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Stable isotope geochemistry of different lithotypes of the Velenje lignite (Slovenia)

Geokemija stabilnih izotopov različnih litotipov velenjskega lignita

Tjaša KANDUČ[1], Miloš MARKIČ[2] & Jože PEZDIČ[3]
[1]Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia,
tjasa.kanduc@ijs.si
[2]Geological Survey of Slovenia, Dimičeva 14, SI-1000 Ljubljana, Slovenia, milos.markic@geo-zs.si
[3]Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana,
Aškerčeva 12, SI-1000 Ljubljana, joze.pezdic@ntfgeo.uni-lj.si

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Abstract

The stable isotope composition of carbon and nitrogen in low-rank coals is often used as a supplementary method to assess coal-forming processes in different paleoenvironments. In this study, carbon and nitrogen isotopes were investigated in different macroscopic varieties i.e. lithotypes, of the Velenje lignite. $\delta^{13}C$ and $\delta^{15}N$ values were determined in 47 samples. The quantity and petrographical variability of the samples is considerably higher than in previous studies. $\delta^{15}N$ characterization of the Velenje lignite is presented in this paper for the first time. It was found that $\delta^{13}C$ and $\delta^{15}N$ values of different lignite lithotypes were influenced by original isotopic heterogeneity of the source plant ingredients, and by biogeochemical processes (gelification, mineralization of organic matter) at the early stage of biomass accumulation and its early diagenesis.

Povzetek

V premogih nizke stopnje karbonizacije uporabljamo stabilne izotope ogljika in dušika kot dopolnilno metodo pri določevanju procesov nastanka premogov v različnih paleookoljih. V naši raziskavi smo določili stabilne izotope ogljika in dušika v 47 vzorcih različnih litotipov velenjskega lignita. Preiskali smo znatno večje število vzorcev kot v predhodnih raziskavah in prvič doslej smo določili $\delta^{15}N$ vrednosti. Ugotovili smo, da na vrednosti $\delta^{13}C$ in $\delta^{15}N$ različnih litotipov lignita vplivajo tako izotopske značilnosti prvotnih rastlinskih komponent kot biogeokemični procesi (gelifikacija, mineralizacija organske snovi) v zgodnji fazi akumulacije biomase in zgodnji diagenezi.

Introduction

The Velenje lignite is palinologically characterized by the predominance of gymnosperms over angiosperms (Šercelj, 1985/86, Hemleben et al., 2000). Recent investigations of biomarkers in the Velenje lignite (Bechtel et al., 2003) indicate that gelification of plant tissues might be governed by the activity of anaerobic rather than by aerobic bacteria. They also indicate that biogeochemical decomposition of plant tissues by bacteria affected $\delta^{13}C$ values of the lignite.

The isotopic composition of carbon in low-rank coals may be used to reconstruct changes in the global carbon cycle, as well as climatic changes (Lücke et al., 1999, Arens et al., 2000). Plants use atmospheric CO_2 to produce carbohydrate (CH_2O) during photosynthesis by three pathways: the C3 or Calvin pathway, the C4 or Hatch–Slack pathway, and CAM cycle photosynthesis. The amount of fractionation depends on the pathway followed. In all cases, photosynthetic uptake of CO_2 is accompanied by significant depletion in ^{13}C. Organic matter produced from atmospheric CO_2 ($\delta^{13}C \sim -7$ ‰) by land plants using the C_3 pathway consequently has an average $\delta^{13}C$ of -27 ‰ (VPDB), and by the C_4 pathway of about -14 ‰ (O'Lary, 1988). It is difficult to determine the specific process governing $\delta^{13}C$ of bulk organic matter since different environmental factors such as atmospheric CO_2, the type of plant material, bacterial degradation and temperature of formation can influence the $\delta^{13}C$ value of coal (Duponey et al., 1993, Schleser, 1995).

Organic nitrogen in sedimentary organic matter represents the transfer of nitrogen from the atmosphere to the lower crust. $\delta^{15}N$ of bulk organic matter in sediments depends on $\delta^{15}N$ of atmospheric nitrogen, the source of the organic matter and on biogeochemical processes such as ammonification, nitrification and denitrification. However, the fate of organic nitrogen and denitrogenation during early and late stages of diagenesis is still poorly understood (Ader et al, 1998). $\delta^{15}N$ can be used to distinguish between either prevailingly algal or land–plant sources of the host organic matter. It was shown (Peterson & Howarth, 1987) that the nitrogen reservoir difference is preserved in the isotopic contents of organic matter produced by plankton ($\delta^{15}N$ of + 8.6 ‰) and C3 plants ($\delta^{15}N$ of + 0.4 ‰) in an estuarine ecosystem.

In comparison to previous isotopic studies of the Velenje lignite (Pezdič et al., 1998; Bechtel et al., 2003) the present one embraces spatially much more widely distributed samples, both vertically and laterally. Since data on $\delta^{15}N$ for world–wide coals are quite scarce, $\delta^{15}N$ for the Velenje lignite were determined for the first time. Sampling of

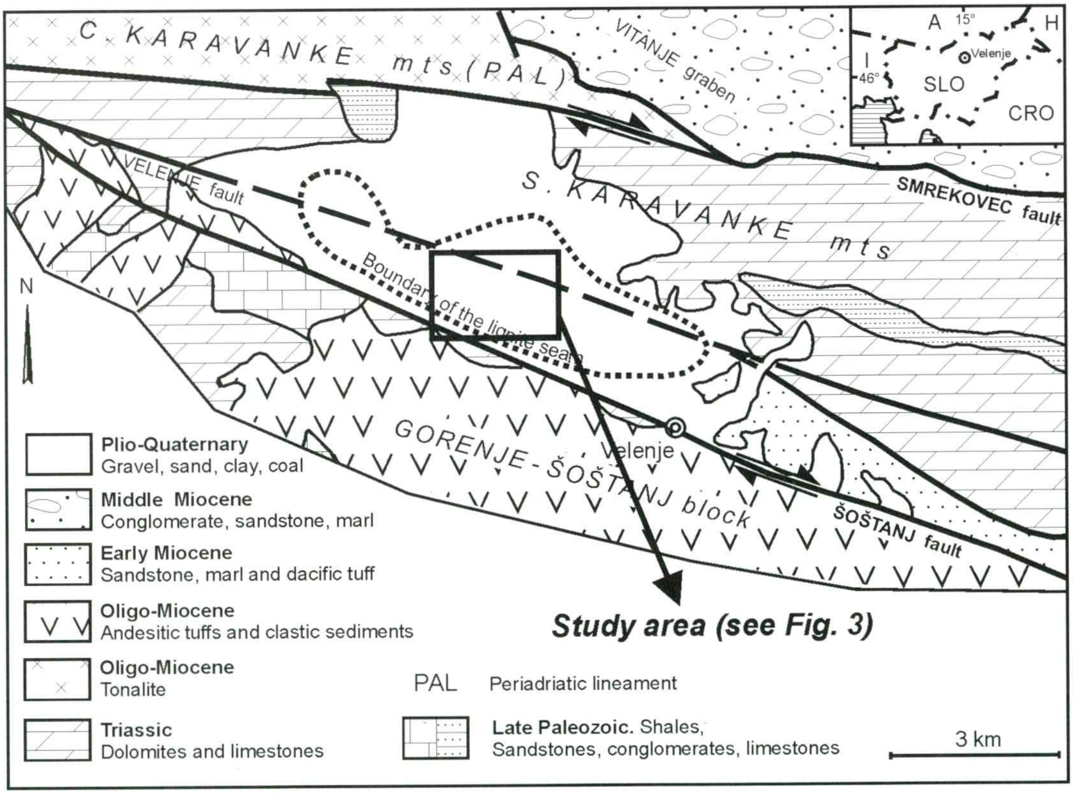

Figure 1. Geological map of the Velenje lignite basin (simplified after Brezigar et. al., 1987).

the lignite was carried out on the basis of its macropetrographic heterogeneity described in terms of lithotypes. Correlation between the lithotypes and their isotopic composition, both resulting from specific vegetal precursors and specific peat/lignite-forming processes, was the main target of this study.

Geological setting and lignite formation

The Velenje basin is situated in the NE part of Slovenia (Fig. 1). It is located between the WNW–ESE trending Šoštanj fault and the E–W trending Smrekovec fault, which represents a segment of the dextral strike-slip Periadriatic lineament. The Periadriatic lineament was formed due to collision of the Adriatic and the European continental plates 35 Ma ago (Fodor et al., 1998). In the Oligocene, the heavier oceanic plate sank into the mantle. Due to partial melting and fracturing, tonalite intrusions and andesitic extrusions with corresponding volcaniclastics were generated and deposited in the wider area. Pre-Oligocene rocks of the Velenje area consist mainly of Triassic limestones and dolomites, whereas the Oligo-Miocene non-volcanic sediments consist of differently lithified marls, silts, clays and sands.

In Pliocene times, tectonic activity gradually ceased. Sedimentary filling of the intermontane depression started with terrigenous coarse clastics (Fig. 2) of the predominantly high energy fluvial environment. Due to the energy decrease of the depositional environment, accumulation of coarse clastics was gradually replaced by finer clastics. As a final result of this tecto-sedimentary process, a peat-forming marshy environment was established. Decimetre to metre thick beds of mineral-rich lignite and claystones represent the record of the initial marshy sedimentation. Due to a further decrease in inorganic input, more and more clean peat was accumulated giving rise to what we know at present as the Velenje lignite seam. Taking into account the maximum lignite seam thickness of 160 m (Brezigar, 1985/86), an estimated 2:1 peat-to-lignite compaction ratio and 1 mm peat growth per year (Taylor et al., 1998), it can be roughly concluded that the time of peat accumulation lasted for about 300,000 years. Considerable ash contents (15–40 weight % on a *dry basis;* increasing with depth) and the petrographic characteristics of the lignite indicate that the original peat-forming environment was in general topogenous, with alternations between the following vegetation subenvironments (based on petrographic indices): wet forest swamp, dry forest swamp, bush moor, and fen (Markič & Sachsenhofer, 1997). As known from palinological investigations (Šercelj, 1985/86, Hemleben et al., 2000) *Taxodium, Sequoia, Osmunda and Tsuga* floristic species were the most important contributors to the forest and bush vegetation. Sulphur contents (Stot, *dry basis,*) in the Velenje lignite mostly vary between 2 and 3 wt. % (Markič & Sachsenhofer, 1997). In the case of freshwater peats, such high S contents are known for Ca-rich environments characterized by neutral or even alkaline pH values (up to

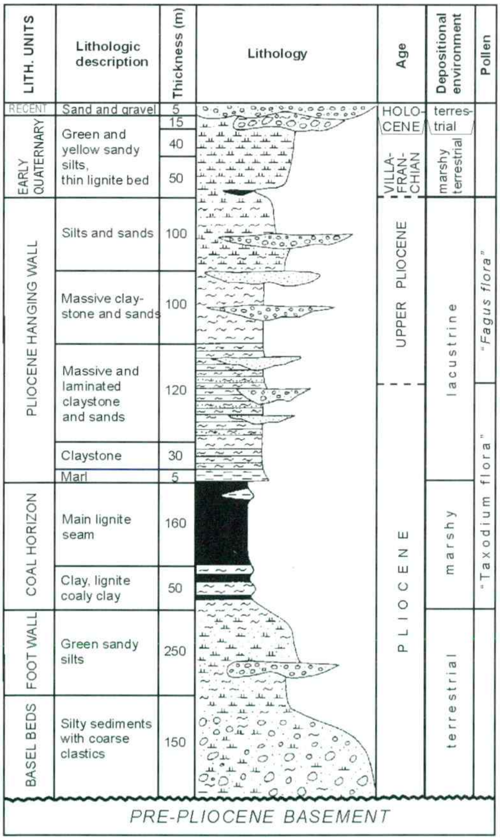

Figure 2. Typical stratigraphic column of the Velenje basin sedimentary fill (after Brezigar 1985/86).

8.6) (Taylor et al., 1998). Calcite replacement and incrustations of vegetal remnants, as well as increased CaO contents in the low-ash Velenje lignite samples (recent investigations) provide support to this thesis. It is well known that alkaline environments promote a high bacterial activity, crucial for reduction of sulphates to sulphides (formation of marcasite/pyrite), as well as for biochemical degradation (gelification) of organic matter.

Variability in vegetal precursors and coalification processes is reflected in the petrography of the lignite. It is characterized by different ratios of xylitic fragments of very different dimensions compared to fine detrital matrix. Fusinitic particles can be mostly observed as incrustations over xylitic lumps. Mineral-rich varieties of fine detrital lignite occur especially at the bottom of the seam. Quite common are xylitic fragments replaced by epigenetic calcite. Such forms occur in separate layers, but are particularly frequent in the close vicinity of faults and fractures (Vrabec, personal communication). Fine detrital lignite is gelified to different degrees. If nongelified, it is dark brown, whereas it is black or even brittle, if strongly gelified. Gelification increases toward the top of the seam (Markič & Sachsenhofer, 1997). However, it is interesting that gelified xylites occur in the lower part of the seam, whereas they are almost absent in the upper part.

Peat accumulation, the thickest in the basin centre and pinching out toward its periphery, was terminated due to its deeper submersion below the water surface. Vegetation development was replaced by a lacustrine sedimentation of marls, clays and silts, sporadically interrupted by fluvial sedimentation of sands and gravels (Brezigar, 1985/86). Accommodation space for the post-peat sedimentation was mainly governed by the syn-sedimentary activity of the Šoštanj and Smrekovec faults.

The total Pliocene to Holocene sedimentary fill of the basin reaches more than 1000 metres.

Dislocations of the lignite seam (up to 70 m) and of the Pliocene to Plio-Quaternary (Villafranchian) hanging-wall strata with the greatest effects along the dextral strike-slip Šoštanj fault and obliquely related ac-

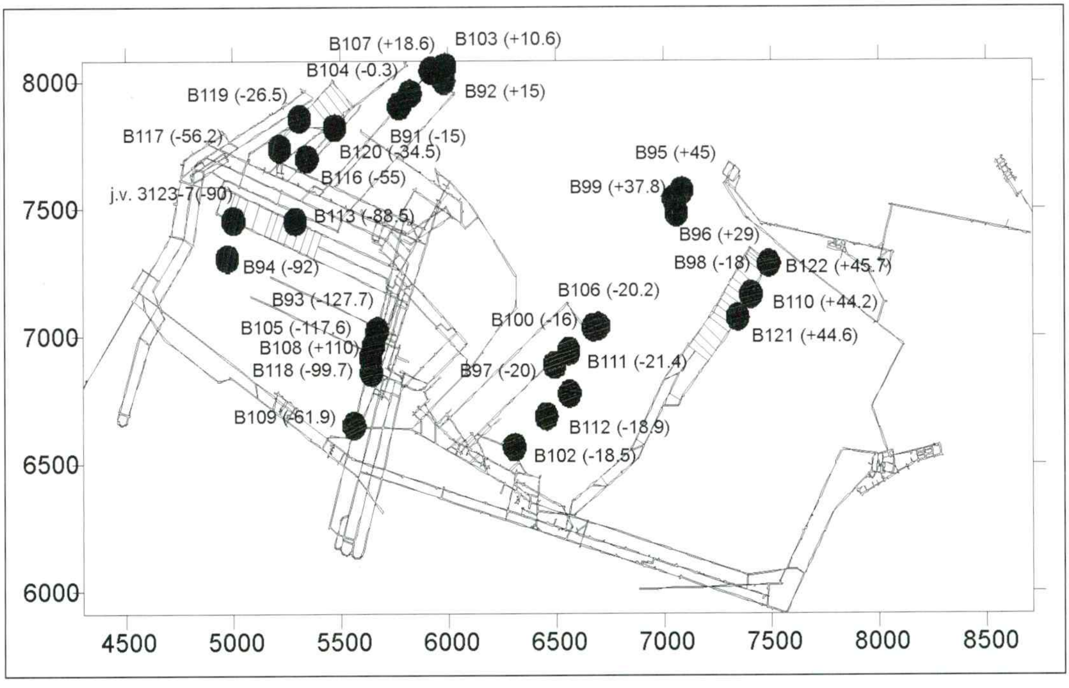

Figure 3. Map of sampling locations (heights relative to the sea level are cited in parentheses); borehole j.v. 3123-7 coincides with boreholes D70 (1-4), L45 (2), 115 (1-4).

companying faults, indicate a strong tectonic activity of the area in its very young geological history (Brezigar, 1985/86; Brezigar et al., 1987; Vrabec, 1999).

Experimental

Lignite samples, representing different lithotypes, were taken from underground roadways ahead of the working faces. The lateral (an area of ca 2 x 2.5 km^2) and vertical (from -128.7 to +110.0 m height a.s.l.) distribution of the samples is plotted on the mining-plan map in Fig. 3. In the W part of the mine-workings, at the locality of a gas outburst in February 2003 (long-wall lignite excavation at the level of -90), numerous samples (18) were taken from the JV 3123-7, JV 115(1-4), L45(2) and D70(1-4) boreholes, which were drilled immediately after the above mentioned event. On a given scale of Fig. 3, all these boreholes coincide.

A macroscopic description of the lignite samples in terms of lithotypes was carried out following the criteria of Markič at al. (2001) (Fig. 4). The following lithotypes were distinguished (with number of samples): xylite (9), poorly gelified fine-detrital lignite (16), moderately gelified fine-detrital lignite (9), strongly gelified fine-detrital lignite (11), fusinite and semidegradofusinitic lignite (2) (Tab 1). In the later two cases, fusinite represents an encrustation over xylite, whereas the semidegradofusinitic (semifusinitic) designation derives from the microscopic inspection.

Heterogeneous lithotypes characterized by different ratios between fine detrital matrix and xylitic fragments (lithotypes coded by values from 4 to 9 in Fig. 4) were not analysed as whole samples. In such cases (samples B93, B97 and B111 in Tab. 1) only their fine detrital matrix was analysed.

As possible lignite precursors, some representative parts of recent plants (trunk of a

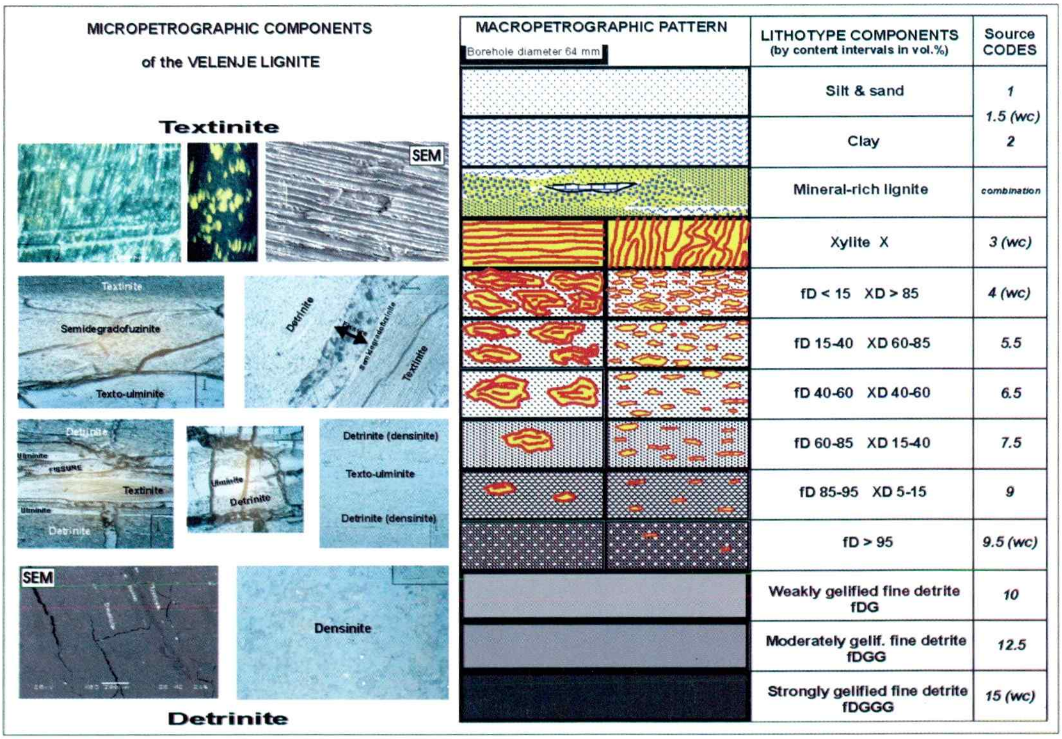

Figure 4. *Right:* Lithotype classification for the Velenje lignite based on different ratios (vol. %) between lithotype components; X - xylite, fD - fine detrite, XD – xylo-detrite, G – gelite (from Markič et al., 2001). *Left:* characteristic micropetrographic components from textinite (xylinite) to detrinite at different magnifications (50 to 200 ×; optic, and SEM - scaning electron microscopy).

Table 1. Macroscopic description and $\delta^{15}N$ and $\delta^{13}C$ values of the analyzed Velenje lignite samples

Num.	Sample	Macroscopic description	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{15}N_{AIR}$ (‰)
1	B91	poorly gelified detrital lignite	-26.8	4.0
2	B92	lamellar xylite	-26.5	4.4
3	B93	strongly gelified fine detrital lignite with xylite inclus.	-27.6	2.5
4	B94	moderately gelified black fine detrital lignite	-27.7	2.9
5	B95	poorly gelified detrital lignite	-27.1	2.8
6	B96	moderately gelified detrital lignite	-27.8	3.0
7	B97	strongly gelified fine detrital lignite with xylite inclus.	-27.4	2.0
8	B98	xylite	-26.6	3.2
9	B99	greyish black xylite	-27.2	2.5
10	B100	strongly gelified detrital lignite	-28.7	2.0
11	B102	strongly gelified fine detrital lignite (mineral-rich)	-28.2	2.0
12	B103	xylite + fusinite	-24.7	4.0
13	B104	moderately gelified fine detrital lignite	-27.9	3.8
14	B105	moderately gelified fine detrital lignite	-27.8	3.3
15	B106	brown xylite	-25.6	3.5
16	B107	poorly gelified fine detrital lignite	-26.9	4.2
17	B108	poorly gelified fine detrital lignite	-27.4	4.2
18	B109	xylite	-25.3	2.1
19	B110	poorly gelified black detrital lignite	-27.1	4.0
20	B111	poorly gelified detrital lignite with xylite inclusions	-26.8	2.6
21	B112	poorly gelified black fine detrital lignite	-26.8	3.1
22	B113	strongly gelified fine detrital lignite	-28.0	2.4
23	B116	strongly gelified black detrital lignite	-28.0	2.2
24	B117	poorly gelified detrital lignite	-26.8	3.5
25	B118	poorly gelified detrital lignite	-27.2	3.6
26	B119	moderately gelified black fine detrital lignite	-27.8	3.1
27	B120	moderately gelified fine detrital lignite	-28.0	4.0
28	B121	poorly gelified black fine detrital lignite	-26.3	2.8
29	B122	poorly gelified blackish - brown fine detrital lignite	-26.7	3.3
30	JV 3123-7	xylite, 0.3 m	-24.2	2.4
31	JV 3123-7	poorly gelified detrital lignite, 0.5 m	-27.3	3.3
32	JV 3123-7	semidegradofusinitic lignite,1.8 m	-25.2	4.6
33	JV 3123-7	xylite, 2.5 m	-23.0	2.0
34	JV 3123-7	xylite, 7.1 m	-23.6	3.9
35	JV 3123-7	moderately gelified detrital lignite, 8.3 m	-28.1	3.2
36	JV 3123-7	poorly gelified detrital lignite, 9.8 m	-27.4	3.3
37	JV 3123-7	strongly gelified detrital lignite, 12.3 m	-28.0	1.8
38	JV 3123-7	xylite, 14 m	-27.5	3.9
39	JV 115(-90)1	poorly gelified detrital lignite	-27.0	3.4
40	JV 115(-90)3	strongly gelificated detrital lignite	-27.6	2.6
41	JV 115(-90)2	poorly gelified detrital lignite	-27.2	3.7
42	JV 115(-90)4	moderately gelified detrital lignite	-27.2	2.4
43	L 45 (2)	strongly gelified detrital lignite, 2.5 m	-27.5	2.6
44	D 70 (2)	strongly gelified detrital lignite, 7.8m	-28.2	2.3
45	D 70 (1)	strongly gelified detrital lignite, 2.5 m	-28.5	2.7
46	D 70 (3)	poorly gelified detrital lignite, 13.5 m	-27.5	3.0
47	D 70 (4)	moderately gelified detrital lignite, 11.5 m	-28.0	2.9

conifer, conifer needles, grass, and bushes) on the present surface of the Velenje basin were collected as additional 4 samples (Tab. 2).

The bulk of the sampled lignite material represents the humic organic matter, except for two samples of fusinite and semidegradofusinitic lignite that represent inertinitic organic matter. The only lipoid-rich material in the study is represented by the recent conifer needles.

Table 2. $\delta^{15}N$ and $\delta^{13}C$ values of recent plant parts collected around the Velenje basin

Type of plant parts	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{15}N_{AIR}$ (‰)
trunk	-28.0	-3.3
conifer needles	-27.0	-3.6
grass	-31.1	-3.7
bush	-25.0	-2.3

After macroscopic description, the samples were ground in an agate crusher to powder for isotopic analyses.

The isotopic composition of carbon and nitrogen in lignite samples (Tab. 1), as well as in recent plant material (Tab. 2), was determined using an Europa 20–20 continuous flow IRMS ANCA–SL preparation module. 10 mg of homogenized sample was weighed in a tin capsule for nitrogen and 1 mg for carbon analysis. Samples for carbon analysis were pre-treated with 1 molar HCl to remove carbonates. The sample residues were washed in distilled water, dried and homogenized. The isotopic composition of nitrogen and carbon was determined after combustion of the capsules in a hot furnace (temperature 1000°C). Generated products were reduced in a Cu tube (600°C), where excess O_2 was absorbed. H_2O was trapped on a drying column composed of $MgClO_4$. Gases were separated on a chromatographic column and ionized. NBS 22 (oil) and IAEA N -1 (ammonium sulfate) reference materials were used to relate the analytical results to the VPDB and AIR standards as follows:

$$\delta^{13}C_{sample}(\delta^{15}N_{sample}) = \frac{R_{sample} - R_{RM}}{R_{RM}} \cdot 1000 \quad [‰],$$

where:

R_{sample} - ratio $^{13}C/^{12}C$ in sample ($^{15}N/^{14}N$ for $\delta^{15}N$ in sample)

R_{RM} - ratio $^{13}C/^{12}C$ in reference material ($^{15}N/^{14}N$ for $\delta^{15}N$ in reference material)

Sample reproducibility for carbon and nitrogen was ± 0.2 ‰.

Results and discussion

In general, the initial peat-forming depositional environment of the studied coal is characterized by its peat–forming plant communities, the ratios between the amount of organic versus inorganic material sedimentation, nutrient supply, pH value, bacterial activity, sulphur supply, temperature and the redox potential (aerobic, anaerobic). After peat accumulation, early diagenesis of organic matter begins with biochemical processes, which last up to the stage of the subbituminous coal rank (Stach et al., 1982; p.38), or according to some authors even up to the stage of the bituminous coal rank (Bustin et al., 1983; p.21). The biochemical stage of coalification is continued by the physicochemical stage of coalification, which is not of a special interest in this paper since we are dealing with a typical ortho-lignite.

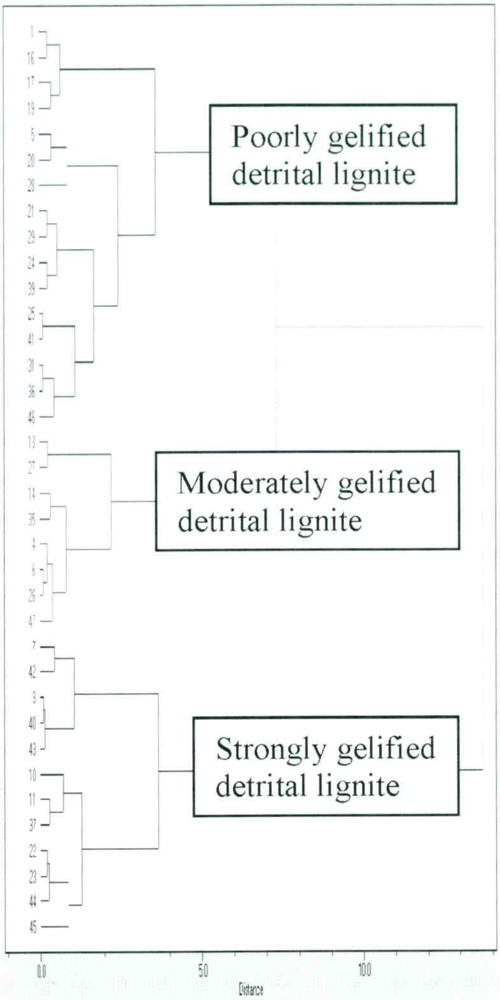

Figure 5. Dendrogram illustrating the results of cluster analysis of $\delta^{13}C$ and $\delta^{15}N$ values of lignite. The association of samples at a low value of the distance coefficient means a high similarity between the respective entities.

As described in Bustin et al. (1983; after Tissot & Welte, 1978), biochemical coalification is characterized by the following two stages: "firstly, plant material is mechanically disintegrated and depolymerized into aromatic, phenolic, and carboxylic groups with the aid of micro-organisms, and secondly, the humic polymers undergo random repolymerisation and polycondensation of the molecular types. With progressive diagenesis, the humic acids (formed during depolymerization) lose their acid groups and turn into humins, which are insoluble in alkalies. The process of humification is followed by gelification, a physico-colloidal process by which the humic matter passes through a soft plastic gel stage and takes on

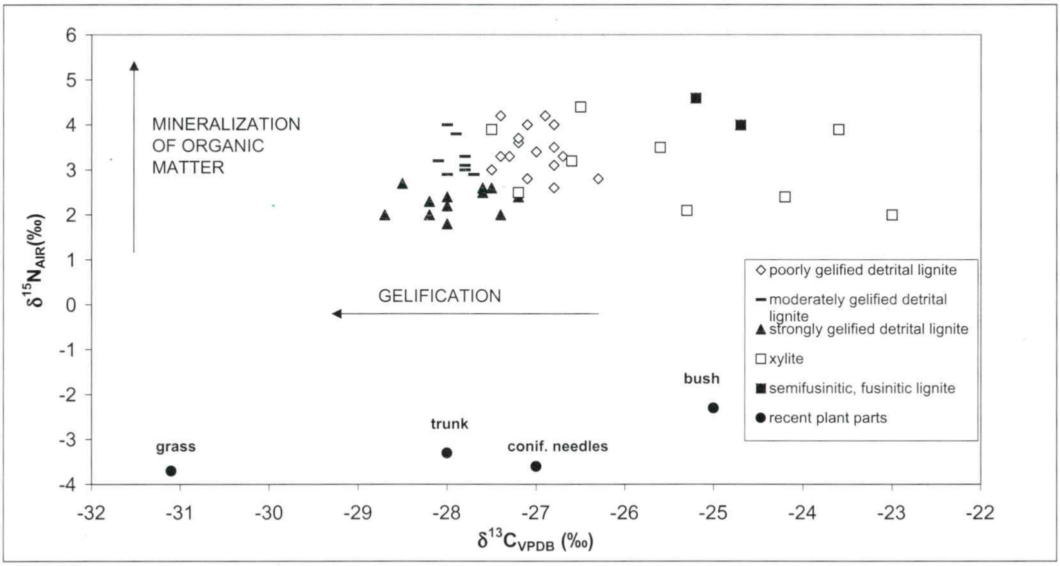

Figure 6. $\delta^{13}C_{VPDB}$ versus $\delta^{15}N_{AIR}$ of different lithotypes of lignite from the Velenje basin. Decreasing $\delta^{13}C$ values indicate the process of gelification. Increasing $\delta^{15}N$ values indicate the process of mineralization of organic matter.

a swollen appearance". According to Diessel (1992), gelification is the result of biochemical processes during the earliest stage of coal diagenesis (early coalification) up to the conversion of vegetal matter into peat and soft brown coal (lignite). As a result of lithification, more or less gelified lithotype / maceral petrographic components are formed. So-called soft tissues (*in sensu* Diessel, 1992), derived from herbaceous plants that are composed mainly of cellulose, undergo the above processes faster than woody tissues rich both in cellulose and lignin, often also in resins. A similar relation is true for smaller (thin cell-walled) versus larger (thick cell-walled and/or resin-rich) woody coal-forming ingredients.

Results of $\delta^{13}C$ and $\delta^{15}N$ measurements are given in Table 1 for the lignite samples and in Table 2 for samples of recent plant parts, and are discussed in what follows.

$\delta^{13}C$ and $\delta^{15}N$ values of different lithotypes of the Pliocene Velenje lignite vary from -28.7 to -23.0 ‰ and from 1.8 to 4.6 ‰, respectively (Table 1).

In order to better ascertain isotopic composition of differently gelified varieties of detrital lignite, 36 samples of detrital lignite were statistically processed by cluster analysis (after procedures in Zupan, 1992). Cluster analysis was processed according to $\delta^{13}C$ and $\delta^{15}N$ variables. The following groups of detrital lignite can be distinguished (Fig. 5, & Fig. 6): poorly gelified detrital lignite with $\delta^{13}C$ from -27.5 to -26.3 ‰ and $\delta^{15}N$ from 2.6 to 4.2 ‰, moderately gelified detrital lignite with $\delta^{13}C$ from -28.1 to -27.7 ‰ and $\delta^{15}N$ from 2.9 to 4.0 ‰, and strongly gelified detrital lignite with $\delta^{13}C$ from -28.7 to -27.2 ‰ and $\delta^{15}N$ from 1.8 to 2.7 ‰. Results of cluster analyses are in good agreement with macroscopic descriptions in Tab. 1, except for sample 42. According to cluster analysis, this sample fits better to strongly than to moderately gelified detrital lignite.

The xylite samples have an extensive range of $\delta^{13}C$ values from -27.5 to -23.0 and $\delta^{15}N$ from 2.0 to 4.4 ‰. In comparison to the detrital lignite samples, xylites have either similar or higher $\delta^{13}C$ values than poorly gelified detrital lignite (Fig. 6). Fusinitic and semifusinitic components, as products of forest fires and oxidation of xylite, are enriched in the heavy carbon as well as in the heavy nitrogen isotope (Fig. 6).

It can be concluded from the above cited $\delta^{13}C$ values that they decrease from xylites toward detrital and strongly gelified detrital lignite. This phenomenon is known from the previous studies (Pezdič et al., 1998,

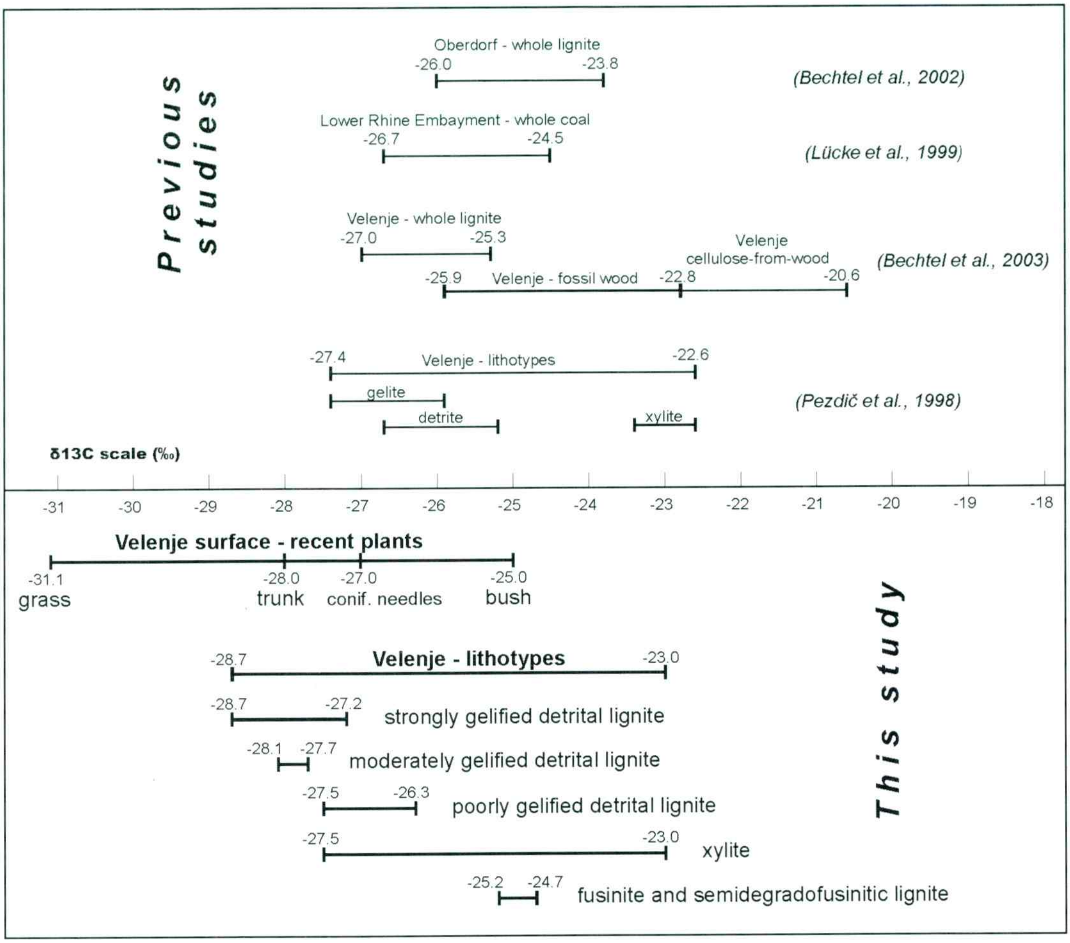

Figure 7. Comparison of $\delta^{13}C$ values between the Velenje lignite (this study and previous studies of Pezdič et. al., 1998, and Bechtel et. al., 2003), the Miocene Lower Rhine Embayment brown coal (Lücke et. al., 1999), and the Oberdorf lignite (Bechtel et. al., 2002).

Bechtel et al., 2003) as well. It is interpreted by the bacterial activity which affects fine detrital organic matter more easily than resistant xylite pieces and/or by the considerable presence of isotopically light organic matter from leafs, resins and bark in fine detrital coal matrix (Bechtel et al., 2003; after Hámor-Vidó & Hertelendi, 1996). Bacterial activity as a key factor of the biochemical gelification process leading into enrichment in the light carbon isotope composition is dependant on the alkalinity and the redox potential of the depositional environment. It is enhanced in more alkaline environments. In the case of the Velenje lignite it was postulated, that gelification was governed especially by the anaerobic bacteria (Bechtel et al., 2003), whereas considerable alkalinity is ascertained by the sulphur (Stot, *dry basis*) contents of 2 to 3 wt. % (Markič & Sachsenhofer, 1997) and considerable CaO (up to 40 wt. %) and MgO (up to 15 wt. %) contents in inorganic matter of low-ash lignite varieties (Markič; recent investigations). Biogeochemical degradation of organic material is also indicated by unexpected organo-arsenic compounds recently found in the Velenje lignite by Šlejkovec and Kanduč (2005).

Concerning the activity of aerobic bacteria it can be concluded, that they were responsible for decreasing cellulose contents during aerobic degradation of wood (Bechtel et al., 2003), which occurred during humification, i.e. before the main gelification process. It is also known, that humic acids form from lignin in the phase of humification only through oxidation (Stach et al., 1982).

A comparison between $\delta^{13}C$ values from this study and $\delta^{13}C$ values from previous studies of the Velenje lignite (Pezdič et al., 1998, Bechtel et al., 2003), as well as a comparison with the Miocene Lower Rhine Embayment brown coal (Lücke et al., 1999), and the Oberdorf lignite (Bechtel et al., 2002) is given in Fig. 7. It should be emphasized that in different studies, coals were analyzed using different sample materials. In the study of Bechtel et al. (2003), homogenized interval (up to 2 m) whole-coal samples, hand-picked wooden (xylite) pieces, and from-the-wood extracted cellulose were analyzed from a representative borehole-core through the entire lignite seam. Data for the Miocene Lower Rhine Embayment brown coal (Lücke et al., 1999) and for the Oberdorf lignite (Bechtel et al., 2002) refer to whole coals.

Recent plant parts around the Velenje basin have $\delta^{13}C$ from -31.1 (grass), -28.0 and -27.0 (a trunk and conifer needles), to -25.0 ‰ (bush), and $\delta^{15}N$ values from -3.7 to -2.3 ‰ (Tab. 2, Figs. 6 and 7). The data on $\delta^{13}C$ correspond to the range of values reported for recent C3 plants, with an average $\delta^{13}C$ around –27 ‰ (Stahl, 1986). According to Lücke et al. (1999), changes in the global carbon cycle and thermal maturity have little effect on changes of $\delta^{13}C$ of coals. Organisms that fix (metabolise) atmospheric nitrogen commonly have $\delta^{15}N$ between -3 and 0 ‰. Most other plants and animals have $\delta^{15}N$ around 0 ‰. Enrichment in the light nitrogen isotope is observed during fixation of atmospheric nitrogen and ammonia in plant parts, forming amino acids and proteins. Atmospheric nitrogen was formed by degassation of the upper mantle during the earth early history (Kroos et al., 1995). Samples of atmospheric nitrogen collected at various times and localities in the Northern Hemisphere are reported to have $\delta^{15}N$ values in the range of 0 ± 0.026 ‰ (Mariotti, 1983).

Among the recent plants involved in this study, a tree trunk and bush exhibit higher $\delta^{13}C$ values than grass. A similar already discussed relationship exists between xylite (derived mostly from paleo-trees and bushes) and fine detrital lignite (derived mostly from paleo-herbaceous flora) (Figs. 6 and 7). Geissler and Belau (1971) observed no carbon isotope fractionation during coalification up to the lignite stage. However, in our study, a representative enrichment in ^{13}C isotope in different lignite lithotypes was found in comparison to recent plants. A shift of about 2 ‰ in $\delta^{13}C$ values between various lithotype varieties and their precursive plant materials is attributed to bacterial activity during lignite formation.

Isotopic differences between recent plants and the Velenje lignite lithotypes are even more contrasted in the case of $\delta^{15}N$ values (Fig. 6). Various lithotypes are isotopically highly enriched in the heavier nitrogen isotope compared to the recent plants. Organic nitrogen isotopes can be used as indicators for reconstruction of the paleoecological and paleodepositional history of the basin (Ader et al. 1998), including the process of mineralization of organic matter i.e. partial loss of organic component and relative enrichment of inorganic component during lignite formation. According to Zhu et al., (2000), mineralization of organic matter is caused by various bacteria in an alkaline environment and is reflected in $\delta^{15}N$ values higher than in their plant precursors. It is also well known that mineralization is more pronounced in aerobic environments leading to formation of fusinite, semidegradofusinite and related inertinitic components in coals. The highest $\delta^{15}N$ values of the fusinite, semidegradofusinite-rich, and some xylite and poorly gelified detrital lignite samples of the studied Velenje lignite (Fig. 6) are in good agreement with the above statement about mineralization in an aerobic environment. On the contrary, depletion with the ^{15}N isotope in the strongly gelified detrital lignite samples is a clear evidence of anaerobic conditions, where the mineralization process is limited. More pronounced gelification is therefore generally accompanied by lower mineralization of organic matter.

Vertical variability of the $\delta^{13}C$ and $\delta^{15}N$ values for the sampled lignites is presented in Fig. 8. It can be concluded that vertical (as well as lateral; Fig. 3) variability in carbon and nitrogen isotopic composition is expressed to a negligible degree in comparison

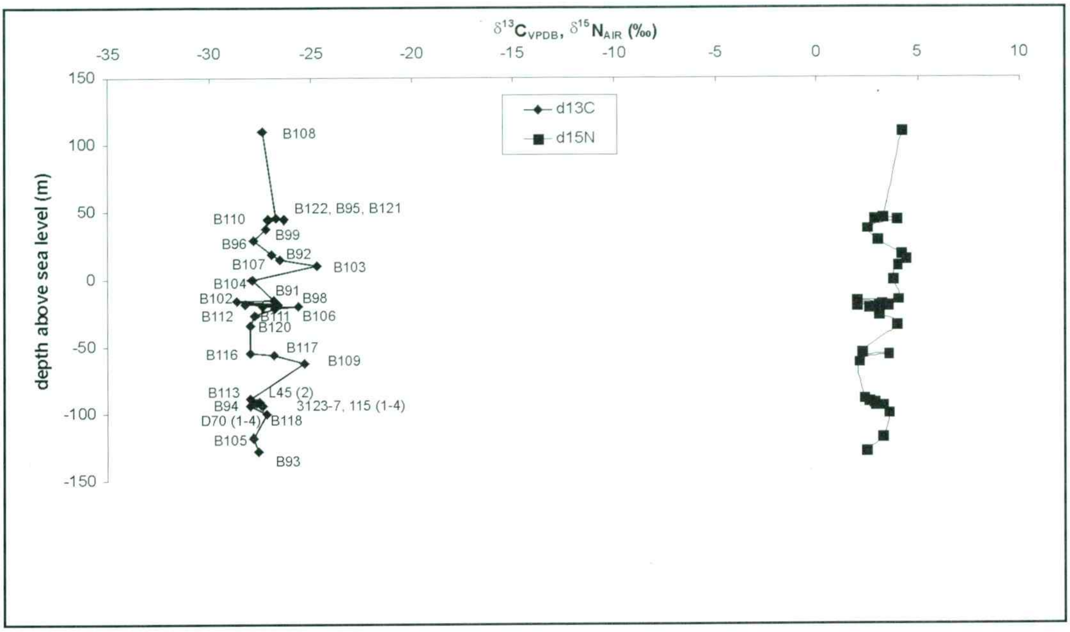

Figure 8. $\delta^{13}C_{VPDB}$ and $\delta^{15}N_{AIR}$ values of lignite versus height relative to the sea level for the Velenje basin (for location of sampling points see Fig. 3).

to the variability between the lithotypes themselves. Therefore, similar partial processes of humification, gelification and mineralization, affecting different lithotype components to different degrees, occurred throughout the formation of the lignite seam - in spite of that it evolved from different peat forming environments (wet and dry forest swamp, bush moor and fen *in sensu* Markič & Sachsenhofer, 1997).

Conclusion

Variability in the stable isotope composition of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) of different lithotypes of the Velenje lignite as well as differences in isotopic composition between the lithotypes and recent plants from the present surface of the study area indicate that both original floristic ingredients and biogeochemical processes (gelification and mineralization) were of great importance in the early diagenesis of the Velenje lignite formation.

Among the recent plant parts, samples of a trunk, conifer needles and a bush have $\delta^{13}C$ values from -28.0 to -25.0 ‰. Grass is depleted in the heavy carbon isotope. Its $\delta^{13}C$ value is in the order of -31.1 ‰.

Xylites, considered as lignite ingredients derived from trunks and bushes, which are considerably resistant to biogeochemical processes of degradation, are characterized by $\delta^{13}C$ values between -27.5 and -23.0 ‰. Xylites therefore express either similar carbon isotopic composition as their precursors or are enriched in the heavy carbon isotope.

Detrital lignites, derived mostly from herbaceous flora, which is biogeochemically less resistant than larger wooden pieces, have $\delta^{13}C$ values between -28.7 and -26.3 ‰. In comparison to a recent grass, they are considerably enriched in the heavy carbon due to bacterial activity during humification and gelification. In comparison to xylites, detrital lignites are depleted in the heavy carbon, similarly as a grass is depleted in the heavy carbon in comparison to a trunk and a bush. The effect of gelification due to activity of anaerobic bacteria in an alkaline environment (*in sensu* Bechtel et al., 2003) is best ascertained from the comparison in $\delta^{13}C$ values between differently gelified detrital lignites. Weakly gelified detrital lignites are characterized by $\delta^{13}C$ values between -27.5

and -26.3 ‰, whereas strongly gelified detrital lignites between -28.7 and -27.2 ‰. However, all detrital lignites do not necessary origin from exactly the same vegetal precursors. Therefore, isotopic differentiation originated from different vegetal ingredients should not be neglected in the case of detrital lignites as well. More precise paleobotanic and micropetrographic investigations are recommended to be carried out in the future to better clarify this question.

Recent plants are characterized by low $\delta^{15}N$ values (-3.7 to -2.3 ‰) in comparison to the lithotypes (1.8 to 4.6 ‰). Enrichment in the heavy nitrogen in the lithotypes is interpreted as a consequence of a mineralization process caused by bacterial activity in an alkaline environment (*in sensu* Zhu et al., 2000), which was proceeded by oxidation in an aerobic environment. High $\delta^{15}N$ values of the fusinite and semidegradofusinite-rich, and some xylite and poorly gelified detrital lignite samples support this interpretation. On the contrary, strongly gelified detrital lignites formed in an anaerobic environment are characterized by the lowest $\delta^{15}N$ values among the lithotypes. More pronounced gelification of organic matter is therefore generally accompanied by its lower mineralization.

Because no significant variability in the isotopic carbon and nitrogen composition versus depth and laterally is detected for the same lithotypes it can be supposed that the processes of humification, gelification and mineralization were temporally and spatially uniformly intensive throughout the formation of the Velenje lignite seam.

Our study confirms that besides the nature of original plant ingredients biogeochemical processes in the early diagenesis of the Pliocene lignite formation in the Velenje basin should not be neglected.

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