The kerogen vanadyl porphyrins: incorporation during catagenesis

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Natural vanadyl (VO^{2+})-deoxophylloerythroetioporphyrins (DPEP) have been shown to be capable of reacting and quantitatively incorporating into immature kerogen model materials (torbanite, lignites, subbituminous coal and immature lacustrine kerogen) at 200 °C for 72 h in the absence/presence of air. Electron spin resonance was 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+}. 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.

Key words: vanadyl porphyrins, kerogen, electron spin resonance.

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 the 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 originated during the very 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 the VO^{2+}-P

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are incorporated into the kerogen matrix through aliphatic bonds as proposed 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 categenesis.

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 were already incorporate 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 insoluble organic matter. Therefore, the identification of VO^{2+}-P in the kerogen framework provided evidence that VO^{2+}-P, were also indigenous to the sediments. Premović *et al.*[9] suggested that a significant amount of alkyl VO^{2+}-P that was not incorporated into the proto/young kerogen during the earlier stages of diagenesis, could be incorporated into 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 (<200 ºC). In addition, Premović *et al.*[9,10] demonstrated that kerogen-like-material could be produced at lower temperatures (≤ 100 ºC) by the oxygenic kerogenization of asphaltenes. In accordance with this concept, the asphaltenes (already enriched in alkyl VO^{2+}–P) could be converted into kerogen (also rich in VO^{2+}–P) during geological heating at temperatures ≤ 100 ºC in the presence of air.

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 ancient kerogen. Thus, while VO^{2+}-P are not commonly found in quantity in proto/young kerogen,[11] these species, in view of their abundance in some ancient sedimentary organic matter (such as the Se material), may be very important in the late stages of kerogen maturation.

The purpose of this communication is to describe the thermal behavior of sedimentary VO^{2+}-DPEP in the presence of kerogen-model materials (hereinafter referred to as kerogen models) separated from coals of various rank and from a lacustrine shale. In general, coal (*i.e.*, its predominant insoluble organic fraciton) may be regarded as a special type of kerogen derived mainly from terrestrial organic matter. The experimental approach described (see experimental section: heating experiment) was designed to model, in an admittedly idealized fashion, possible the VO^{2+}-DPEP/kerogen interactions (at eventual disposal sites). Thus, our laboratory experiments, heating coals in the presence of VO^{2+}-DPEP, model the geological thermal incorporation of VO^{2+}-DPEP into kerogen. We employed in our thermal experiments VO^{2+}-DPEP as a type VO^{2+}-P. This is particularly appropriate because this type of porphyrin is the predominant VO^{2+}-P in most petroleum source rocks.

The coals were chosen to model immature kerogen (algal coals, lignites, subbituminous coal) and very mature kerogen (anthracite) found in sedimentary environments.

EXPERIMENTAL

Samples

The Triassic Se marl sample used was from the outcrop site. The bitumen fraction of this rock is characterized by a high concentration of VO^{2+}-P (mostly of the DPEP-type, *i.e.*, DPEP/ETIO porphyrin ratio >100).[5]

The samples selected for the present study ensured a large range of geochemical composition of the coals to be examined. 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. The eight coal samples used in this work are described briefly in Table I.

Separation and extraction

The whole rock/coal sample were crushed/powdered and the minor carbonates/silicates were removed with HCl/HF, and the pyrite decomposed with LiAlH$_4$.[12] The residues were dissolved by refluxing (Soxlet) for 48 h in benzene:methanol (6:1 v/v), centrifuged (2 h), the supernatants filtered (5 cm pore filter) and the solvent evaporated. The isolated coal residues were examined by X-ray diffraction.

Ultraviolet (UV)-visible (VIS) spectrophotometry

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

Electron spin resonance (ESR)

The 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. The signal intensities (proportional to the VO^{2+}-P concentraiton) were calculated by double integration of the first derivative ^{51}V hyperfine ($m_I = -5/2$) line using the COMPUTER DESIGN system.

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

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

Heating experiment

        The simulated geothermal experiments were performed on the DPEP concentrate (hereinafter referred to 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 × 100 mm), flushed with O_2-free N_2 and sealed under vacuum. The sealed glass tubes were then heated at 200 °C for up to 72 h. After cooling, the extractable part of the VO^{2+}-DPEP coated on the 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 content using ESR.

RESULTS AND DISCUSSION

        The ESR spectrum of the VO^{2+}-P incorporated into the Se kerogen structure(s) is shown in Fig. 1a. The reaction of VO^{2+}-DPEP and torbanite results in the almost
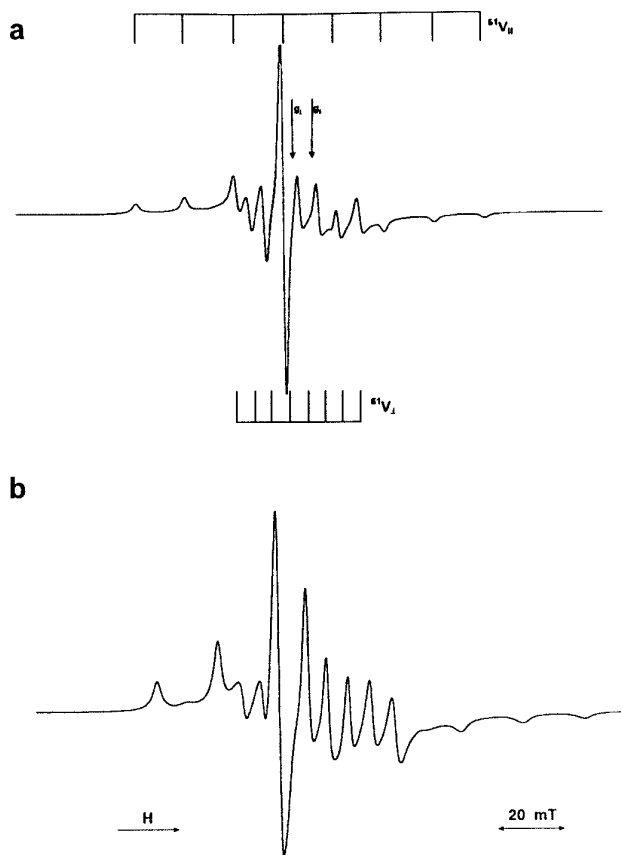

Fig. 1. First derivative room temperature X-band anisotropic ESR spectra of: (a) VO^{2+}-P of the Se kerogen, (b) VO^{2+}-P incorporated into the torbanite macromolecular structures by laboratory thermal treatment.

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. 1b, which can be seen to be almost identical to the VO^{2+}-P within the Se kerogen (Fig. 1a). 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 the incorporation of VO^{2+}-DPEP into both tasmanite and anthracite were unsuccessful.

Although the above results must be considered initial they show that VO^{2+}-DPEP reacts 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 reach temperatures of 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 categenesis is applied to the transformation occuring between approximately 60 °C, and 150 °C, depending an the geologic age of the rock.[7] According to current thinking, during early catagenesis (at temperatures within the range 60 °C and 90 °C), a heavy (and immature) petroleum containing rather large molecules with heteroatoms (O, N, S) (such as asphaltene molecules) is released. Thus, 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 sedimentary carbonaceous rocks, which are commonly regarded as source beds of petroleum. Obviously, the reactions at temperatures 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 the 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 of reacting with VO^{2+}-DPEP at temperatures $\leq$ 200 °C and to incorporate VO^{2+}-DPEP into the polyaromatic network of this coal. This fact implies that VO^{2+}-DPEP cannot be thermally incorporated 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 the 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) with 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.

TABLE I. Coals/kerogen used for the VO^{2+}-DPEP incorporation

Name Coal/kerogen	Location	Age	Type
Torbanite	Scotland	Carboniferous	Algal coal[1]
Tasmanite	Tasmania	Permian	Spore coal[2]
Kostolac	Serbia	Tertiary	lignite[3]
Kolubara	Serbia	Tertiary	lignite[3]
Kosovo	Serbia	Tertiary	lignite[3]
Soko	Serbia	Tertiary	subbituminous (brown) coal[3]
Vrška Čuka	Serbia	Jurassic	anthracite[3]
Aleksinac	Serbia	Tertiary	immature lacustrine kerogen[4]

[1]Cane and Albion, 1971. [2]Aquino Neto *et al.*, 1992. [3]Pantić and Nikolić, 1973. [4]Djuričić *et al.*, 1971.

The unreactivity of tasmanite towards VO^{2+}-DPEP may be due to the fact that this coal contains, chemically speaking, very resistant and tough organic materials.[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 only with certain types of kerogen (*e.g.*, torbanite *vs.* tasmanite) which were particularly predominant in certain sedimentary basins.

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 ºC: *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 type of bonding but chemical. Furthermore, exhaustive refluxing (Soxhlet) extraction treatment (*c.f.* heating experiments) provides strong experimental evidence that the VO^{2+}-DPEP are bound *via* covalent bonds to the kerogen-like materials studied.

It is likely that the incorporation of VO^{2+}-DPEP into the kerogen model macromolecules will depend heavily upon the nature of the functional groups on their periphery. Evidently, 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 regorous manner. Perhaps the chemical reaction of the alkadiene type of C=C bonds might be involved in the torbanite case.[14] Namely, it is possible that the reduction of the torbanite alkadiene

C=C bonds during laboratory heating results in VO^{2+}-DPEP being attached to the torbanite nucleus. The interaction of VO^{2+}-DPEP with the lignites/subbituminous coal studied, however, indicates that the oxygen-containing functional groups in these materials might be involved in its binding to their macromolecules. Namely, one of the most characteristic features of these low rank coals is their relatively high content of oxygen-containing functional groups[15] (especially CO_2/phenolic OH). It may be tentatively concluded that the funcitonal 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 C=C bonds nor are they 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, as well as lipids and dextran are capable of incorporating 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 obtain evidence as to whether VO^{2+}-DPEP can be incorporated into an immature kerogen during categenesis, we thermally treated an immature kerogen, isolated from the Aleksinac shale, in the presence of VO^{2+}-DPEP. The result indicates that the 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_2/phenolic OH units.[16] It is apparent that these groups might act as covalent bonding sites for the 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.

Summarizing up to this point, it may be concluded that, given a kerogen with appropriate functional groups, VO^{2+}-DPEP could be naturally incorporated into the matrix of relatively immature kerogens. This has considerable significance in the geochemistry of VO^{2+}-P because it demonstrates a mechanism for the evolution of kerogen VO^{2+}-P and, at the same time, gives a good indication of the stability of VO^{2+}-P, once formed, to the geochemical exposure to which they are subjected. In this way VO^{2+}-DPEP can easily be 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 the VO^{2+}-DPEP themselves and, thus, have a large potential for survival during catagenesis. Namely, recent thermal ESR experiments have shown the partial decomposition of the kerogen VO^{2+}-P when heated at 300 ºC, 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 the thermal incorporation of VO^{2+}-DPEP into the kerogen-model/kerogen frameworks are also relevant to natural/laboratory 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 experiments 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 above. A preliminary kinetic study shows that the incorporation rate of VO^{2+}-DPEP into the models during laboratory heating at 200 ºC is about 500 × faster in the presence than in the absence of air. Thus, these results suggest that oxidation of the kerogen models by air O_2 may play an essential role for the incorporation of VO^{2+}-DPEP into their macromolecular structures in the presence of air. In general, oxidation of coal at 200 ºC 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 VO^{2+}-DPEP binding. According to Kalema and Galavas,[18] the 200 ºC oxidation incorporates a variety of new oxygen funcitonalities (the carboxylic, carbonyl and phenol units) resulting in the formation of so-called "regenerate humics/protokerogen". Thus, 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 macromolecular structures.[20] Unless the coal VO^{2+}-P are generated during the very early stages of diagenesis, we may tentatively propose that opportunities also existed for the incorporation of VO^{2+}-DPEP into the structures of these two coal materials during catagenesis.

CONCLUSIONS

1. The simulation experiments described in this paper clearly show that VO^{2+}-DPEP readily reacts 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 the intensive-oil production stage (catagenesis) as secondary kerogen VO^{2+}-P.

И З В О Д

КЕРОГЕНСКИ ВАНАДИЛ ПОРФИРИНИ: УГРАДЊА ТОКОМ КАТАГЕНЕЗЕ

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Показано је да су природни ванадил (VO^{2+})-деоксофилоеритроетиопорфирини (DPEP) способни да се квантитативно уграђују у структуре незрелих модел керогена (торбанита, лигнита, мрког угља и незрелог језерског керогена) на 200 ºC за 72 h у присуству/одсуству ваздушног кисеоника. Коришћена је метода електрон спин резонанције да би се одредило да ли је дошло до уградње VO^{2+}-DPEP у наведене моделе. Производ уградње подсећа на природни кероген обогаћен са VO^{2+}-DPEP. Описани експерименти јасно показују да керогенски VO^{2+}-P могу потицати од уградње VO^{2+}-DPEP у макроструктуре керогена током катагенезе.

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