The Vrška Čuka anthracite shows contents of 16% inorganic compound and 84% organic matter, out of which 82% is kerogen and <2% is bitumen. X-ray diffraction (XRD) indicates the presence of the graphitic structures. The electron spin resonance (ESR) shows a high concentration of polyaromatic paramagnetic structures (PPS; $4.5 \times 10^{19}$ spins g$^{-1}$). The Fourier transform infrared spectroscopy (FTIR) reveal that the Vrška Čuka kerogen contains predominantly aromatic/polyaromatic structures. Analysis of the aromatic area shows both the absence of aromatic substituents and the presence of aromatic polycondensation (average 3-4 rings; $\geq 17$ carbon atoms). The spectrum also shows considerably reduced absorptions corresponding to the presence of aliphatic groups. Most of the aliphatic carbon is present as CH$_3$ (probably in short alkyl chains- methyl/methylene attached to polyaromatic structures) as indicated by the CH$_3$/CH$_2$ value 0.7 of the appropriate absorptions. It was suggested that polyaromatic structures were formed by polycondensation of aromatics during kerogen maturation. Low atomic values of H/C and O/C (0.45 and 0.07) indicate a high degree of genesis (metagenesis). The result of these analyzes are in agreement with each other and show that the maturation of this kerogen led to the formation of polyaromatic structures from aromatic.

**Introduction**

Except for industrial purposes, the study of coal is significant, because based on their geochemistry, ancient geochemical records from the past can be determined. Coal changes its properties with increasing thermal maturities. The availability and combination of various modern analytical techniques enable a detailed study of the geochemical conditions of its sedimentation and genesis. Also, polyaromatic structures in the kerogen could be identified more accurately in coal and organic-rich sediments.

Geological research by J. Žujović at the end of the XIX century showed that the carbonaceous formations from this area were from the Jurassic Period. Later research has shown that during the Late Triassic Period, the regression of the Carpathian Sea to the east occurred, from many parts of Eastern Serbia [1-3]. During the Early Jurassic, transgression of the Carpathian sea has occurred in the studied area. On the coasts of the Jurassic Sea, over time, organic-rich sediments were deposited [4]. Anthracite was formed from these deposits at Vrška Čuka, Dobra and Jerma.

Anthracite coal from Vrška Čuka is suitable for geochemical and technological research, as well as flotation kinetics, but it is little known as such in the world [5,6].

The overview of mineral resources of Serbia defines Vrška Čuka anthracite as high-rank bituminous coals with vitrinite reflection $\geq 2.20\%$ Rr, moisture $\leq 5\%$, carbon content $\geq 80\%$ with net calorific value $\geq 35$ MJ/kg [7]. Premović et al. [8,9] were studying the organic free radicals in Worldwide Precambrian and Paleozoic kerogen samples. The results of this investigation show that Vrška Čuka kerogen has the biggest concentration of PPS of the investigated samples. Recent research of polyaromatic hydrocarbons of anthracite from Chengzhuang (China) and the Czestochowa region (Polish Jura) showed that the aromatic layers tended to be parallel by intramolecular or intermolecular π-π interaction [10,11]. For this reason, a detailed analysis of the polyaromatic structures was done.

Geological and tectonic settings

The Vrška Čuka mine is a Lower Jurassic coal basin located 250 km southeast of Belgrade and 12 km east of Zaječar (Figure 1.). A complete Jurassic section is exposed in Vrška Čuka anticline. They include Liasic clastites with coal and Jurassic limestone. The Vrška Čuka anthracite has black-grey color, metallic-glass shine, and depending on its metamorphosis can appear...
as graphite. The area of Vrška Čuka is a complex anticline structure stretches SE-NW, with the axis sinking to NW under Neogene sediment. The most important fault is Velika raselina, which divided the NE anticline limb from the anticline core [12]. Strong tectonic movement and lithological diversity characterized this area. From the aspect of tectonic activities, this area can be divided into several coal areas [13]: east anticline limb or Velika Čuka area, Limestone plateau (Krečnjački plato); Kantarji hill (Kantarjiško brdo) and Mala Čuka area. Today, the Mala Čuka area is the only exploitation area. The oldest rock in the research area is a low crystalline complex presented by phyllitoid and green rocks (F) and pGama Plagiogranite (py). These rocks are from the anticline core of Vrška Čuka. Gabro (νC) was impressed in the phyllitoid of the anticline, while diabase (bbC) was poured over the phyllitoid. Upper Carboniferous (C) is presented by sandstone, conglomerates, and shale with thin layers of hard coal. The formation of Red Permian sandstone (P) lies over the carboniferous series of Quartz-porphyrite breaking through the older rock.

The period of Jurassic has a complete development. Lower Jurassic (J1 or Liassic) sediments, conglomerates, quartz sandstone and clay contain fossil flora and fauna originating from carbonaceous shale accompanying the coal layers. Middle Jurassic (J2) sediments are presented by the limestone of the Upper Jurassic. Jurassic sediments are spatially well-developed in the area of Vrška Čuka. Detailed lithostratigraphic Jurassic epoch (Middle and Upper) of the Vrška Čuka was described by Veselinović, Andjelković, et al, and Tcoumatcenco [14-16]. The authors distinguished six distinctive layers: 1) Vratnac limestones: reef and sub-reef limestones (J2), 2) Greben ammonitic limestones: clayey nodular limestones with cherts (J2+3), 3) Sandy limestones (J2), 4) Staro Selo Beds: yellow marine sandstones (J2+3), 5) Vrška Čuka coal beds: yellow sandstones, coal schists and sandstones lying discordantly over Permian rocks.

Figure 1. - Location and geological map of Vrška Čuka (based on [12]).

The lower Cretaceous is the best developed in the north of Vrška Čuka. Valanginian (K1) and Heterirvan (K1+2) stages are presented by flysch, sedimentary rocks deposited in deep marine facies. Aptian (K1) sandstone represents the end of sedimentation Jurassic-Lower Cretaceous rocks. Marls, fine-grained clay sandstone of Albian (K1) lie over Jurassic limestone. The Upper Cretaceous is not as widespread as the Lower Cretaceous in the area of Vrška Čuka. Sediments of the Upper Cretaceous (K1, K2) are present in the southern part and presented by sandstone, shale, conglomerates with volcano-clastic rocks as well as andesite, basalt and trachites (xB). Neogen is presented with Miocene sediments (M2,3) and is widespread in the west of Vrška Čuka. These sediments represent sandstone, sandy clay, marls with coal, conglomerate, sand and gravel. Quaternary sediments appear next to Beli Timok, as terrace sediments (t, and f) presented by gravel and sand,
as well as prolluvial (pr) and alluvial sediments (al).

**Experimental**

Sample preparation and fractionation.

The kerogen extraction procedure was previously described by Premović et al. [18] and Wolbach and Andres [19]. The anthracite sample (handpicked from a convey- or) was ground to a fine powder (200-400 mesh) with a ball mill. After that, this sample was treated with boiling HCl (6 M, 8 h, 80 °C). This acid solution removes the carbonates and oxides. The insoluble portion comprises the HCl-insoluble fraction. A solid remnant of this and all subsequent fractions were filtered, washed and dried in a laboratory oven at a temperature of 102 °C. Thereafter, the remaining inorganic compounds were acid leached by digestion for 8 h at 80 °C using a 3:1 (v/v) mixture of HF (22 M) and HCl (12 M) and then again with boiling HCl (6 M, 8 h, 80 °C). In this way, organic concentrate was produced, which is not pure kerogen so it is necessary to purify it from organic admixture (mainly bitumen). Pure kerogen was obtained by extracting impurities from the concentrate with an azeotrope benzene/methanol mixture.

X-ray diffraction (XRD).

This analysis was used to determine the content and amount of inorganic and organic components in the Vrška Čuka coal as well as the presence of graphitic structures in its kerogen. The Rigaku Ultima IV powder diffractometer (Rigaku Corporation, Tokyo, Japan) was used. The X-ray beam was nickel-filtered CuKα radiation (λ = 0.1540 nm, operating at 40 kV and 40 mA). The results were done 5-90° (2θ) in a continuous scan mode (0.02°, 5°/ min). The results have been checked to the patterns of the International Centre for Diffraction Database.

Electron spin resonance.

The ESR spectrum was done on finely ground pow- ders of the Vrška Čuka anthracite, which was placed in pure silica tubes. The Spectrum was done on a Bruker ER-200 instrument (100 kHz field modulation).

**Fourier Transform Infrared Spectroscopy.**

Coal samples were finely powdered and dispersed evenly in anhydrous potassium bromide (KBr) pellets (1.5 mg/150 mg KBr). FTIR Spectra were taken at room temperature using a Bomem (Hartmann & Braun) MB-100 instrument with a resolution ± 4 cm⁻¹.

**Ultimate analysis.**

Ultimate analysis was performed on a Vario EL III C, H, N, S/O Elemental Analyzer (Elementar Analyseanalyse Systeme GmbH, Hanau-Germany) under the following conditions: the combustion temperature is 1150 °C, a carrier gas-helium and a detector-TCD. The dynamic working range of the apparatus is as follows: C: 0.03-20 mg; H: 0.03-3 mg; N: 0.03-2 mg; S: 0.03-6 mg.

**Results and discussion**

**Inorganic mineral vs. Kerogen**

Selective leaching procedures and results of Vrška Čuka anthracite show contents of 16% inorganic compound and 84% organic matter, out of which 82% is kerogen and <2% is bitumen. Figure 2 shows the XRD pattern of anthracite. On the diagram, one can distinguish very sharp peaks and broad ones. The very sharp and intense peak 0.02 (2θ) indicates the presence of a well-crystallized graphite phase (sp² hybridization). Apart from it, there are low-intensity peaks of graphite 100 at about 42 °2θ, 101 at about 45 °2θ and 004 at 55 °2θ. The peak at 30 °2θ is CaCO₃ which is an anthracite admixture. Other peaks were attributed to different forms of sedimentary carbon. Mechanisms of graphite formation from kerogen were described by Bustin et al. [20]. According to these authors, graphite was produced from anthracite starting material at temperatures <600 °C.

**Aromatics in the Vrška Čuka kerogen**

The ESR spectrum of the Vrška Čuka anthracite is devoid of any hyperfine structure and can be described as a nearly Lorentzian symmetrical signal (Figure 3.). This line is characterized by the following ESR parameters: g-value (2.0034 ±0.003) and line widths 0.49 (±0.05) mT. This finding is in agreement with the ESR study of the Vrška Čuka anthracite by Premović [13], which implies that high polyaromatic character having a very high content of PPS (4.5×10¹⁵ spins g⁻¹).
Moreover, the FTIR spectrum of kerogen is dominated by a strong band centered in the 1602 cm\(^{-1}\) region (Figure 4.), which is characteristic of solid carbonaceous systems and is generally assigned to large polyaromatic carbon skeletons \([21]\). A weak band at 1700 cm\(^{-1}\) is usually ascribed to the carbonyl groups. Three considerably reduced absorption bands in the 3100 cm\(^{-1}\) to 2700 cm\(^{-1}\) zone indicate the presence of aliphatic structures in the kerogen and a weak absorption at 3050 cm\(^{-1}\) is related to aromatic/polyaromatic structures \([21,22]\). Further evidence for aromatization/poly-aromatization is seen in absorption bands in the 900-700 cm\(^{-1}\) region. These bands are assigned to aromatic/polyaromatic structures with isolated aromatic hydrogen atoms (870 cm\(^{-1}\)), two adjacent hydrogen atoms per ring (810 cm\(^{-1}\)) and four adjacent aromatic hydrogen atoms (750 cm\(^{-1}\)) \([23]\). The number of adjacent hydrogen atoms per ring provides an estimate of the degree of aromatic substitution/polyaromatization. The Vrška Čuka aromatic/polyaromatic has the most intense band at 750 cm\(^{-1}\). This band is attributed to average aromatic sizes of 3 to 4 rings or more (\(\geq 17\) carbon atoms). Thus condensed aromatic nuclei (3 to 4 rings) should be present in the Vrška Čuka kerogen.

For the region of 3100 cm\(^{-1}\) to 2700 cm\(^{-1}\) in the FTIR spectra of three kerogen samples, there are three principal bands, near 2955 cm\(^{-1}\), 2920 cm\(^{-1}\) and 2860 cm\(^{-1}\), that can be clearly assigned to methyl/methylene groups attached to alkyl chains/aromatic rings. In general, from curve-fitted various FTIR bands of kerogen a series of relationships defined as ratios of integrated absorbance areas may be used to quantify the structural characteristics. The relationship used here was the following: the \(\frac{\text{CH}_3}{\text{CH}_2}\) ratio = 2955 cm\(^{-1}\) band/2920 cm\(^{-1}\) band. For most of the kerogenous materials of the Vrška Čuka anthracite kerogen, the \(\frac{\text{CH}_3}{\text{CH}_2}\) ratio is 0.7. This is probably due to the loss of alkyl chains and conversion of various aromatic methylene structures to polyaromatic rings during catagenesis of the Vrška Čuka kerogen. This claim is consistent with the structural characterization of the organic species in Jincheng No.15 anthracite, with the fact that this sample contains five rings on average \([24]\).

Overall, the FTIR spectrum supports the concept of an aromatic/polyaromatic macrostructure, in accord with mature kerogen assignment based on elemental analysis. This finding is in agreement with ESR observations that the Vrška Čuka kerogen has reached its aromaticity with increasing natural maturation as evidenced by the higher content of polyaromatic structures.

Depositional environments and maturity of kerogen

Saxby \([25]\) lists five basic mechanisms by which organic matter can become part of sediment: direct supply of organisms, absorption of dissolved organic molecules, precipitation, detrital supply, and hydrocarbon migration. With increasing temperature and depth of burial, this organic material undergoes changes analogous to coalification or maturation.

One of the requirements for the formation and preservation of both bio-organic substances (as the proto-
kerogen precursor and proto-kerogen during early diagenesis) are anoxic conditions at the water/sediment interface and within the upper part of the sediment [26]. The high content of kerogen strongly suggests that their depositional environment was anoxic conditions [27]. This type of environment is also suitable for the preservation/maturation of kerogen during the latter stages of genesis [9].

During the genesis and maturation, the resulting kerogen undergoes structural changes that were detected in the previous analysis. In order to interpret these changes, a decrease in O/C and H/C ratio is observed. Analytical data for Elemental analysis of the Vrška Čuka kerogen are N 0.7%, C 86.7%, H 3.3%, and S 1.0%. In a van Kreleven diagram the three types of kerogen are plotted (Figure 5.). Obviously, kerogen shows a small concentration of H and a therefore low H/C ratio (0.45). According to Tissot and Welte [27], this low ratio is characteristic of mature kerogens. By reading the data from the van Kreleven diagram, it can be seen that Vrška Čuka is a kerogen in the phase of metagenesis, which is characteristic of kerogens of the highest maturity only.

**Conclusions**

The Vrška Čuka anthracite shows a content of 16% inorganic compound and 84% organic matter, out of which 82% is kerogen and <2% is bitumen. The percentage of C increases with thermal maturity, mainly in the form of condensed aromatic moieties, as reflected by the ESR and FTIR. Organo-geochemical evidence suggests that kerogen contains predominantly polyaromatic structures with a relatively high concentration of PPS and ≥20 carbon atoms. The low atomic H/C ratio of the Vrška Čuka kerogen indicates that the degree of genesis is quite advanced (metagenesis).

**References**


[12] Veselinović M, Divljan M, Đorđević M, Kalenić M, Milošković R, Rajčević D, Popović R, Rudolf LJ. Tumač za osnovnu geološku kartu SFRJ 1:100.000, list Zaječar L63 [Explanatory booklet of the basic geological map of the SFRJ 1:100.000, Zaječar sheet-In Serbian]. Savezn
POLIAROMATIČNE STRUKTURE U KEROGENU ANTRACITA SA LOKALITETA VRŠKA ĆUKA (KARPATO-BALKAN REGION, SRBIJA)

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Vrška Ćuka antracit sadrži 16% neorganskih minerala i 84% organske materije od koje je 82% kerogena i <2% bitumen. XRD analiza ovog kerogena ukazuje na prisustvo grafitnih struktura. Analiza aromatičnog područja pokazuje prisustvo grafitnih struktura. ESR analiza pokazuje visoku koncentraciju radikala PPS.

Izvodom

Vrška Ćuka antracit sadrži 16% neorganskih minerala i 84% organske materije od koje je 82% kerogena i <2% bitumen. XRD analiza ovog kerogena ukazuje na prisustvo grafitnih struktura. ESR analiza pokazuje visoku koncentraciju radikala PPS (4,5×1019 spins g-1) u uzorku. FTIR istraživanja pokazuju da Vrška Ćuka kerogen sadrži pretežno aromatično/kariorganatične strukture. Analiza aromatičnog područja pokazuje odsustvo aromatičnih supstituenata i prisustvo aromatične polikondenzacije (prosečno 3-4 prstena, ≥17 C atoma). Spektroscopicni alifatični ugljenik je prisutan kao CH3, koji je u aromatičnim strukturama većina alifatičnih ugljenika.

Ključne reči: Vrška Ćuka, antracit, kerogen, poliaromatici, metageniza

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