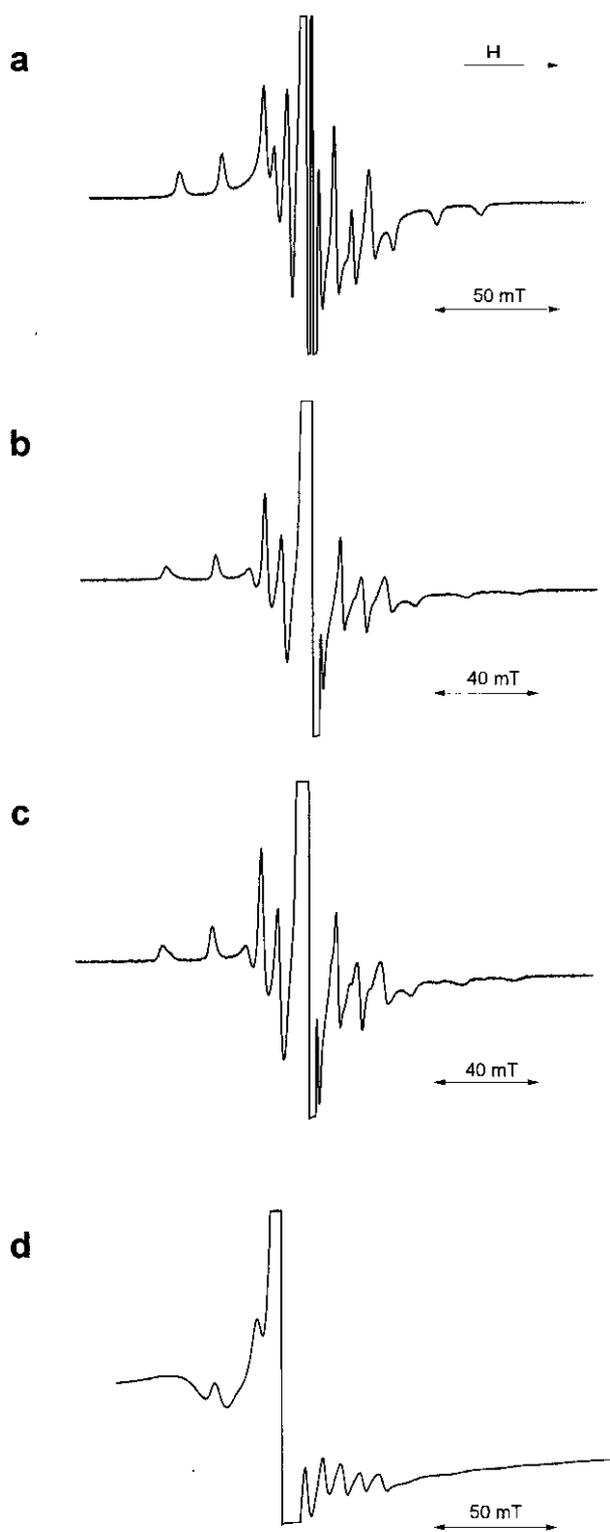


Fig. 1. First derivative, room temperature, X-band ESR spectra of: (a)  $\text{VO}^{2+}$ -P in Ma kerogen; (b)  $\text{VO}^{2+}$ -non-P in pyrolyzed Ma kerogen; (c)  $\text{VO}^{2+}$ -non-P in the Western Kentucky coal (the Millport mine), and (d) first derivative, room temperature, Q-band ESR spectrum of  $\text{VO}^{2+}$ -non-P of pyrolyzed Ma kerogen. ESR parameters:  $A_{\parallel} = 17.6 \pm 0.2$  mT, and  $A_{\perp} = 5.7 \pm 0.4$  mT;  $g_{\parallel} = 1.951 \pm 0.003$ , and  $g_{\perp} = 1.985 \pm 0.010$  (for the  $\text{VO}^{2+}$ -P [4]);  $A_{\parallel} = 19.2 \pm 0.3$  mT, and  $A_{\perp} = 6.9 \pm 0.5$  mT;  $g_{\parallel} = 1.937 \pm 0.005$ , and  $g_{\perp} = 1.991 \pm 0.010$  (for the  $\text{VO}^{2+}$ -non-P).

( $x$ ,  $y$ ) components of  $g$  and  $^{51}\text{V}$  hyperfine coupling tensors, respectively.  $H_i$ ,  $S_i$  and  $I_i$  represent the vector components of the magnetic field, electron spin, and  $^{51}\text{V}$  nuclear spin along the  $i$  ( $= x, y, z$ ) axes.

A comparison of the spin-Hamiltonian parameters for  $\text{VO}^{2+}$ -P of unheated Ma kerogen (Fig. 1(a)) and heated Ma kerogen (Fig. 1(b)) suggests that the  $\text{VO}^{2+}$  compounds in thermally treated kerogen are of non-porphyrin type. In fact, the ESR spectrum of heated Ma kerogen is similar to those reported by Premović et al. [17] for  $\text{VO}^{2+}$ -non-P ions incorporated into the structure of the Western Kentucky coal enriched with V from the Providence Mine (Union county). According to these authors, the  $\text{VO}^{2+}$  ions within the structure of this coal are, probably, complexed with the oxygenated functional groups (e.g. carbonyl/carboxylic/phenolic groups).

Our earlier study has demonstrated that on pyrolysis in vacuo at temperatures up to  $400^{\circ}\text{C}$  the ESR signals given by  $\text{VO}^{2+}$ -P in the LL/Se kerogens undergo no change [8–10]. This fact indicates that air plays an essential role in the observed conversion of  $\text{VO}^{2+}$ -P into  $\text{VO}^{2+}$ -non-P. In separate experiments it was also demonstrated that the active component of air is molecular oxygen ( $\text{O}_2$ ) since pure  $\text{O}_2$  at a pressure corresponding to the partial pressure in air was equally effective. Similar experimental results and observations are found for the asphaltenes studied.

In Fig. 2(a) we see the changes of the normalized ESR signal intensities of  $\text{VO}^{2+}$ -P,  $\text{VO}^{2+}$ -non-P, and total  $\text{VO}^{2+}$  in the Se kerogen as heating time increases. The  $\text{VO}^{2+}$ -P ESR signals decrease monotonically and become quite small after six days of heating. Concomitantly,  $\text{VO}^{2+}$ -non-P appear and, at longer heating times, dominate the spectrum. Similar  $\text{VO}^{2+}$  ESR signal changes are observed during heating of the LL/Ma kerogens (not shown). Clearly, the secondary  $\text{VO}^{2+}$ -non-P must have been formed from the principle  $\text{VO}^{2+}$ -P in the ESR spectrum, since the minor  $\text{VO}^{2+}$  species would not have been present in sufficient quantity to account for these large secondary ESR signals.

$\text{VO}^{2+}$ -non-P formed at the expense of  $\text{VO}^{2+}$ -P during laboratory pyrolysis of the LL/Se kerogens amounted to ca. 80% of initial  $\text{VO}^{2+}$  in  $\text{VO}^{2+}$ -P (Fig. 2(a)). This fact indicates that in this material there are, at least, either two different types of incorporated  $\text{VO}^{2+}$ -P or two different oxygenic degradation pathways of  $\text{VO}^{2+}$ -P. In both cases a less plausible alternative yields  $\text{V}^{5+}$  compounds, which are “invisible” to ESR. In striking contrast to the kerogens, the pyrolyzed Se (Fig. 2(b)) and LL (not shown) asphaltenes yield only ca. 25% of  $\text{VO}^{2+}$ -non-P at the expense of initial  $\text{VO}^{2+}$ -P. This marked difference in yielding of  $\text{VO}^{2+}$  in  $\text{VO}^{2+}$ -non-P (and other pyrolytic features) of these (and similar) carbonaceous geological materials will be discussed in detail elsewhere. The  $\text{VO}^{2+}$ -non-P ESR signals of the LL/Ma/Se kerogens diminished after about 20 days of laboratory heating in air atmosphere at  $250^{\circ}\text{C}$ .

Thermal conversion of the kerogen/asphaltene  $\text{VO}^{2+}$ -P into  $\text{VO}^{2+}$ -non-P could be approximated by the first order

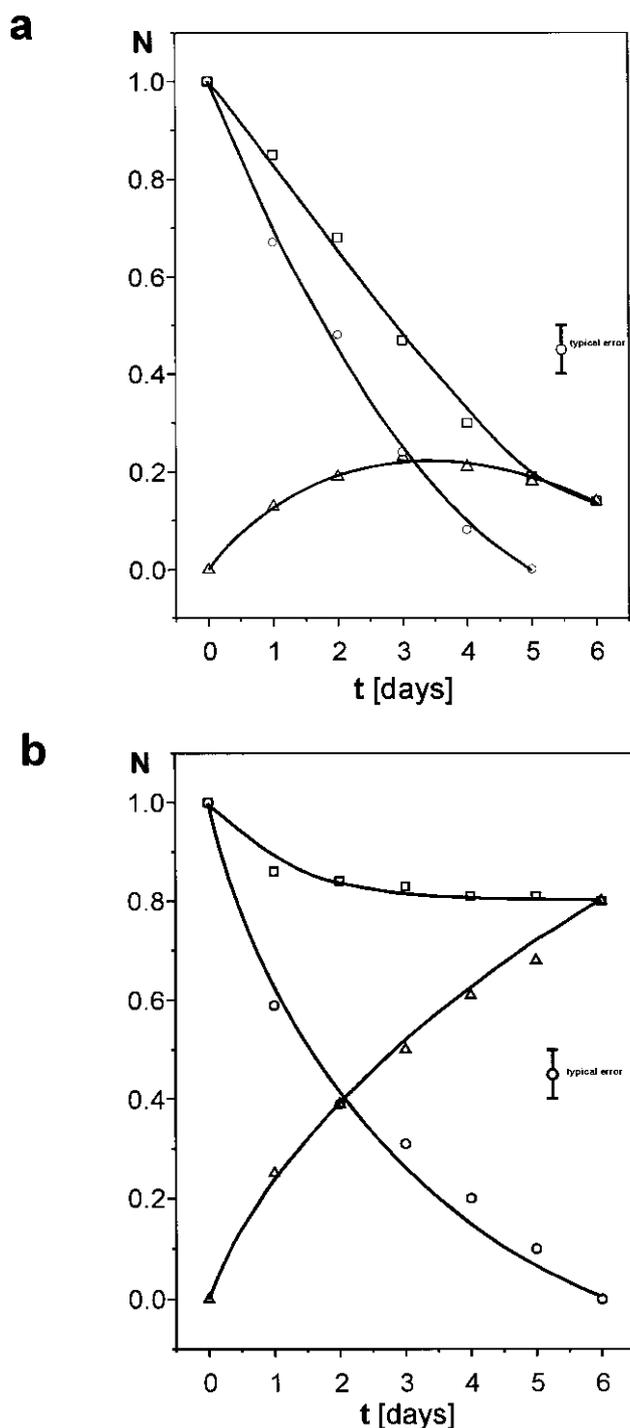


Fig. 2. Changes of normalized ESR signal intensity ( $N$ ) for total  $VO^{2+}$  (□);  $VO^{2+}$ -P (○); and  $VO^{2+}$ -non-P (△) for (a) the Se kerogen and (b) the Se asphaltene.

kinetics at 250°C with a half-life ( $t_{1/2} \sim 2$  days) of  $VO^{2+}$ -P. Porphyrins are known to undergo thermal degradation at relatively low temperatures in the presence of air. This process is also known to cause the scission of the porphyrin ring [19]. Consequently, we suggest that the thermal conversion described above occurs through the scission of the porphyrin ring of  $VO^{2+}$ -P, leading to the formation of a

hexadentate  $VO^{2+}$ -non-P complex made of oxygen ligand donor atoms.

Weathering is the natural oxidation of kerogen that takes place at low temperatures ( $<30^\circ\text{C}$ ), while oxidation is a higher temperature ( $>70^\circ\text{C}$ ) event. The natural (mild) oxidation of kerogens, in which the related temperatures do not exceed  $150^\circ\text{C}$ , leads to changes of the original chemical structure with an increase in the content of oxygenated (carbonyl/carboxylic/phenolic) functional groups. On the other hand, modern studies of changes in the kerogen composition during air oxidation at  $200$ – $250^\circ\text{C}$  have indicated a dramatic increase in oxygenated (carbonyl/carboxylic/phenolic) groups whose concentrations are strictly dependent on the oxidation temperature. According to Kalema and Gavalas [20], the  $200^\circ\text{C}$  oxidation incorporates a variety of new oxygen functionality (the carbonyl/carboxylic/phenol units) resulting in the formation of so-called “regenerate humics/protokerogen”.

The demineralized Oklahoma impsonite/grahamite samples were examined by ESR. This examination reveals the presence of  $VO^{2+}$ -P in amounts comparable to those in the kerogens of the LL/Ma/Se rocks [5,6]. Kinetic parameters from our very recent pyrolysis experiments show that some asphaltic oil (including asphalts) can be completely converted into a kerogen-like (amorphous) material at a temperature of  $70^\circ\text{C}$  (for  $<100$  days) up to  $250^\circ\text{C}$  (for  $<2$  days) in the presence of air  $O_2$  [8,9]. In the light of these experimental results, we are led to the view that the conversion of soluble asphaltic petroleum into insoluble (kerogen-like) solid bitumen (such as the Oklahoma impsonite/grahamite) had to occur through natural thermal kerogenization of asphaltic petroleum in the presence of air  $O_2$  [16].

It is generally accepted that the minimum temperature at which irreversible chemical changes of carbonaceous geological materials are observed in the laboratory must be considerably higher than the maximum temperature to which these materials had been exposed in the previous geological history [21]. Our ESR investigation indicates that the temperature of about  $150^\circ\text{C}$  must be reached before the conversion of the kerogen/asphaltene  $VO^{2+}$ -P into  $VO^{2+}$ -non-P at a rate that can be observed in the laboratory (about 20 days). Therefore, we may hypothesize that if this conversion has occurred in particular geological materials then this material had to be exposed to much lower temperatures than  $150^\circ\text{C}$  over geological time (say,  $<100^\circ\text{C}$ ). Therefore, we can suggest that if the aerobic conversion of asphaltic oil into the Oklahoma impsonite/grahamite has occurred [16], then the parent asphaltic petroleum had to be exposed to temperatures much lower than  $150^\circ\text{C}$  over geological time (e.g.  $<100^\circ\text{C}$ ).

The ESR spectra of the Western Kentucky coal samples studied were similar to the spectrum of  $VO^{2+}$ -non-P (Fig. 1(c)). However, in addition to the hyperfine coupling, each of the  $VO^{2+}$  lines of the coal samples spectra from some sites are either broadened or are further split into a

number of sublines, belonging to the hyperfine lines from two different  $\text{VO}^{2+}$  subspectra, the minor  $\text{VO}^{2+}$ -P and the predominant  $\text{VO}^{2+}$ -non-P. Finally, in contrast to the results for the LL/Ma/Se kerogens,  $\text{VO}^{2+}$ -non-P of the pyrolyzed Western Kentucky coal diminished after 6 h of laboratory heating at 250°C in the presence of air  $\text{O}_2$ . The lower stability of  $\text{VO}^{2+}$ -non-P of the Western Kentucky coal than those of the LL/Se kerogens can be rationalized by their structural differences.

One of the possible explanations for the Western Kentucky coal  $\text{VO}^{2+}$ -non-P origin presumes that the parent coal (or part of it) enriched with  $\text{VO}^{2+}$ -P was exposed to natural heating temperatures  $\leq 150^\circ\text{C}$  in the presence of air  $\text{O}_2$ . A more detailed discussion is, however, beyond the scope of this paper, but will be published elsewhere.

#### 4. Conclusion

Isothermal laboratory heating of the LL/Ma/Se kerogens at 150 and 250°C for 1–20 days in the presence of air  $\text{O}_2$  converts the kerogen  $\text{VO}^{2+}$ -P into  $\text{VO}^{2+}$ -non-P. Similar conversion is observed under the same experimental conditions for the asphaltenes extracted from the LL/Se rocks, and floating asphalt from the Dead Sea.

The samples of the Western Kentucky No. 9 coal (enriched with V) from six mines show the presence of predominant  $\text{VO}^{2+}$ -non-P similar to those generated through oxygenic heat treatment of the kerogen/asphaltene materials (besides minor  $\text{VO}^{2+}$ -P) described above.

#### Acknowledgements

This research was supported by grant number 02E38 from the Ministry of Science (Serbia). The authors are grateful for financial supports to the Ministry of Industry (Montenegro) and Consejo de Desarrollo Científico y Humanístico, Universidad Central de Venezuela (Venezuela). We thank Drs A. Sandler (DS), H. Rieber (Se), D.H. Maylotte (W. Kentucky) and B.J. Cardott (impsonite/grahamite) for supplying geological samples. Funding support from le

Ministère Français de l'Éducation Nationale, de l'Enseignement Supérieur et de la Recherche to P.I.P. for his stay at the Université Pierre et Marie Curie (Paris) is gratefully acknowledged.

#### References

- [1] O'Reilly DE. *Journal of Chemical Physics* 1958;29:1188.
- [2] Premović PI. In: *Proceedings of VIIth Yugoslav Conference on General and Applied Spectroscopy (plenary lecture)*, Niš, Yugoslavia, 1978, 11 p.
- [3] Hocking MB, Premović PI. *Geochimica et Cosmochimica Acta* 1978;43:359.
- [4] Premović PI. *Geochimica et Cosmochimica Acta* 1984;48:873.
- [5] Premović PI, Pavlović MS, Pavlović NZ. *Geochimica et Cosmochimica Acta* 1986;50:1923.
- [6] Dordevic DM. MSc Thesis, University of Niš, Yugoslavia, 2000.
- [7] Nissenbaum A, Aizenshtat Z, Goldberg M. In: Douglas AG, Maxwell JR, editors. *Advances in organic geochemistry*. Oxford: Pergamon, 1980. p. 157.
- [8] Premović PI, Jovanović LjS, Zlatković SB. *Journal of Serbian Chemical Society* 1996;61:149.
- [9] Premović PI, Jovanović LjS, Zlatković SB. *Organic Geochemistry* 1996;24:801.
- [10] Premović PI, Jovanović LjS. *Fuel* 1997;76:267.
- [11] Rieber H. *Eclogae Geologicae Helveticae* 1973;66:667.
- [12] Premović PI. In: Rodríguez-Clemente R, Tardy Y, editors. *Geochemistry and mineral formation of the earth surface*. Madrid: CSIC, 1987. p. 431.
- [13] Premović PI, Tonsa IR, Pavlović MS, López L, Lo Monaco S. *Fuel* 1998;77:1769.
- [14] Aizenshtat A, Dinur D, Nissenbaum A. *Chemical Geology* 1979;24:161.
- [15] Cardott BJ, Ruble TE, Suneson NH. *Energy Sources* 1993;15:239.
- [16] Premović PI, Jovanović LjS, Zlatković SB, Premović MP, Tonsa IR. *Journal of Petroleum Geology* 1998;21:289.
- [17] Premović PI, Jovanović LjS, Premović MP, Pavlović MS. *European Coal Geology and Technology* 1997;125:273 (Geological Society Special Publication).
- [18] Faber RJ, Fraenkel GK. *Journal of Chemical Physics* 1967;47:2462.
- [19] Yen TF. In: Yen TF, editor. *Role of trace metals in petroleum*. Michigan: Ann Arbor Science, 1975. p. 1.
- [20] Kalema WS, Gavalas GR. *Fuel* 1987;66:158.
- [21] Tissot BP, Welte DH. *Petroleum formation and occurrence*. Berlin: Springer, 1984.