

Incorporation of vanadyl porphyrins into kerogen structures during catagenesis

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Received 15 February 1999; accepted 30 September 1999

Abstract

Natural vanadyl (VO^{2+})-deoxophylloerythroetioporphyrins (DPEP) are shown to be capable of reacting and quantitatively incorporating into the immature kerogen model materials (torbanite, lignites, subbituminous coal and an immature lacustrine kerogen) at 200°C for 72 h in the absence/presence of air oxygen. Electron spin resonance is used to monitor the incorporation of VO^{2+} -DPEP into the kerogen models. The products of the incorporation resemble natural kerogen enriched with VO^{2+} -DPEP. The simulation experiments described in this paper clearly show that the kerogen VO^{2+} -P may originate from VO^{2+} -DPEP incorporation into the kerogen macromolecular structures during catagenesis. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Vanadyl porphyrins; Kerogen; Electron spin resonance

1. Introduction

In his pioneering research performed in the mid-1930s Treibs [1–3] demonstrated the presence of VO^{2+} -porphyrins (P) in a wide variety of ancient sedimentary carbonaceous rocks. Treibs [3] also showed that major components were the alkylporphyrins: VO^{2+} -DPEP and etioporphyrins (ETIO). The geoporphyrins may be classified according to their physicochemical properties into the following two groups: extractable alkyl VO^{2+} -P with: (a) relatively low molecular weight and (b) minor VO^{2+} -P with relatively high molecular weight [4]. Most researchers believe that sedimentary alkyl VO^{2+} -P have originated during the early stages of diagenesis, long before the long term effects of heat and other processes of diagenesis/catagenesis were brought to bear on the sediment.

Premović et al. [5] determined the distribution of VO^{2+} -P in various fractions of the La Luna limestone and Serpiano (Se) marl by employing a variety of geochemical and spectroscopic techniques: the existence of VO^{2+} -P in the kerogen/asphaltene fractions was shown using electron spin resonance (ESR) spectrometry. The maltene fractions of these rocks are characterized by a high concentration of alkyl VO^{2+} -P (mostly the DPEP-type) [5]. They suggested that VO^{2+} -P are incorporated into the

kerogen matrix through aliphatic bonds as suggested by Mackenzie et al. [6]. Baker and Louda [4] reasoned that alkyl VO^{2+} -P were released to the evolving bitumen only by thermal cracking of kerogen during catagenesis.

Geochemists consider that kerogen formation is the result of either a series of consecutive/random repolymerization and polymerization reactions of a very small fraction of the (bio)degradation products of extant biomacromolecules [7] or the accumulation of selectively preserved resistant biomacromolecules [8]. According to the first concept, alkyl VO^{2+} -P have been incorporated already into the proto/young kerogen whereas, according to the second concept, the kerogen VO^{2+} -P are associated with macromolecular structures which were highly resistant to degradation.

Kerogen should be indigenous to the original sediment, because kerogen is an insoluble organic matter. Therefore, the identification of VO^{2+} -P in the kerogen framework has provided evidence that VO^{2+} -P were indigenous to the sediments. Premović et al. [9] suggested that a significant amount of alkyl VO^{2+} -P that were not incorporated into the proto/young kerogen during earlier stages of diagenesis could be incorporated into a secondary kerogen (asphaltene-derived kerogen) in deeper sedimentary strata either before or during the petroleum generation stage: catagenesis. According to these authors the geochemical process responsible for such an incorporation is anaerobic kerogenization of asphaltenes under mild thermal conditions

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Table 1
Coals/kerogen used for the VO²⁺-DPEP incorporation

Coal/kerogen	Location	Age	Type
Torbanite	Scotland	Carboniferous	Algal coal ^a
Tasmanite	Tasmania	Permian	Spore coal ^b
Kostolac	Serbia	Tertiary	Lignite ^c
Kolubara	–	–	Lignite ^c
Kosovo	–	–	Lignite ^c
Soko	–	–	Subbituminous (brown) coal ^c
Vrška Čuka	–	Jurassic	Anthracite ^c
Aleksinac	–	Tertiary	Immature lacustrine kerogen ^d

^a Ref. [14].

^b Ref. [13].

^c Ref. [15].

^d Ref. [16].

(<200°C). In addition, Premović et al. [9,10] demonstrated that kerogen-like-material could be produced at lower temperatures ($\leq 100^\circ\text{C}$) by the oxygenic kerogenization of asphaltenes. In accordance with this concept, the asphaltenes (enriched already in alkyl VO²⁺-P) could be converted into kerogen (also rich in VO²⁺-P) during geological heating at temperatures $\leq 100^\circ\text{C}$ in the presence of air O₂.

Therefore, in considering processes of kerogen formation one must account for the presence, and nature, of the chemical components, which, while not recognizably present in quantity in proto/young kerogens, are important parts of the ancient kerogen. Thus, while VO²⁺-P are not commonly found in quantity in proto/young kerogens [11], these species, in view of their abundance in some ancient sedimentary organic matter (such as the Se material), may be important in the late stages of kerogen maturation.

It is the purpose of this communication to describe the thermal behavior of sedimentary VO²⁺-DPEP in the presence of the kerogen-model materials (hereinafter referred as the kerogen models) separated from coals of various ranks and from a lacustrine shale. In general, coal (i.e. its predominant insoluble organic fraction) may be regarded as a special type of kerogen derived mainly from terrestrial organic matter. The experimental approach described (see Section 2: heating experiment) was designed to model, in an admittedly idealized fashion, the possible VO²⁺-DPEP/kerogen interaction (at eventual disposal sites). Thus our experiments of laboratory heating of the coals in the presence of VO²⁺-DPEP model a geological thermal incorporation of the VO²⁺-DPEP into the kerogen. We have employed in our thermal experiments VO²⁺-DPEP as type VO²⁺-P. This is particularly appropriate because these types of porphyrins are predominant VO²⁺-P in most of the petroleum source rocks. The coals were chosen to model an immature kerogen (algal coals, lignites, subbituminous coal) and very mature kerogen (anthracite) found in sedimentary environments.

2. Experimental

2.1. Samples

The Triassic Se marl sample used was from the outcrop site. Bitumen fraction of this rock is characterized by a high concentration of VO²⁺-P (mostly DPEP-type, i.e. DPEP/ETIO porphyrin ratio > 100) [5].

Samples selected for the present study allowed a large range of geochemical composition of coals to be heated. Algal coals (torbanite/tasmanite), lignite (Kostolac/Kolubara/Kosovo), subbituminous (brown) coal (Soko) and the Vrška Čuka anthracite were selected for the heating experiments. In addition, a kerogen concentrate of the lacustrine shale from the Aleksinac Formation was also included. Eight coal samples used in this work are described briefly in Table 1.

2.2. Separation and extraction

Whole rock/coal sample was crushed/powdered and minor carbonates/silicates were removed with HCl/HF, and the pyrite was decomposed with LiAlH₄ [12]. The residue 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) and solvent evaporated. Isolated coal residues were examined by X-ray diffraction.

2.3. Ultraviolet (UV)-visible (VIS) spectrophotometry

UV-VIS spectrum of the Se VO²⁺-DPEP concentrate was recorded on a Zeiss Specord Model. In general, the spectrum with maxima occurring at about 409 (Soret), 534 (β) and 573 nm (α) is typical of VO²⁺-DPEP. Concentrations of extractable VO²⁺-P were calculated from the UV-VIS spectra, using both the α -peak (573 nm, $\epsilon = 2 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$) and Soret peak (409 nm, $\epsilon = 3.3 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1}$) [11]. The presence of VO²⁺-DPEP was confirmed by observing diagnostic shifts in the Soret band on complexation with piperidine [5].

2.4. Electron spin resonance (ESR)

ESR measurements were performed on unheated and heated samples in a quartz tube (4 mm o.d.) using a Bruker ER 200D ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz interfaced to a COMPUTER DESIGN computer. Signal intensities (proportional to the VO²⁺-P concentration) were calculated by double integration of the first derivative ⁵¹V hyperfine ($m_I = -5/2$) line using the COMPUTER DESIGN system.

2.5. Isolation of the Se VO²⁺-P concentrate

The Se bitumen fraction (remained after the above solvent evaporation) was refluxed (Soxhlet) for 90 h in methanol to obtain the methanol soluble fraction (after

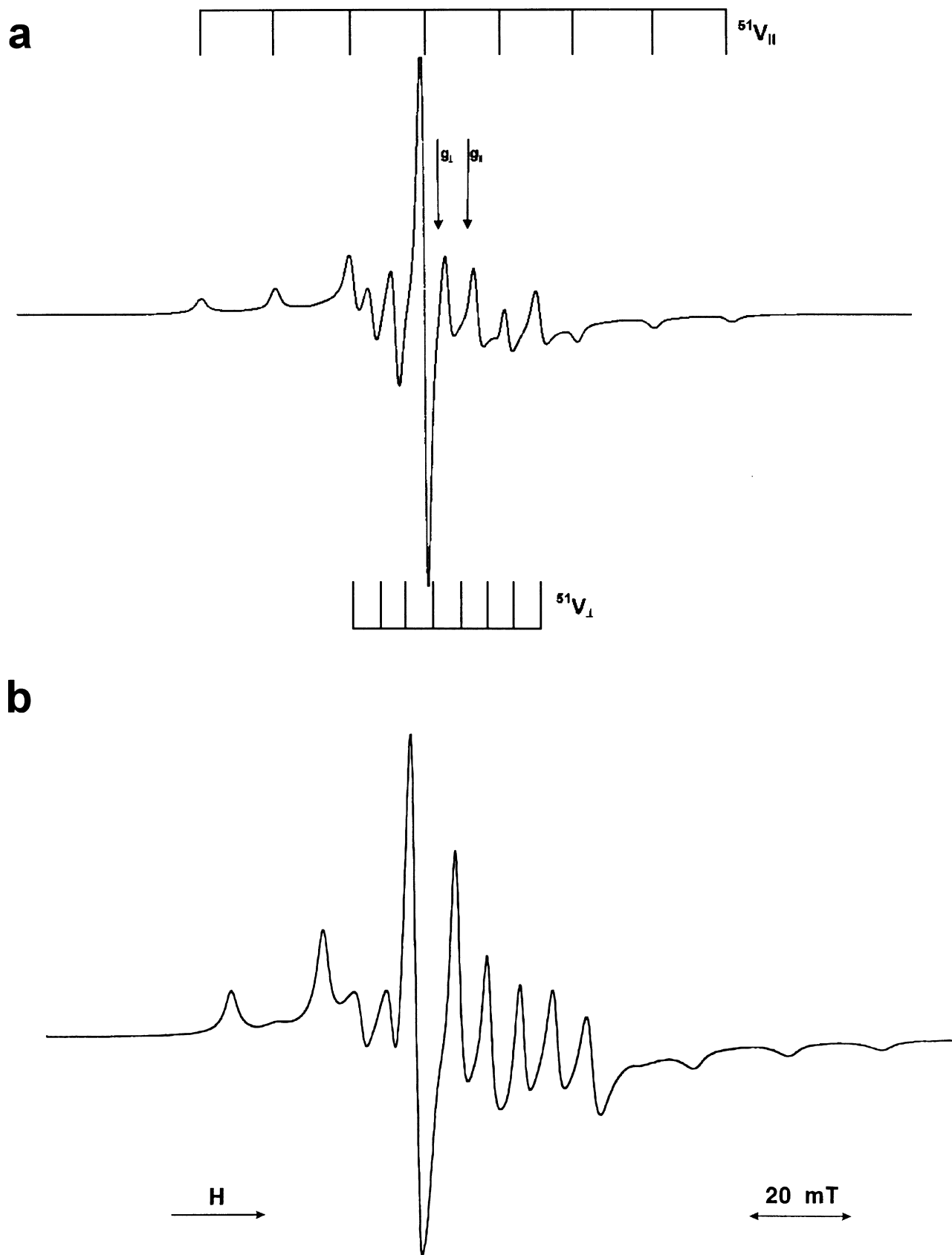


Fig. 1. First derivative room temperature X-band anisotropic ESR spectra of: (a) $\text{VO}^{2+}\text{-P}$ of the Se kerogen; and (b) $\text{VO}^{2+}\text{-P}$ incorporated into the torbanite macromolecular structures by laboratory thermal treatment. The ESR parameters ($^{51}\text{V}_{\parallel}$, $^{51}\text{V}_{\perp}$, g_{\parallel} , g_{\perp}) are given in Ref. [5].

solvent evaporation). This fraction was weighed and examined by ESR/UV–VIS spectrophotometry to determine its VO^{2+} –P content.

To a column (1 cm i.d. \times 30 cm) containing Merck Kieselgel 60 (10 g) the Se methanol fraction was applied in 3 \times 2 ml of toluene:chloroform (3:1): this was eluted at 1 ml min^{-1} with toluene, toluene:chloroform (3:1) and toluene:methanol (9:1). Fractions (1–2 ml) were evaporated in a stream of nitrogen to near dryness for examination by ESR to determine relative VO^{2+} –P content, most of which was eluted in the toluene fraction. The toluene fraction was further purified by preparative thin layer chromatography (TLC) using Merck precoated silica plates and toluene:chloroform (3:1) as eluent. The VO^{2+} –P compounds were recovered from the upper red porphyrin band using benzene:methanol (3:1). The presence of predominant VO^{2+} –DPEP was confirmed by UV–VIS and by observing diagnostic shifts in the Soret band on complexation with piperidine [5].

2.6. Heating experiment

The simulated geothermal experiments were performed on the DPEP concentrate (hereinafter referred as VO^{2+} –DPEP) of the Se marl. The VO^{2+} –DPEP concentrated extract was deposited on prewashed (redistilled hexane) and vacuum-dried coal/kerogen materials to give a concentration of about 150 ppm of metalloporphyrin. Aliquots of coated kerogen/coal were placed in heavy-walled glass tubes (4 mm \times 100 mm), flushed with O_2 -free N_2 and sealed under vacuum. The sealed glass tubes were then heated at 200°C up to 72 h. After cooling, the extractable part of VO^{2+} –DPEP coated on coal/kerogen was extracted with benzene:methanol (3:1 (v/v)) (Soxhlet) for 72 h. The remaining kerogen + non-extractable VO^{2+} –P (incorporated into the coal/kerogen structures) was examined for its VO^{2+} –P using ESR.

3. Results and discussion

The ESR spectrum of VO^{2+} –P incorporated into the Se kerogen structure(s) is shown in Fig. 1(a). The reaction of VO^{2+} –DPEP and torbanite results in almost complete incorporation of the porphyrin species into the torbanite structure(s) within 72 h at 200°C in the absence of air. The ESR spectrum of the VO^{2+} –DPEP incorporated into the algal coal matrix is shown in Fig. 1(b) and it is almost identical VO^{2+} –P within the Se kerogen (Fig. 1(a)). Similar results/spectra were obtained for the incorporation of VO^{2+} –DPEP into the structures of the Kostolac/Kolubara/Kosovo lignites and Soko coal. On the contrary, attempts to observe incorporation of VO^{2+} –DPEP into both tasmanite and anthracite were, however, unsuccessful.

Although the results mentioned-above must be considered initial they show that VO^{2+} –DPEP react at 200°C with the kerogen models to form products similar to sedimentary kerogen enriched with VO^{2+} –P: such as the Se

kerogen. In the first stage, corresponding to diagenesis, the transformation of humic materials (as the kerogen precursors) is mainly by means of biological processes as the materials are buried at depths up to 1000 m and reaches temperatures up to 60°C. Deeper burial (due to further accumulation of sedimentary overburden, tectonic activity, or both) increases the temperature of the sedimentary rock and its kerogen. The term catagenesis is applied to transformation occurring between approximately 60 and 150°C, depending on the geologic age of the rock [7]. According to the current thinking during early catagenesis (at temperature range 60–90°C) a heavy (and immature) petroleum containing rather large molecules with heteroatoms (O, N, S) (such as asphaltene molecules) are released. Thus, the kerogen-like materials enriched with VO^{2+} –P are produced relatively rapidly by the reactions of VO^{2+} –DPEP and the kerogen models at temperatures less than about 100°C above those prevailing in the sedimentary carbonaceous rocks which are commonly regarded as source beds of petroleum. Obviously, the reactions at a temperature near 100°C would take place very slowly but over a long (geological) time period may be expected to produce the same or similar kerogen-like material. Thus, the most favorable natural conditions for thermal incorporation of VO^{2+} –DPEP as described will exist in the later, more severe, stages of the maturation processes. The failure of the incorporation of VO^{2+} –DPEP into anthracite shows that its polyaromatic units are not capable to react with VO^{2+} –DPEP at temperature \leq 200°C and to incorporate into the polyaromatic network of this coal. This fact implies that VO^{2+} –DPEP cannot be incorporated thermally into polyaromatic kerogen (similar to Vrška Čuka anthracite) formed prior/subsequent to metagenesis. Thus, we may reason that: (a) thermal incorporation of VO^{2+} –DPEP into the kerogen macromolecular framework which occurs easily in the laboratory may occur rapidly/efficiently (geologically speaking) in natural sedimentary environment during catagenesis; and (b) the VO^{2+} –P components of kerogen are not derived exclusively from the kerogen precursors (humic materials, proto/young kerogen enriched with VO^{2+} –P) themselves and/or reactions from the kerogen precursors (with or without VO^{2+} –P) VO^{2+} –DPEP during early diagenesis (primary kerogen VO^{2+} –P). The extent to which the process during catagenesis (as described above), however, contributes to the incorporation of VO^{2+} –DPEP into sedimentary kerogen (secondary kerogen VO^{2+} –P) is difficult to assess now since no criteria exist for differentiating between primary and secondary kerogen VO^{2+} –P.

The unreactivity of tasmanite with VO^{2+} –DPEP may be due to the fact that this coal contains, chemically speaking, a resistant and tough organic material [13]. This evidence appears to indicate that kerogen enriched with VO^{2+} –P could be formed by natural heating (during catagenesis) of VO^{2+} –DPEP with only a certain type of kerogen (e.g. torbanite vs. tasmanite) which was mainly predominant in a particular sedimentary basin.

It is apparent that the incorporation of the VO^{2+} -DPEP into the kerogen models involves the formation of a bond between VO^{2+} -DPEP and their macromolecular structures. The thermal incorporation of VO^{2+} -DPEP into the kerogen models occurs at 200°C: i.e. at a temperature at which C–C bond breaking is negligible (in the absence of mineral catalysts). On the other hand, the irreversible and complete thermal incorporation of VO^{2+} -DPEP into the kerogen models cannot be explained by any other bonding but chemical. Furthermore, exhaustive refluxing (Soxhlet) extraction treatment (cf. heating experiments) provides strong experimental evidence that VO^{2+} -DPEP are bound via covalent bonds to the kerogen-like materials studied.

Clearly, the incorporation of VO^{2+} -DPEP into the kerogen model macromolecules will depend heavily upon the nature of functional groups on their periphery. Obviously, the incorporation of VO^{2+} -DPEP into the kerogen models is a result of a specific reaction(s). However, the possible chemical pathway(s) by which VO^{2+} -DPEP is incorporated into the kerogen model macromolecular structure(s) during thermal treatment is difficult to envisage because several mechanisms may be involved with a number of functional groups of these models. We also attempted to develop a treatment based on thermochemistry/chemical kinetics to describe this process, but were unable to do so because of the same complexity. It is for this reason that we are reporting our results in a less rigorous manner. Perhaps chemical reaction of the alkadiene type of C=C bonds might be involved in the torbanite case [14], i.e. it is possible that the reduction of the torbanite alkadiene C=C bonds during laboratory heating results in VO^{2+} -DPEP attached to the torbanite nucleus. The interaction of VO^{2+} -DPEP by lignites/subbituminous coal studied, however, indicates that oxygen-containing functional groups in these materials might be involved in its binding to their macromolecules. That is, one of the most characteristic features of these low rank coals is their relatively high content of oxygen-containing functional (especially CO_2H /phenolic OH) groups [15]. It may be tentatively concluded that functional groups of these materials interact with VO^{2+} -DPEP to form particular kerogen/ VO^{2+} -DPEP bond association. On the other hand, the unreactivity of anthracite/tasmanite with VO^{2+} -DPEP may be due to the fact that these materials do not have any alkadiene type of the C=C bonds or they are not rich in oxygenic functional groups.

Additional work is being carried out to test the ability of various structural types of sedimentary relevant oxygenic chemicals to bind to VO^{2+} -DPEP. For instance, our preliminary results indicate that phenols, salicylic and oxalic acids, lipids and dextran are capable of incorporation of VO^{2+} -DPEP into their structures. Consequently, thermal reactions of simple compounds (such as those above) appear to be a likely pathway for VO^{2+} -DPEP to form in natural milieu compounds that do not immediately reflect their chlorophyll precursors. This work is still in progress.

To find evidence that VO^{2+} -DPEP tend to be incorpo-

rated into an immature kerogen during catagenesis, we have conducted thermal treatment of immature kerogen isolated from the Aleksinac shale in the presence of VO^{2+} -DPEP. The result indicates that thermal incorporation of VO^{2+} -DPEP into an immature kerogen (under relatively mild thermal conditions) could take place also in young sediments. As an immature kerogen the Aleksinac material contains various amounts of reactive oxygenic functional groups, including CO_2H /phenolic OH units [16]. It is apparent that these groups might act as covalent bonding sites for laboratory thermal incorporation of VO^{2+} -DPEP into the Aleksinac kerogen structures. Thus, an immature kerogen (using its oxygen functionalities as a “geochemical glue”) may serve as a sink for the VO^{2+} -DPEP incorporation into the kerogen macromolecular structure(s) during catagenesis.

In summary, we may conclude that, given kerogen with the appropriate functional groups, VO^{2+} -DPEP could be naturally incorporated into the matrix of a relatively immature kerogen. This has considerable significance in the geochemistry of VO^{2+} -P because it shows a mechanism for the evolution of the kerogen VO^{2+} -P and at the same time gives a good indication of the stability of VO^{2+} -P, once formed, in the geochemical exposure to which they are subjected. In this way VO^{2+} -DPEP can be easily preserved in source rocks (or in any sedimentary carbonaceous rock, in general) because the kerogen VO^{2+} -P formed will be more resistant to thermal decomposition than VO^{2+} -DPEP themselves and thus have a large potential for survival during catagenesis. Our recent thermal ESR experiments show that the kerogen VO^{2+} -P decompose partly when heated at 300°C, but under the same conditions complete decomposition of VO^{2+} -DPEP alone occurred [9].

Finally, according to the current thinking, kerogen and the associated asphaltenes originate from the same precursor(s) and asphaltenes represent small fragments of the kerogen macromolecules: i.e. in terms of structure, asphaltenes are similar to kerogen [17]. For this reason, we are of the opinion that our experimental results concerning thermal incorporation of VO^{2+} -DPEP into the kerogen-model/kerogen frameworks are also relevant to laboratory/natural incorporation of VO^{2+} -DPEP into the asphaltene macromolecules. Further work is being carried out to see if petroleum/source rock asphaltenes can also bind VO^{2+} -DPEP and the results will be reported later.

In the second part of the experiment we heated VO^{2+} -DPEP with the kerogen models in question in the presence of air O_2 . The results clearly show that VO^{2+} -DPEP readily react with the kerogen models under the same thermal conditions as mentioned-above. Preliminary kinetic study shows that the incorporation rate of VO^{2+} -DPEP into the models during laboratory heating at 200°C is about $500\times$ faster than that in the absence of air. Thus, these results suggest that oxidation of the kerogen models by air O_2 may play an essential role in the incorporation of VO^{2+} -DPEP into their macromolecular structures in the presence of air. In general, oxidation of coal at 200°C is believed to

influence many coal properties [18]. For instance, at this temperature oxidation increases the heteroatom (especially oxygen) content of the coal resulting in a greater number of sites available for chemical reactions and thus for the VO^{2+} -DPEP binding. According to Kalema and Gavalas [18], the 200°C oxidation incorporates a variety of new oxygen functionality (the carboxylic, carbonyl and phenol units) resulting in the formation of the so-called “regenerate humics/protokerogen”. Thus, the VO^{2+} -DPEP incorporation into the kerogen model matrix during laboratory heating in air is not an unexpected result. On the other hand, this further supports our notion that oxygenic functionalities of the kerogen models play an important role in the VO^{2+} -DPEP binding to their macromolecular structures. This is consistent with the presence of decarboxylation/decarbonylation reactions some of which might result in crosslink formation which may also include the VO^{2+} -DPEP binding to the kerogen model framework [18]. This work is also still in progress.

Many studies have shown that coals, especially lignites, subbituminous and bituminous coals, yield small but significant amounts of alkyl VO^{2+} -P. Early work in our laboratory has shown that the coal/coal inclusion associated with the Athabasca tar sand (Canada) contain small amounts (<20 ppm) of VO^{2+} -P incorporated into the coal structures [19]. In addition, very recent work in our laboratory has demonstrated that some samples of bituminous Western Kentucky No. 9 coal (USA) enriched with V also contain small but significant amounts (<100 ppm) of VO^{2+} -P incorporated into the coal macromolecular structures [20]. Unless the coal VO^{2+} -P are generated during very early stages of diagenesis, we may tentatively propose that opportunities had existed for the incorporation of VO^{2+} -DPEP into the structures of these two coal materials during catagenesis.

4. Conclusions

1. The simulation experiments described in this paper clearly show that VO^{2+} -DPEP readily react with the kerogen-model materials (torbanite, lignites, subbituminous brown coal and a lacustrine immature kerogen) under relatively mild thermal conditions (200°C, 72 h) comparable to those prevailing during catagenesis.
2. This implies that a major part of VO^{2+} -DPEP which were saved from incorporation into kerogen precursors

(humics or proto/young kerogen) during early diagenesis can be incorporated into kerogen in deep sedimentary layers during intensive-oil production stage (catagenesis) as secondary kerogen VO^{2+} -P.

Acknowledgements

We are deeply grateful to Drs G. Eglinton (tasmanite), A.G. Douglas and the late P. Aspen (torbanite) and the late R. Petrović (the Serbian coals) for providing us with the geological samples. The Ministry of Science (grant No. 02E38) supported the study.

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