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# Isotopic composition of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) of petrologically different Tertiary lignites and coals

## Izotopska sestava ogljika ($\delta^{13}C$) in dušika ($\delta^{15}N$) petrološko različnih terciarnih lignitov in premogov

Tjaša KANDUČ[1]* & Miloš MARKIČ[2]

[1]Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, SI–1000 Ljubljana, Slovenia; *corresponding author: tjasa.kanduc@ijs.si
[2]Geological Survey of Slovenia, Dimičeva ulica 14, SI–1000 Ljubljana, Slovenia; e-mail: milos.markic@geo-zs.si

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### Abstract

This study investigates the carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N$) isotopic composition of tertiary lignites and coals from six sedimentary basins: Velenje, Mura-Zala, and Zasavje in Slovenia; Sokolov in Czech Republic, Barito in Indonesia; and Istria in Croatia. The aim is to investigate the correlation between the fine detrital (fD) component and $\delta^{13}C$ and $\delta^{15}N$ in Velenje lignite samples. Additionally, we aim to evaluate the biogeochemical processes of organic substances during their deposition in all analyzed samples, calculate their $\delta^{13}C_{CO2}$ values and compare the analyzed values of $\delta^{13}C$ and $\delta^{15}N$ to those reported in the literature. Thirty-two samples were analyzed, predominantly from the Velenje ortho-lignite (Pliocene), with additional lignites and coals from the Pannonian to Paleocene epochs for comparison. Carbon isotopic composition ($\delta^{13}C_{org}$) ranged from -27.9 to -23.6 ‰, and nitrogen isotopic composition ($\delta^{15}N$) ranged from 1.8 to 7.4 ‰. The fine-detrital lithotypes of the Velenje ortho-lignite exhibited the most negative $\delta^{13}C_{org}$ values due to anaerobic bacterial activity in an intramontane alkaline lake environment influenced by the carbonate hinterland. Moreover, gelification processes affected fine-detrital organic matter more than larger wooden pieces. Terbegovci, Hrastnik meta-lignites, and Barito sub-bituminous coal also displayed low $\delta^{13}C_{org}$ values, indicating limited gelification, while variations in the $\delta^{15}N$ values suggested differences in mineralization. The Velenje xylitic lithotypes have higher $\delta^{15}N$ values, indicating a more intense mineralization under aerobic conditions. Raša ortho-bituminous coal, deposited in a brackish environment, displayed the highest $\delta^{13}C_{org}$ values and a wide range of $\delta^{15}N$ values due to fluctuating water tables in a paralic carbonate platform environment. The lowest $\delta^{15}N$ value was observed in the Sokolov Basin lignite coal, indicating minimal mineralization and low bacterial activity. The isotopic composition of $CO_2$ in air ($\delta^{13}C_{air}$), which was calculated using the $\delta^{13}C$ values in lignites and coal, ranged from -8.4 to -3.4 ‰, with Velenje lignite displaying the minimum value and Raša coal showing the maximum value. The determined $\delta^{13}C$ and $\delta^{15}N$ values of the coal and lignite samples in this research fall within the typical range of world coals.

### Izvleček

Ta raziskava proučuje izotopsko sestavo ogljika in dušika ($\delta^{13}C_{org}$ in $\delta^{15}N$) terciarnih lignitov in premogov iz šestih sedimentacijskih bazenov: Velenje, Mura-Zala in Zasavje v Sloveniji; Sokolov na Češkem; Barito v Indoneziji; in Istri na Hrvaškem. Cilj je iskati korelacijo med fino detritno (fD) komponento in $\delta^{13}C_{org}$, $\delta^{15}N$ v velenjskih lignitnih vzorcih ter oceniti biogeokemične procese organske snovi med odlaganjem v vseh analiziranih vzorcih, izračunati $\delta^{13}C_{CO2}$ ter primerjati analizirane vrednosti $\delta^{13}C$ in $\delta^{15}N$ z objavljeno literaturo. Analiziranih je bilo dvaintrideset vzorcev, večinoma iz Velenjskega orto-lignita (pliocen), za primerjavo pa še ligniti in premogi od panonijske do eocenske starosti. Izotopska sestava ogljika ($\delta^{13}C_{org}$) vseh vzorcev se je spreminjala od -27,9 do -23,6 ‰, in izotopska sestava dušika ($\delta^{15}N$) od 1,8 do 7,4 ‰. Fino-detritni litotipi Velenjskega orto-lignita so pokazali najbolj negativne vrednosti $\delta^{13}C_{org}$ zaradi anaerobne bakterijske aktivnosti v intramontanem alkalnem jezerskem okolju pod vplivom karbonatnega zaledja. Procesi gelifikacije bolj vplivajo na drobno-detritno organsko snov kot na večje lesne ostanke. Meta-ligniti iz Terbegovcev in Hrastnika ter Barito sub-bituminozni premog so prav tako pokazali nizke vrednosti $\delta^{13}C_{org}$, kar kaže na omejeno gelifikacijo. Spremembe v $\delta^{15}N$ kažejo na razlike v mineralizaciji. Velenjski ksilitski litotipi so pokazali višjo $\delta^{15}N$, kar kaže na bolj intenzivno mineralizacijo v aerobnih pogojih. Raški orto-bitumenski premog, odložen v brakičnem okolju, je pokazal najvišjo $\delta^{13}C_{org}$ in širok razpon $\delta^{15}N$ vrednosti zaradi nihajočih vodnih nivojev v paraličnem karbonatnem platformnem okolju. Najnižja $\delta^{15}N$ je bila opažena v lignitnem premogu iz Sokolovskega bazena, kar kaže na minimalno mineralizacijo in nizko bakterijsko aktivnost. Izotopska sestava $CO_2$ v zraku ($\delta^{13}C_{air}$), ki je bila izračunana iz $\delta^{13}C$ v lignitih in premogih se je spreminjala od -8,4 do -3,4 ‰, pri čemer je velenjski lignit pokazal najnižjo vrednost, raški premog pa najvišjo. Določene vrednosti $\delta^{13}C$ in $\delta^{15}N$ vzorcev lignita in premoga v tej raziskavi padejo znotraj razpona svetovnih premogov.

## Introduction

Coal, which accounts for 65 % of the world's total fossil fuel resources, is widely distributed globally and accounts for 40 % of global power generation (Shafiee & Topal, 2009; Hariana et al., 2021). Coal is a sedimentary rocks that has evolved from compressed vegetation, trapped between layers of rocks over millions of years and is combustible. Among geological materials, it is among the most intricate, composed of organic matter, elements (C, H, O, N, S), water, oil (CH), gases (mainly $CH_4$ and $CO_2$), and a variety of minerals (Rađenović, 2006). The initial phase of the coalification process (e.g. Diessel, 1992) involves the microbial degradation of plant ingredients into peat, occurring either aerobically or anaerobically. Subsequent changes in temperature with depth under overlying strata and pressure modify the physical and chemical characteristics of the sedimentary environment, during which the peat transforms into lignite and higher-ranking coals. Variations in geochemical conditions and the heterogeneity of plant tissues contribute to different coal types (Kirby et al., 2010), which comprise varying proportions of macerals (organic components) and inorganic minerals. The primary maceral groups are the huminite to vitrinite, exinite or liptinite, and inertinite groups (Stach et al., 1982; Diessel, 1992; Taylor et al., 1998; Speight, 2013; Flores & Moore, 2024).

Stable isotopes play a significant role in paleoclimate studies, as they are commonly used to track biogeochemical processes, including peatification and coalification processes (Hoefs, 1987).

It is known that photosynthesis leads to an enrichment of light isotopes, namely $^{12}C$ and $^{14}N$, in plants (O'Leary, 1988). The typical value of $\delta^{13}C$ for C3 plants is approximately -27 ‰ (expressed relative to the Vienna Peedee Belemnite, VPDB), while for C4 plants like *Zea mays*, $\delta^{13}C$ is around -14 ‰. The range of $\delta^{15}N$ in the biosphere varies from -10 ‰ to 10 ‰ (Peterson & Fry, 1987). The $\delta^{13}C$ values for most coals fall within the range of -29 to -20 ‰, aligning with that of modern C3 vegetation, i.e., -34 ‰ to -23 ‰ (Ding et al., 2019). However, during the early stages of organic matter diagenesis, isotopic fractionation occurs due to bacterial activity, leading to an enrichment in the heavier ($^{13}C$ and $^{15}N$) isotopes. Numerous studies have been conducted on the $\delta^{13}C$ and $\delta^{15}N$ values of the coal matrices in different sedimentary basins, and both $\delta^{13}C$ and $\delta^{15}N$ have been utilized to evaluate and understand the evolution of ecological environments. For example, $\delta^{15}N$ is employed to trace the sources of organic matter and the vegetation involved in peat formation and to assess the extent of bacterial activity during the peat-forming stage (Taylor et al., 1998), while $\delta^{13}C$ is used to trace air temperature, humidity, soil moisture, and precipitation rates (Bechtel et al., 2008; Xu et al., 2020; Li et al., 2022; Lin et al., 2022; Masood et al., 2022; Panda et al., 2022). Furthermore, $\delta^{13}C$ values can be used to estimate the $\delta^{13}C_{air}$ values of ancient atmospheres (Arens et al., 2000; Gröcke, 2002).

In the Velenje Basin, Pezdič et al. (1998) initiated the study of biogeochemical processes of various lithotypes (xylite, detrital lignite, fuzinite) of the ortho-lignite using $\delta^{13}C$ analysis. Subsequent research by (Kanduč et al., 2005; Kanduč et al., 2007; Kanduč et al., 2012) expanded on this work by investigating the Velenje ortho-lignite, as well as other coals such as meta-lignites from Kanižarica and Senovo, and plant tissues using both $\delta^{13}C$ and $\delta^{15}N$ tracers. These studies consistently revealed distinct $\delta^{13}C$ and $\delta^{15}N$ values among the different lignite lithotypes from the Velenje Basin, indicating variations in biochemical reactions during coalification, specifically gelification resulting in $^{12}C$ enrichment and mineralization processes leading to $^{15}N$ enrichment (Kanduč et al., 2005; Kanduč et al., 2012; Kanduč et al., 2018). Kanduč et al. (2018) also conducted a detailed investigation of authigenic mineralization associated with organic matter in lignite from the Velenje Basin, while Bangjun et al. (2019) focused on determining biomarkers in the Velenje lignite samples, which were first studied together with stable carbon isotope composition to interpret paleo-environmental conditions and early coalification processes (Bechtel et al., 2003). A similar study was performed on the Trbovlje (Zasavje) coal by Bechtel et al. (2004). The isotopic composition of sulphur ($\delta^{34}S$) and elemental composition of carbon and nitrogen in several Slovenian coals, including Velenje, Trbovlje, Senovo, and Kanižarica, were examined by Šturm et al. (2009), who observed variations between the coal seams and different coal types. These differences were attributed to $SO_4^{2-}$ and $Fe^{2+}$ availability and microbial activity.

The objective of the present study is to isotopically characterize ($\delta^{13}C_{org}$ and $\delta^{15}N$) samples of lignite and coals from six geological basins: Velenje, Mura-Zala, and Zasavje in Slovenia, Sokolov in Czechia, Barito in Indonesia, and Raša (Istria) in Croatia. The primary focus was to search for a correlation between the fine detrital (fD) component and their $\delta^{13}C$ and $\delta^{15}N$ values in Velenje lignite samples. Further, we determined the extent of bio-geochemical processes, such as gelification and mineralization of organic matter. To achieve this, we compared our results with previously published isotopic data on lignites and coals and to the isotopic composition of recent plant samples to elucidate any discrepancies and highlight the degradation of organic matter during the coalification process. Additionally, we calculated $\delta^{13}C$ values in relation to atmospheric carbon dioxide ($\delta^{13}C_{CO2}$) to determine potential differences in paleo-air among the studied coals.

## Geological characteristics of sampling locations

Sampling locations from six coal-bearing sedimentary basins (Velenje, Mura-Zala, Zasavje, Sokolov, Barito, and Istria), with basic information on locality, coalification rank, and age are presented in Table 1 and Figure 1.

Knowing the geological characteristics and paleo-environment of the sampling locations in the separate basins is essential for interpreting the bio- and physicochemical coalification processes within different geological realms.

Table 1. Characteristics of studied lignites and coals.

| Abbreviation of samples (and number of samples analyzed) | Lignite / Coal from a basin | Locality - seam | Coalification Rank | Age |
|---|---|---|---|---|
| VL (22) | Velenje (Slovenia) | Pesje – Velenje seam | Ortho-lignite | Pliocene |
| TL (2) | Mura-Zala (Slovenia) | Terbegovci lignite from a borehole. | Meta-lignite | Pannonian ("Pontian") |
| HC (1) | Zasavje (Slovenia) | Laško syncline Hrastnik seam Terezija field | Meta-lignite / sub-bituminous coal | Oligocene |
| JC (1) | Sokolov (Czechia), | Josef seam | Meta-lignite / sub-bituminous coal | Oligocene |
| BC (1) | Barito (Indonesia) | Barito seam | Sub-bituminous coal | Miocene |
| RC (5) | Istria (Croatia)RC | Raša – in-limestone seam | Ortho-bituminous coal | Paleocene |

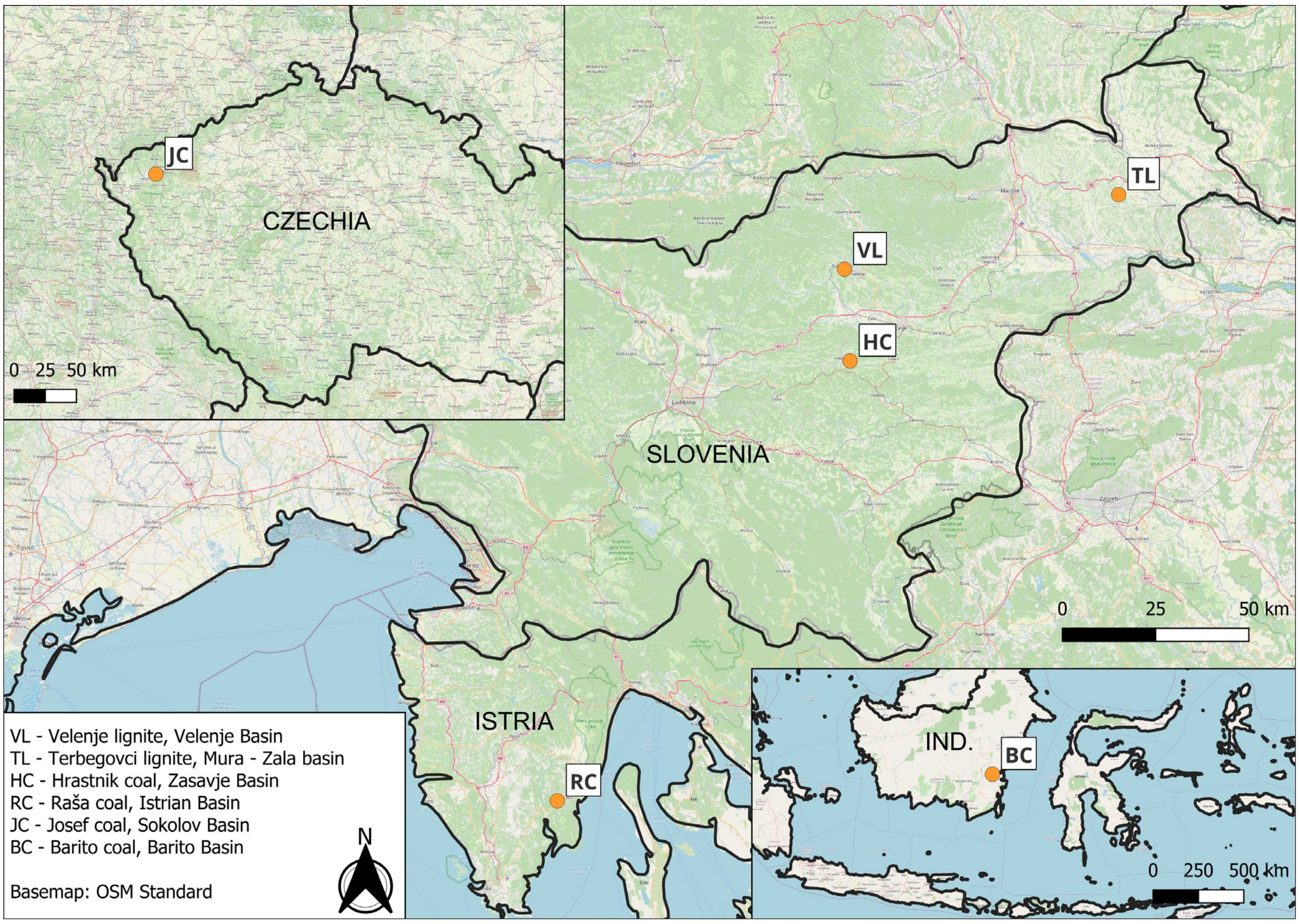



Fig. 1. Sampling locations from the six coal-bearing sedimentary basins in Slovenia, Czechia, Indonesia (Ind.) and Istria.

## Velenje ortho-lignite (VL), Velenje basin, N Slovenia

The Velenje lignite-bearing basin is a typical intramontane freshwater lacustrine basin formed as a pull-apart basin (Vrabec, 1999) during the Pliocene to Quaternary times. It was created by polyphase dextral strike-slip fault tectonics between the Smrekovec and Šoštanj faults (Fig. 2). The basin contains a sequence of clastic sediments that can reach up to 1000 meters in thickness and host a single lignite seam that is exceptionally thick, measuring extremelly, up to 165 meters (Brezigar, 1985).

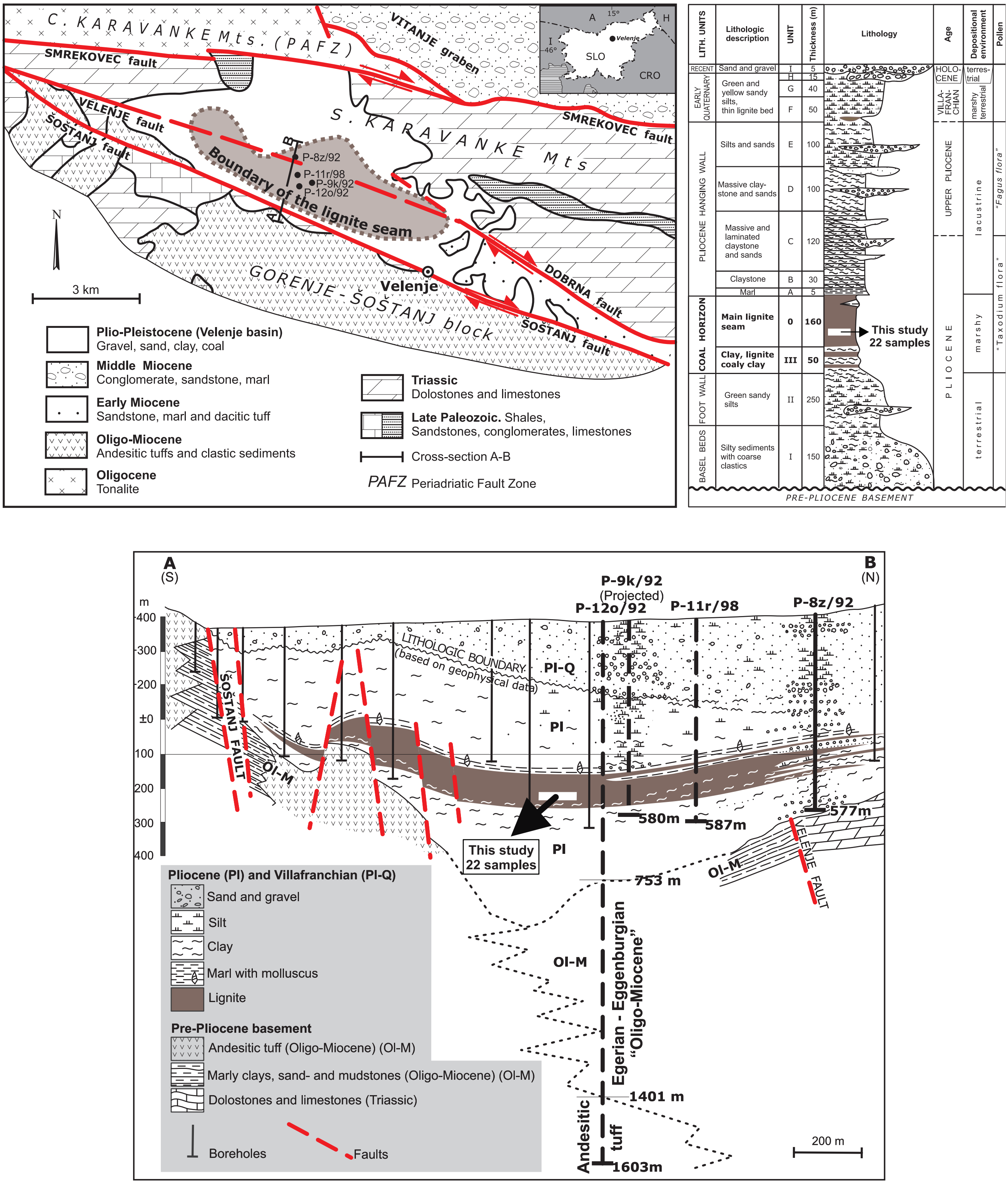



Fig. 2. The Velenje lignite basin: geological map (upper left), lithologic column (upper right), and cross-section (bottom) (Brezigar, 1985).

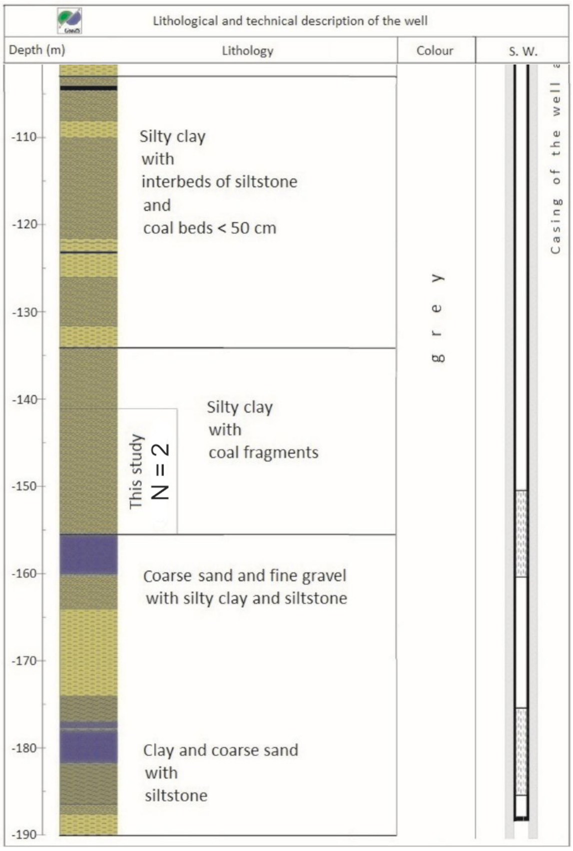



Fig. 3. Lithologic column of TER-1/03 well. The sampled coal material is from a depth interval of 141.0–155.5 m; N = number of samples; the whole column is given in Markič & Brenčič (2014).

According to the literature data, the average calorific value of the lignite, on an as-received basis (based on core data), is 10.7 MJ/kg, with a moisture content of 33.5 % and an ash content of 18.0 % (RCMWRA, 2002; Veber & Dervarič, 2004; Papež, 2019). The sulfur content, on a dry basis (db), varies from around 1.0 % to 5.5 %, with the latter being mainly detected where the lignite seam is close to the carbonate bedrock (Markič & Sachsenhofer, 2010). The Velenje lignite is classified as a typical ortho-lignite in terms of coalification rank, characterized by approximately 45 % bed moisture (ash-free basis), 62.7–66.4 % carbon content (dry, ash-free basis), 58.3–57.7 % volatile matter (dry, ash-free basis), and the gross calorific value (GCV) ranging from 12.23 to 15.25 MJ/kg (bed moist, ash-free basis) (Markič & Sachsenhofer, 2010). The reflectance (Rm %) of huminite (ulminite B) varies from 0.34 to 0.41 %, suggesting that this lignite can be classified as a meta-lignite. However, this range can also result from optical effects, such as subtle oxidation caused by pronounced aerobic bacterial and fungal activity during peatification and early coalification (Markič & Sachsenhofer, 2010).

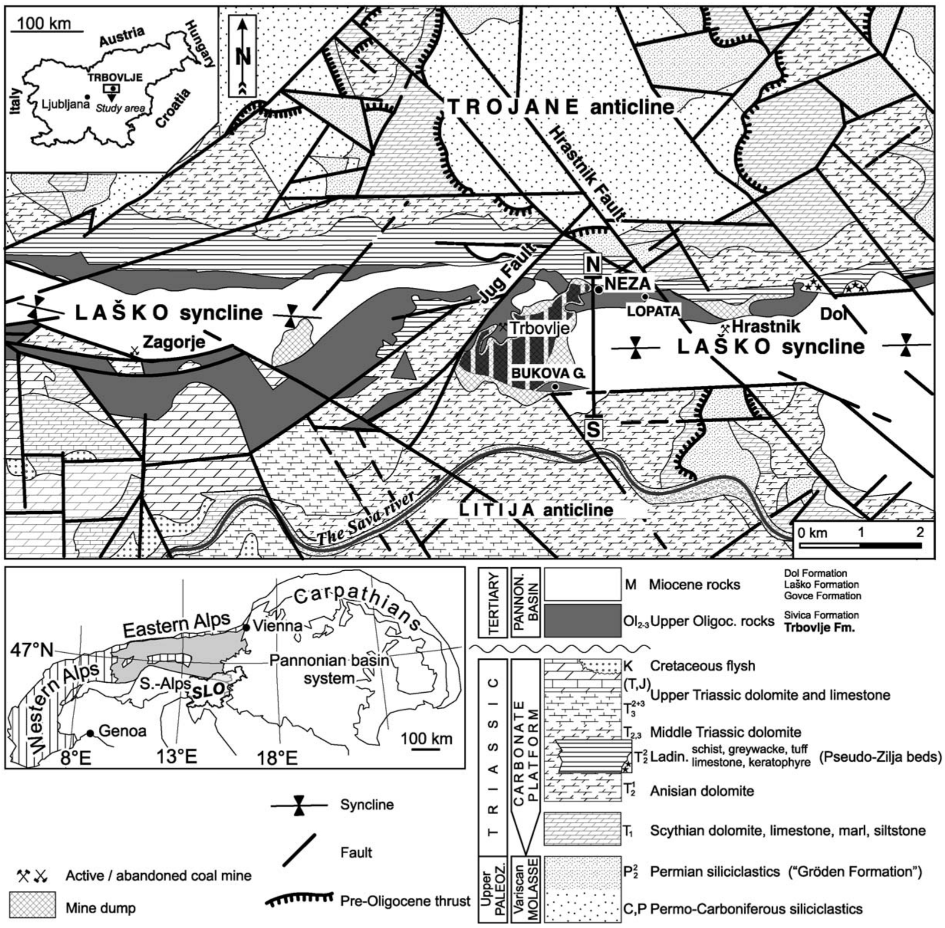



Fig. 4. Geological map of the Zasavje Basin – Laško Syncline (adapted from Buser, 1978 and Premru, 1983, taken from Bechtel et al. (2004)). Notable is the Hrastnik coal mine in the central-eastern part of the map.

### Terbegovci lignite (TL), Mura–Zala Basin, NE Slovenia

Based on the gross calorific value on a dry, ash-free basis ($GCV_{dafb}$) of 28.137 MJ/kg, the coal material was classified as a humic high-grade meta-lignite, similar in rank to the meta-lignites in the Mura Formation formed during the late Panonian (Markič et al., 2011).

### Hrastnik coal (HC), Zasavje Basin, Central Slovenia

The E-W trending Laško syncline (Fig. 4) of the Zasavje Basin is about 40 km long and up to 3 km wide, bounded by the Trojane and Litija anticlines to the north and the south, respectively (Kuščer, 1967; Buser, 1978; Premru, 1983; Placer, 1998 and references therein). The lithologies and formations

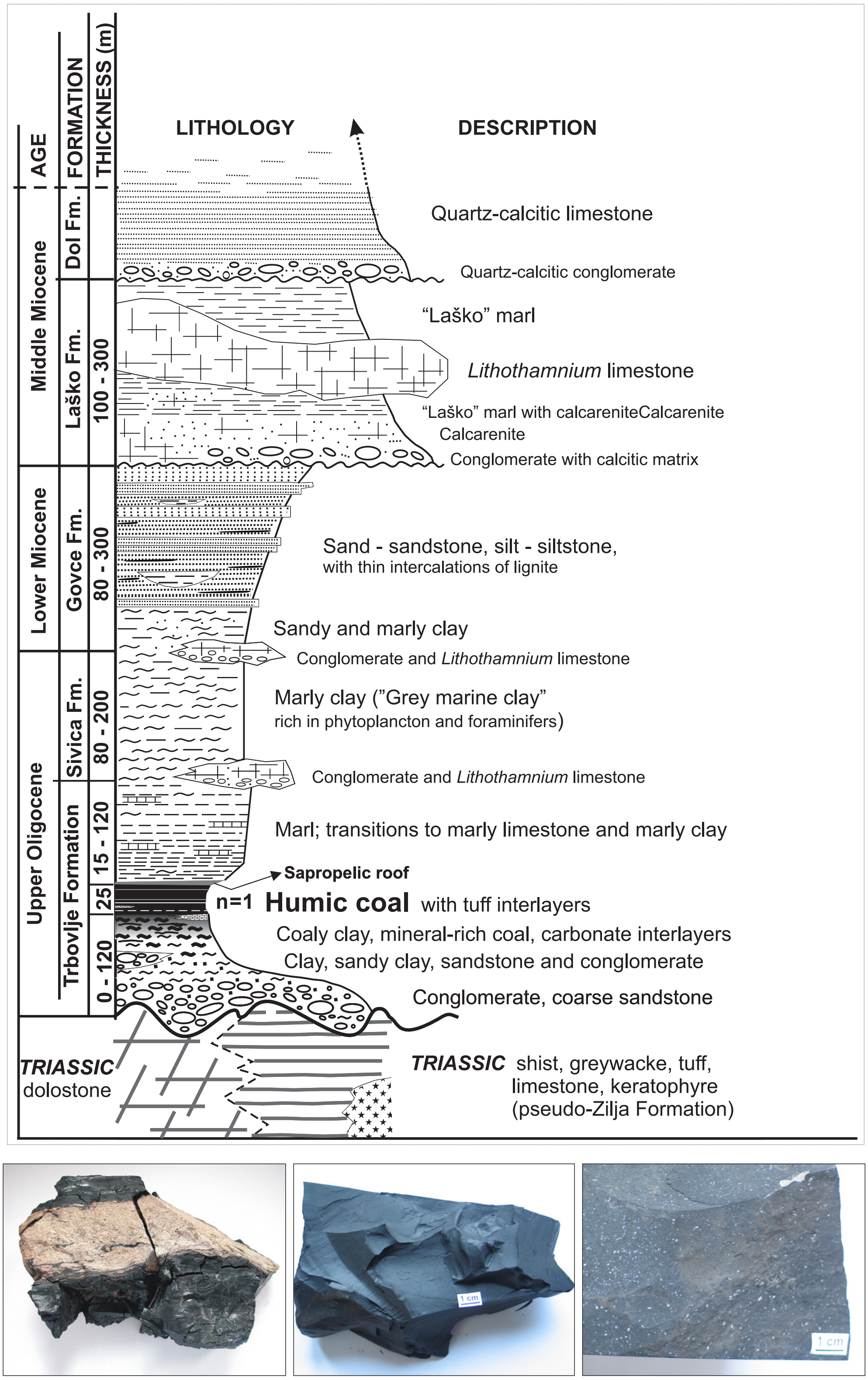



Fig. 5. Above: Schematic lithologic column of Tertiary strata in the Zasavje basin – Laško Syncline (modified after Kuščer, 1967). Below left: Zasavje humic coal with an andesitic tuff interlayer (7 cm thick). Below middle: sapropelic coal. Below right: sapropelic coal with sub-millimetre fragments of lake molluscs (“white dots”). The sample was taken from the humic coal seam.

above the coal seam are shown in the lithologic column in Figure 5.

The average coal grade and calorific value (as received basis) for the k. 34 Terezija polje (Hrastnik), from which the sample was taken, are as follows: coal moisture 19.7 %, ash yield 33.1 %, S content 4.2 %, and the net calorific value 12.8 MJ/kg (RTH d.o.o., 2013). Using the formula in (Thomas, 1992, p.30), the gross calorific value at the dry, ash-free basis (GCVdafb) is 30.2 MJ/kg, ranks the Hrastnik coal into the sub-bituminous coalification rank. This rank is generally consistent with the rank determined by vitrinite reflectance of 0.5 % Rm, as reported in Bechtel et al. (2004) for the Zasavje-Trbovlje seam.

### Josef coal (JC), Sokolov Basin, W Czechia

Lignites from Czechia are thoroughly described in Pešek (2014). The Nove Sedlo Formation is composed of effusive and volcanoclastic rocks, marking the first significant stage of the extension of the Sokolov Basin associated with intense tectonic movements and volcanic activity. The lower part hosts the Josef coal seam, from which the sample was taken (Fig. 6). Its moisture content (as received basis) ranges between 28 and 43 %, the ash content (dry basis) between 2.6 and 27.3 %, and the sulphur content (dry basis) between 0.5 and 11.8 % (Rojík et al., 2014). Its gross calorific value (dry, ash-free basis) is between 29.1 and 31.5 MJ/kg, and its reflectance (Rm %) ranges from 0.3 to 0.45 %. The coal is ranked as a metalignite to sub-bituminous coal (Rojík et al., 2014; p. 134).

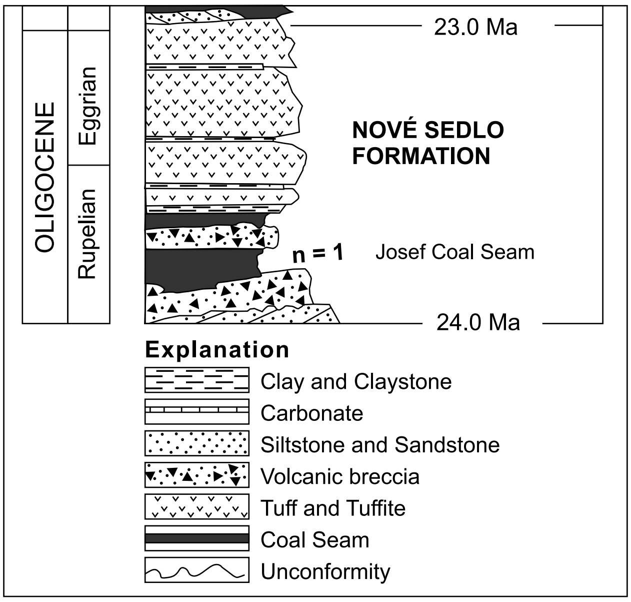



Fig. 6. Stratigraphic scheme of the Upper Oligocene of the Sokolov Basin fill, (after Rojík et al., 2014); n = number of samples taken from the Josef Coal Seam. (The Stare Sedlo Fm below the Nove Sedlo Fm is not shown).

### Barito coal (BC), Barito Basin, Indonesia

The Barito Basin is located in South Kalimantan (Fig. 1). It is one of the main geological basins in the region, containing abundant coal resources and reserves. Within the basin, the Warukin Formation is among those where coal is present (Fig. 7). The rocks in the Warukin Formation primarily comprise sandstones and claystones with coal deposits (Supandi & Hartono, 2020).

The coal imported from Indonesia to Slovenia is excavated in the open-cast Pasir Mine, Indonesia's third largest single mine, operated by the Kideco Jaya Agung Company. The geology of the Pasir Mine is summarized here from the work of Choi et al. (2013) and Supandi and Hartono (2020). The Barito Basin coal from the Pasir Mine is known for its low sulphur content (<0.2 %) and is considered an environmentally friendly coal-energy source due to an ash content of <5 %. The Barito coal in

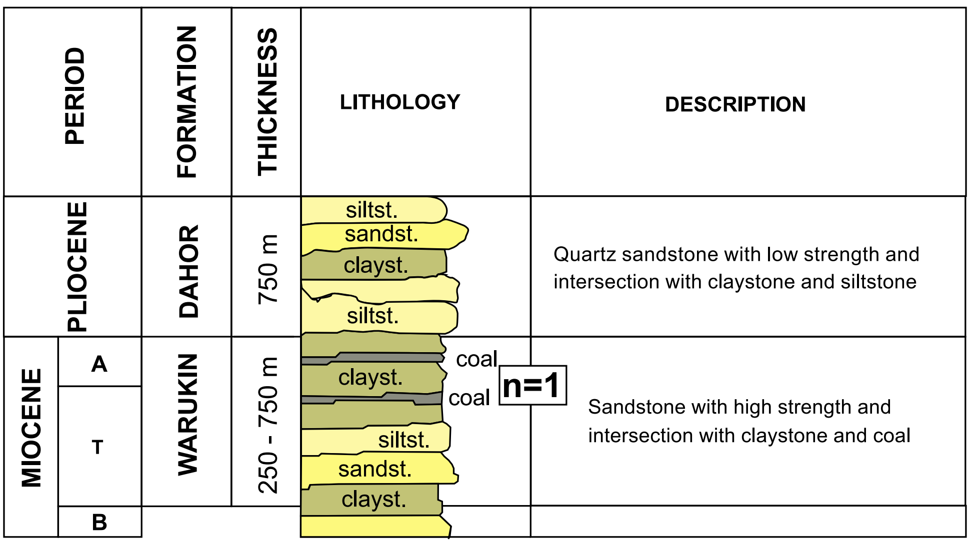



Fig. 7. Regional stratigraphic column of the Barito Basin showing the coal seams in the Warukin Formation (modifed after Supandi & Hartono, 2020); n = number of samples taken.

Southern Kalimantan occurs in several widely developed beds up to 10 m thick and is sub-bituminous (Thomas, 1992; Internet 2).

### Raša Coal (RC), Istrian Basin, Croatia

The Istrian coal mines in the eastern part of the Istrian Peninsula in Croatia's Northern Adriatic Sea region (Fig. 1) held the largest economically viable anthracite coal deposits in Croatia from the 18th century until 1999. One distinctive characteristic of the Raša coal is its high organic sulfur content, reaching up to 14 % (Medunić et al., 2016). During the initial phase of coalification, known as humification, organic sulphur compounds are generated as plant debris decomposes due to bacterial activity. Hamrla (1960) determined that the Raša coals were formed under anaerobic conditions. The substantial organic sulphur content in these coals is attributed to the bacterial reduction of marine sulphates, which became incorporated into the organic matrix (Medunić et al., 2016).

Raša coal is classified as an ortho-bituminous coal (Table 1) with a gross calorific value (dry, ash-free basis) of 34.3 MJ/kg and a vitrinite reflectance (Rr %) of 0.64 (Hamrla, 1959; Hamrla, 1985).

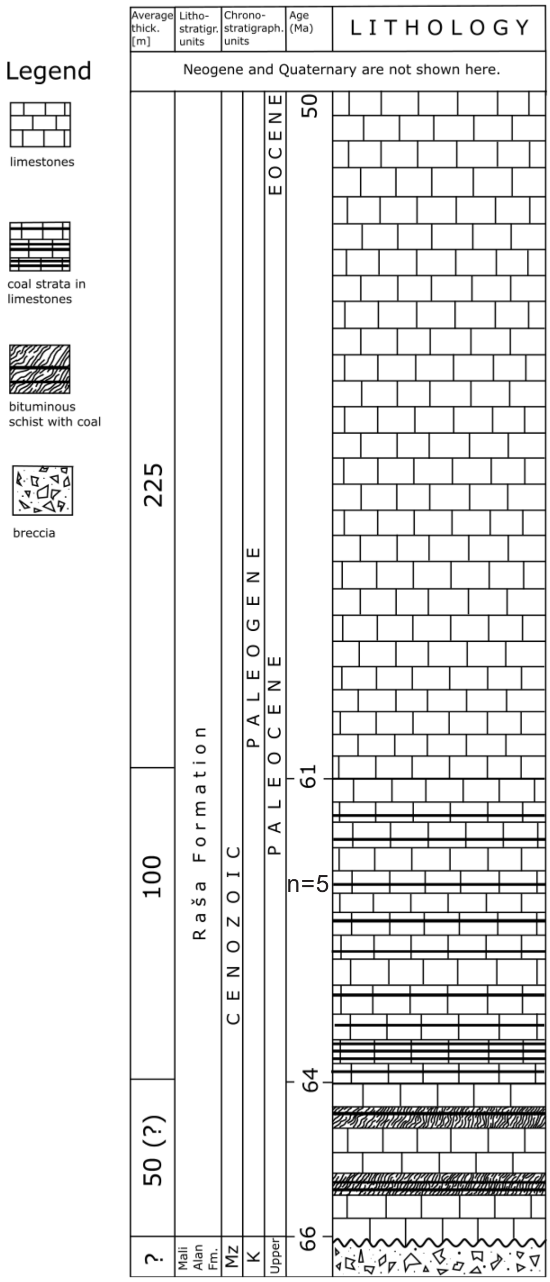



Fig. 8. Regional stratigraphic column from Medunić 2016, after Velić et al., 2015, n = number of samples taken.

## Sampling and methods

Thirty-two lignite and coal samples from six diverse sedimentary basins were collected for this study (Fig. 1). Detailed data, e.g., coordinates of origin with mine sampling locations and sampling date, are presented in the data repository (Kanduč et al., 2023). The coal samples were obtained from various locations, including underground mining areas (Velenje lignite – VL, Hrastnik coal – HC, Raša coal – RC), open-pit mines (Josef coal – JC), and boreholes (Terbegovci lignite – TL).

Twenty-two samples (Table 1) of the ortho-lignite from Velenje were collected during the macro-petrographic logging of three nearly horizontal boreholes from the Pesje and Preloge excavation fields: JPK-52 (+2°) (excavation field B-65/A, Pesje), JGM-55 (+10°) (excavation field B K. -130 Preloge, south wing), and JPK-60 (+10°) (excavation field F K.-65 Pesje). All these cores were collected in the southern central and lower part of the lignite seam (Fig. 2). The boreholes passed through intervals with different lithotype compositions, which have a more significant influence on the isotopic composition than with seam depth (Kanduč et al., 2005; Markič & Sachsenhofer, 2010). The Terbegovci meta-lignite samples (TL) were taken from a depth of 141.0–155.5 m as a composite sample of coal cuttings during the drilling of the TER-1/03 water supply well (Fig. 3), while a single bulk sample of meta-lignite/sub-bituminous coal from the Hrastnik mine was collected just before the mine ceased operation in 2012. A sample from the Josef meta-lignite/sub-bituminous coal seam was also collected (Table 1), and the Thermal-Heat Power Station Ljubljana - Termoelektrarna Toplarna Ljubljana provided a coal sample identified as a sub-bituminous coal from the Barito Basin (Pasir Mine) in Indonesia. Additionally, five samples (Table 1) of ortho-bituminous coal from Raša were collected from different seams of unique petrologic composition (Hamrla, 1959; Medunić et al., 2016).

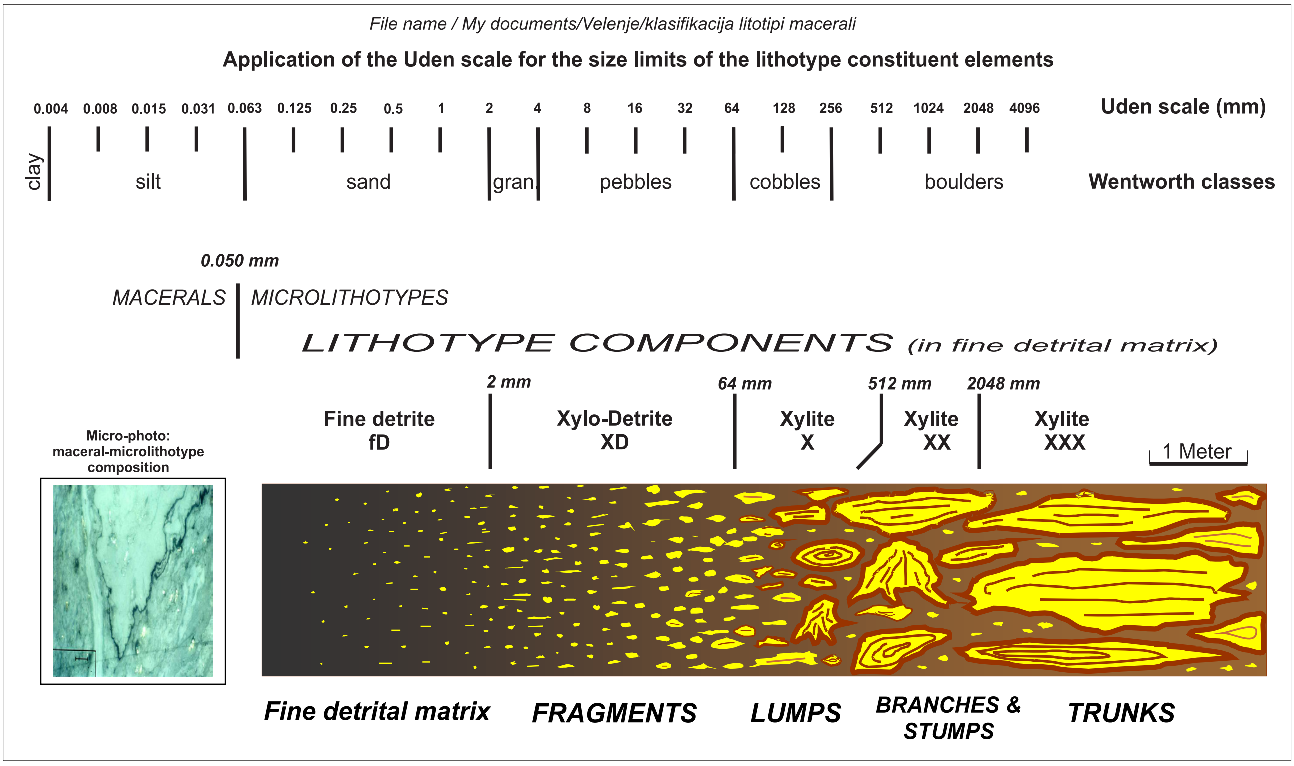



Fig. 9. Basic concept of macropetrographic classification for the Velenje ortho-lignite (Markič et al., 2001; Markič & Sachsenhofer, 2010) using a concept of lithotype components and the Uden scale for dimension limits.

## Macropetrographic description of the Velenje ortho-lignite

Macropetrographic classification of the lithotype heterogeneity of the Velenje ortho-lignite has been defined and described in detail by Markič et al. (2001) and Markič & Sachsenhofer (2010). For its macropetrographic description and composition, a concept of lithotype components was introduced (Fig. 9). The classification is somewhat broader than the “official” classification by the (ICCP, 1993).

Microscopic descriptions of samples (VL3 and VL5, Table 2a) were prepared by crushing the material (<2 mm), embedding it in epoxy resin, subjecting it to vacuum, drying, and then creating polished blocks of size 2.5×2.5 cm. The investigation was conducted using Zeiss Opto Axiophot conventional optical microscopy in polarised reflected light under normal atmospheric conditions, and the results were documented photographically.

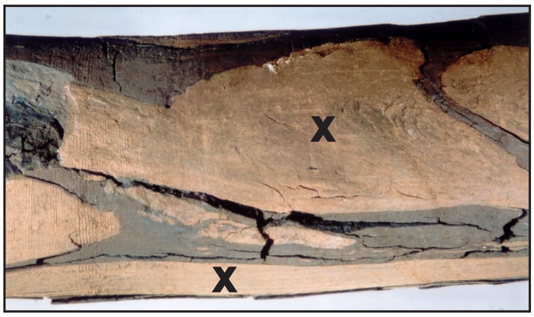
## Isotopic composition of organic carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N_{bulk}$)

The stable isotopic composition of organic carbon ($\delta^{13}C_{org.}$) and nitrogen ($\delta^{15}N_{bulk}$) in different lignite and coal lithotypes was analyzed using the Europa 20–20 isotope-ratio mass spectrometer connected to an ANCA-SL preparation module. To prepare the lignite and coal samples, they were initially homogenized by grinding in an agate mortar. For $\delta^{13}C_{org}$ analysis, the samples were treated with 3M HCl at 60 °C overnight to eliminate carbonates. The remaining residues were washed with distilled water, dried, and homogenized. The organic fraction was filtered through a GF/F filter, and chloride ions were removed with triple washing with distilled water. The residue was then dried at 60–70 °C. Approximately 1–2 mg of the residue was used for $\delta^{13}C_{org}$ measurements. Approximately 8 mg of powdered lignite and coal were used for $\delta^{15}N$ analyses with no pretreatment. The carbon and nitrogen isotopic compositions were determined by combusting the samples in sealed tin capsules in an oxidation column using pure oxygen at 1000 °C. The generated products went throw a reduction column filled with Cu at 600 °C and then separated on a chromatographic column. IAEA CH-3 ($\delta^{13}C$ = -24.724 ‰ ±0.041 ‰) and CH-6 ($\delta^{13}C$ = -10.449 ‰ ±0.033 ‰) reference materials were employed to convert the analytical results to the VPDB scale. IAEA N-1 ($\delta^{15}N$ = +0.4 ‰ ±0.2 ‰) and IAEA N-2 ($\delta^{15}N$ = +20.41 ‰ ±0.12 ‰) were used as reference materials to relate the analytical results to AIR (atmospheric nitrogen) (Coplen, 1996). The reproducibility of the samples was ±0.2 ‰ for carbon isotopes and ±0.3 ‰ for nitrogen isotopes. The results are expressed in the standard $\delta$ notation (in per mil, ‰) as the deviation of the sample (sp) from the standard (st) according to the following equation (Brand et al., 2014):

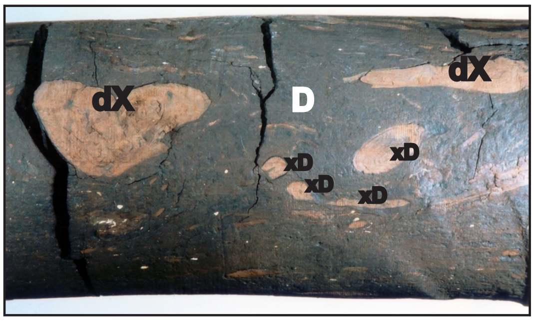
Basic organo-clastic lithotype components

64 mm · 1 mm Scale ~ 1:2 (if not cited differently)


**1:** Xylite **(X)**, wholy extending over dimensions of core diameter.

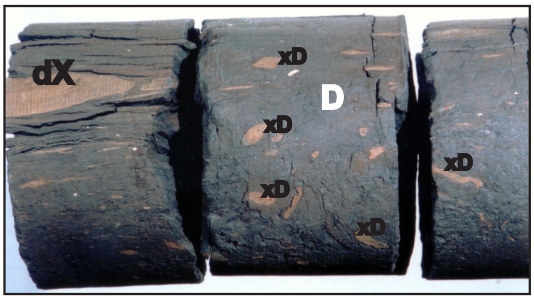



**2:** Xylite fragments **(X)** of different shapes, all longer than 64 mm.

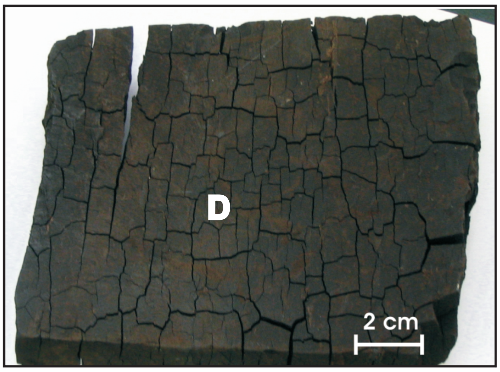



**3:** The biggest two, larger than 32 mm pieces are detro-xylite **(dX)**. Pieces between 1 and 32 mm in size are termed xylo-detrite **(xD)**. Dark homogeneous groundmass (matrix) and the smallest (<1 mm) xylite lenses are termed fine detrite **(D)**.

Extremely small white spots on figs. 3 and 4 are calcite.




**4:** Same components as in fig. 3


**5:** Homogeneous fine detrital lignite - as a whole fine detrite (D). On the left is tyipically crushed, whereas on the right typically fractured fine detrital lignite.

Fig. 10. Lithotype classification is employed in macro-petrographic core logging of the Velenje ortho-lignite. JGM-55 borehole (excavation field B k.-130) (this study) (see appendix) is an example of petrographic well-logging.

$$\delta^{y}X(‰) = (R_{sp}/R_{st}-1)*1000 \quad (1)$$

Where $^{y}X$ is carbon ($^{13}C$) or nitrogen ($^{15}N$), and R the $^{13}C/^{12}C$ or $^{15}N/^{14}N$, respectively.

The $\delta^{13}C$ of air (atmospheric $CO_2$) was then calculated using the equations proposed by Arens et al. (2000) (equation 2) and Gröcke (2002) (equation 3).

Gröcke, 2002 suggested that the carbon isotopic composition of ancient $CO_2$ can be estimated using the $\delta^{13}C$ value of fossil organic matter. In this study, it is assumed that the samples with $\delta^{13}C$ values from -27 ‰ to -22 ‰ were derived from terrestrial/freshwater C3 plants ($\delta^{13}C_{plant}$) and that in Equ. 2, any carbon isotope fractionation during plant metabolism is similar to that of modern C3 plants and that the primary control on plant C isotopes is the carbon isotopic composition of atmospheric $CO_2$ ($\delta^{13}C_{air}$).

$$\delta^{13}C_{air} = (\delta^{13}C_{plant}+18.67)/(1.10) \quad (2)$$

$$\delta^{13}C_{air} = \delta^{13}C_{plant} + 20.22 \quad (3)$$

## Results

The results of the macropetrographic classification and the associated $\delta^{13}C_{org}$ and $\delta^{15}N$ values of lignites and coals and calculated $\delta^{13}C_{air}$ according to equations (2) and (3) from the six selected locations are presented in Tables 2a and 2b. The isotopic data ($\delta^{13}C_{org.}$ and $\delta^{15}N$), the macropetrographic composition data obtained in this study, and previously published data have been uploaded to a public repository (Kanduč et al., 2023).

Table 2a. Results of macropetrographic composition of the Velenje lignite (this study) according to decreasing share of xylite (X) and increasing share of fine detrite (fD), with associated $\delta^{13}C_{org}$ and $\delta^{15}N$ values, $\delta^{13}C_{air}$ values calculated after Arens et al. (2000) and Gröcke (2002), and ash yields from Hann et al. (2020). Ash yields were analyzed as composites of two to five samples with similar petrographic composition.

| **Sample/Location** | **Macropetrographic composition** | | | | | **$\delta^{13}C_{org.}$ (‰)** | **$\delta^{15}N$ (‰)** | **After Arens et al. (2000)** | **After Gröcke (2002)** | **From Hann et al. (2020)** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Interval (m)** | **X (%)** | **dX (%)** | **xD (%)** | **fD (%)** | | | **$\delta^{13}C_{air}$ (‰)** | | **Ash yield (%)** |
| VL2, Velenje JPK 60 | 21.5-21.9 | 95 | | | 5 | -25.3 | +5.6 | -6.4 | -5.5 | 2.69 |
| VL1, Velenje JPK 52 | 16.2-13.3 | 90 | | | 10 | -26.6 | +3.4 | -7.2 | -6.4 | |
| VL3, Velenje JGM 55 | 7.0-7.2 | 85 | | | 15 | -25.7 | +7.4 | -6.4 | -5.5 | 4.93 |
| VL4, Velenje JGM 55 | 9.6-9.9 | 85 | | | 15 | -25.7 | +4.0 | -6.0 | -5.1 | |
| VL15, Velenje JPK 52 | 24.75-24.9 | 70 | | | 30 | -25.5 | +3.5 | -6.2 | -5.3 | 4.45 |
| VL16, Velenje JPK 60 | 8.95-9.15 | 70 | | 5 | 25 | -25.0 | +4.8 | -5.8 | -4.8 | |
| VL13, Velenje JPK 60 | 5.5-5.85 | 20 | 10 | 30 | 40 | -26.2 | +4.4 | -6.8 | -6.0 | 9.91 |
| VL12, Velenje JPK 52 | 22.8-22.95 | 40 | | 15 | 45 | -26.6 | +3.9 | -7.2 | -6.4 | |
| VL14, Velenje JPK 60 | 11.5-11.7 | 35 | | 15 | 50 | -25.5 | +4.6 | -6.2 | -5.3 | |
| VL19, Velenje JPK 60 | 6.6-6.75 | 10 | 5 | 10 | 75 | -27.2 | +3.0 | -7.8 | -7.0 | 9.81 |
| VL20, Velenje JPK 60 | 15.8-16.0 | 10 | 5 | 10 | 75 | -26.5 | +4.5 | -7.1 | -6.3 | |
| VL18, Velenje JPK 60 | 5.85-6.15 | | 5 | 15 | 80 | -27.0 | +3.6 | -7.6 | -6.8 | 9.83 |
| VL17, Velenje JGM 55 | 1.35-1.55 | | 5 | 10 | 85 | -27.3 | +3.5 | -7.8 | -7.1 | |
| VL6, Velenje JPK 52 | 20.35-20.55 | | | 10 | 90 | -27.9 | +2.6 | -8.4 | -7.7 | 9.63 |
| VL8, Velenje JPK 60 | 19.65-19.8 | | | 10 | 90 | -27.4 | +4.1 | -7.9 | -7.2 | |
| VL9, Velenje JPK 60 | 20.6-21.0 | | 5 | | 95 | -26.9 | +2.7 | -7.5 | -6.7 | |
| VL5, Velenje JPK 52 | 17.7-17.8 | | | 5 | 95 | -27.7 | +2.7 | -8.2 | -7.5 | |
| VL7, Velenje JPK 60 | 10.0-10.5 | | | 5 | 95 | -27.2 | +3.0 | -7.8 | -7.0 | |
| VL10, Velenje JPK 52 | 21.4-21.55 | | | 5 | 95 | -27.1 | +5.3 | -7.7 | -6.9 | 14.73 |
| VL11, Velenje JGM 55 | 7.2-7.4 | | | | 100 | -26.9 | +3.5 | -7.5 | -6.7 | |
| VL21, Velenje JGM 55 | 19.5-19.7 | Geloxylite (X65 G35) | | | | -27.5 | +3.6 | -8.0 | -7.3 | |
| VL22, Velenje JPK 60 | 2.5-2.7 | | | 5 | 55min | -27.5 | +3.7 | -8.0 | -7.3 | 23.30 |

X – xylite, dX – detro-xylite, XD – xylo-detrite, fD – fine detrite

Table 2b. Results of macropetrographic composition analysis: TL – Terbegovci lignite (n = 2), HC – Hrastnik coal (n = 1), JC – Josef coal (n = 1), BC – Barito coal (n = 1), RC – Raša coal (n = 5) with associated $\delta^{13}C_{org}$ and $\delta^{15}N$ values, and $\delta^{13}C_{air}$ values as calculated after Arens et al. (2000) and Gröcke (2002).

| Sample/Location | Coalification rank and lithotypes<br>All are humic lignites and coals | $\delta^{13}C_{org.}$ (‰) | $\delta^{15}N$ (‰) | $\delta^{13}C_{air}$ (‰) After (Arens et al., 2000) | $\delta^{13}C_{air}$ (‰) After (Gröcke, 2002) |
|---|---|---|---|---|---|
| TL – Terbegovci lignite, Terbegovci (TER-1/03), Mura Zala basin, NE Slovenia | Meta-lignite, high grade (high grade; <10 % ash db) | -27.0 | +4.4 | -7.6 | -6.8 |
| TL – Terbegovci lignite, TER-1/03, Mura Zala basin, NE Slovenia | Meta-lignite, high grade (high grade; <10 % ash db) | -27.1 | +4.2 | -7.7 | -6.9 |
| HC- Hrastnik coal Terezija polje - Hrastnik, Laško syncline, Central Slovenia | Meta-lignite- Durain | -27.2 | +4.3 | -7.8 | -7.0 |
| JC – Josef coal, Sokolov Basin, Czech Republic | Meta lignite - Durain | -25.6 | +1.8 | -6.3 | -5.4 |
| BC – Barito coal, Barito Basin, Indonesia | Sub-bituminous coal | -27.5 | +2.7 | -8.0 | -7.3 |
| RC – Raša coal, Istrian Basin, Croatia | Ortho-bituminous coal – Vitrain | -23.6 | +3.2 | -4.5 | -3.4 |
| RC – Raša coal, Istrian Basin, Croatia | Ortho-bituminous coal – Vitrain | -23.7 | +4.6 | -4.6 | -3.5 |
| RC – Raša coal, Istrian Basin, Croatia | Ortho-bituminous coal – Vitrain | -23.9 | +3.8 | -4.8 | -3.7 |
| RC – Raša coal, Istrian Basin, Croatia | Ortho-bituminous coal – Vitrain | -24.0 | +5.5 | -4.8 | -3.8 |
| RC – Raša coal, Istrian Basin, Croatia | Ortho-bituminous coal – Vitrain | -24.0 | +2.9 | -4.8 | -3.8 |

The Velenje lignite comprises xylitic components of varying dimensions, shapes, packing, and orientations within a fine detrital matrix. These lithotype components can be categorized as fine detrite (fD), xylo-detrite (XD), and xylites of different sizes (X, XX, XXX) (Fig. 9). Fusite (F) often occurs as incrustations over xylite. Fusite is obtained from the so-called fusinitization pathway (Diessel, 1992), which proceeds under relatively oxygen-enriched conditions. Fusinitization may cause a loss of organic matter and relative enrichment in residual mineral matter (mineralization process). The mineral components typically consist of various forms of calcite (Markič & Sachsenhofer, 2010; Kanduč et al., 2018), consistent with the classification of this lignite as Ca-rich lignite (Markič & Sachsenhofer, 2010). Also, organic components may exhibit different degrees of gelification, classified as weak (G), moderate (GG), and strong gelification (GGG). In the Velenje lignite, huminite macerals (textinite, texto-ulminite, ulminite, attrinite, and densinite) largely predominate, with a share in a total maceral composition ranging between 85 and 95 % by volume, while liptinite and inertinite macerals are highly subordinated (Markič & Sachsenhofer, 1997, 2010).

Xylite refers to fossilized wood pieces larger than 64 mm, i.e., larger than an average borehole-core diameter. In contrast, the detrite consists of fine plant detritus that underwent a coalification process known as biochemical gelification more readily and rapidly compared to xylites (Diessel, 1992; Stach et al., 1982; Taylor et al., 1998), resulting in structural homogeneity of the lignite. The color of detrite ranges from homogeneously dark brown (poorly gelified) to black (if strongly gelified). Detro-xylite and xylo-detrite are xylitic pieces within a fine-detrital matrix. In the case of detro-xylite, the woody pieces are larger than 32 mm, while in xylo-detrite, they are <32 mm (Figs. 9 and 10).

Other lignites and coals in this study are classified by rank (ECE-UN,1998), for example, ortho-lignite, meta-lignite, sub-bituminous coal, bituminous coal and ortho-bitumnous coal (Table 1), and in terms of well-known hard-coal lithotypes: vitrain, clarain, durain and fusain (Stach et al., 1982; Diessel, 1992; Taylor et al., 1998; Flores, 2014).

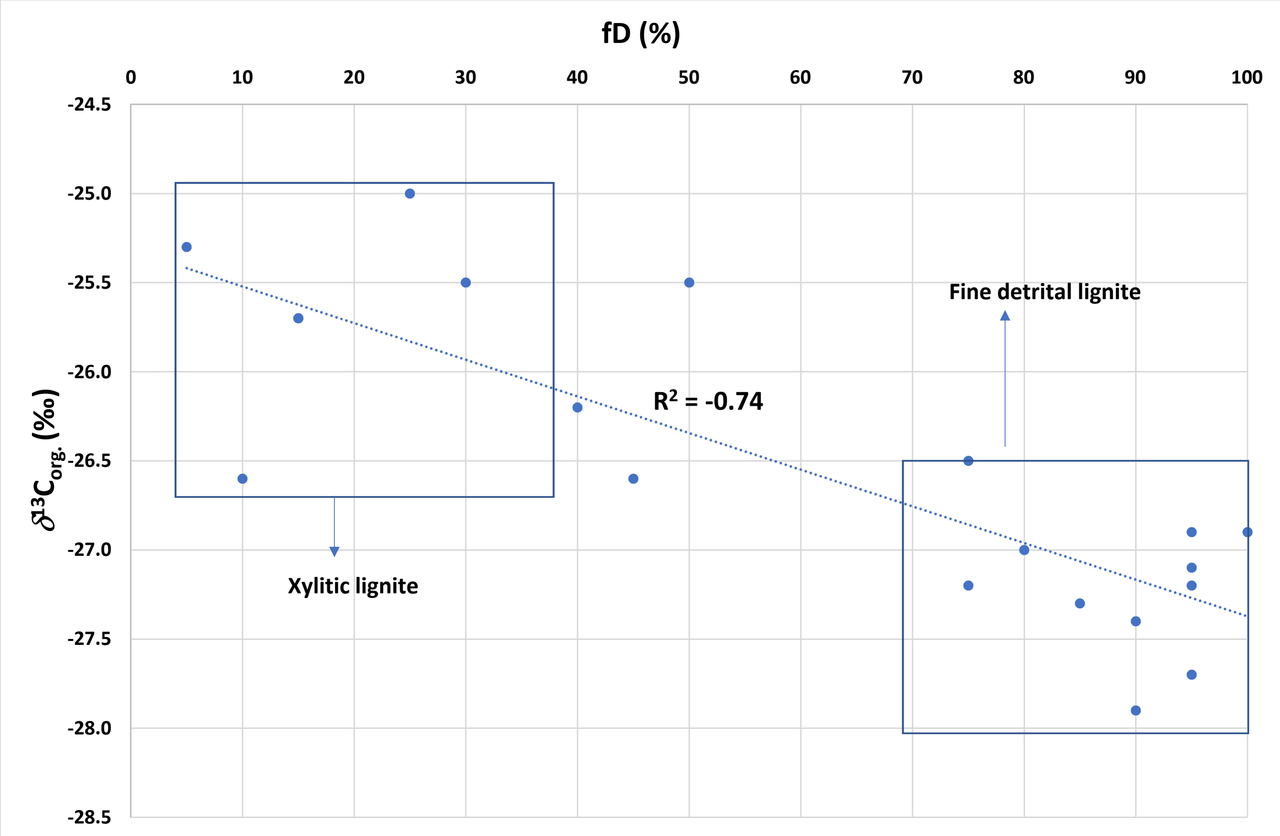



Fig. 11. $\delta^{13}C_{org}$ values vs the share of fine detrital (fD) component of the investigated Velenje lignite samples.

## Discussion

### Relation between xylite, detro-xylite, xylo-detrite and fine-detrite components and associated $\delta^{13}C_{org}$, and $\delta^{15}N$ in the Velenje lignite samples

Among the twenty-two samples of the Velenje ortho-lignite (Table 2a), the following samples with distinct lithotype compositions can be distinguished: six samples of xylite-rich lignite (X >70 %), eleven samples of fine-detrital lignite (fD >75 %) and three samples with a xylite-rich composition (X + dX + xD) 50–60 %, fD 40–55 %, one sample of highly gelified xylite, and one mineral-rich fine detrital sample. In order to look for a possible relationship between fD (fine-detrital component) and $\delta^{13}C_{org.}$ in the Velenje lignite samples, we applied the Mann-Whitney U test. However, no significant difference was identified at the 0.05 significance level. The relationship between fD and $\delta^{13}C_{org.}$ (Fig. 11), using Spearman's non-parametric coefficient is -0.74. The Spearman's correlations ($p<0.05$) for Velenje lignite samples revealed the following correlations: X (%) vs fD (%) -0.97, X+dX (%) vs $\delta^{13}C$ (‰) 0.66 and $\delta^{15}N$ (‰) vs $\delta^{13}C$ (‰) 0.65. dX component is not significantly correlated with any parameter at a $p<0.05$.

Samples of geloxylite (VL 21) and samples enriched with mineral matter (VL 22) are not included in Fig. 11, while two xylite samples with $\delta^{13}C_{org.}$ of -25.7 ‰ and fD 15 % overlap. As observed from Figure 11, xylite-rich lignites (X + dX + xD) ≥50 % vs fD ≤50 % are characterized by $\delta^{13}C_{org}$ values from -26.6 to -25.0 ‰, while those of fine-detrital lignite (fD ≥75 %) are mostly between -27.9 and -26.9 ‰, with one exception with a $\delta^{13}C_{org}$ of -26.5 ‰.

The ash content (Table 2a) in the fine-detrital lignite is higher than in xylitic lignite. Also, the xylite samples (X >70 %) have ash content from 2.69 to 4.45 % and $\delta^{13}C_{org.}$ from -26.6 to -25.0 ‰, while samples enriched with detrital component (fD >40 %) have ash contents from 9.91 to 14.73 % (Table 2a) and are enriched with light $^{12}C$ isotope. The higher ash content for fD (Table 2a) results from water flow influx, with the lake water being subsequently alkaline, promoting gelification, which is discussed in continuation.

### Biogeochemical processes reflected by $\delta^{13}C_{org.}$ and $\delta^{15}N$ in lignites and coals

Mineralization, i.e. microbial degradation of organic matter (enrichment with $^{13}C$ and $^{15}N$ isotope) and gelification processes (enrichment with

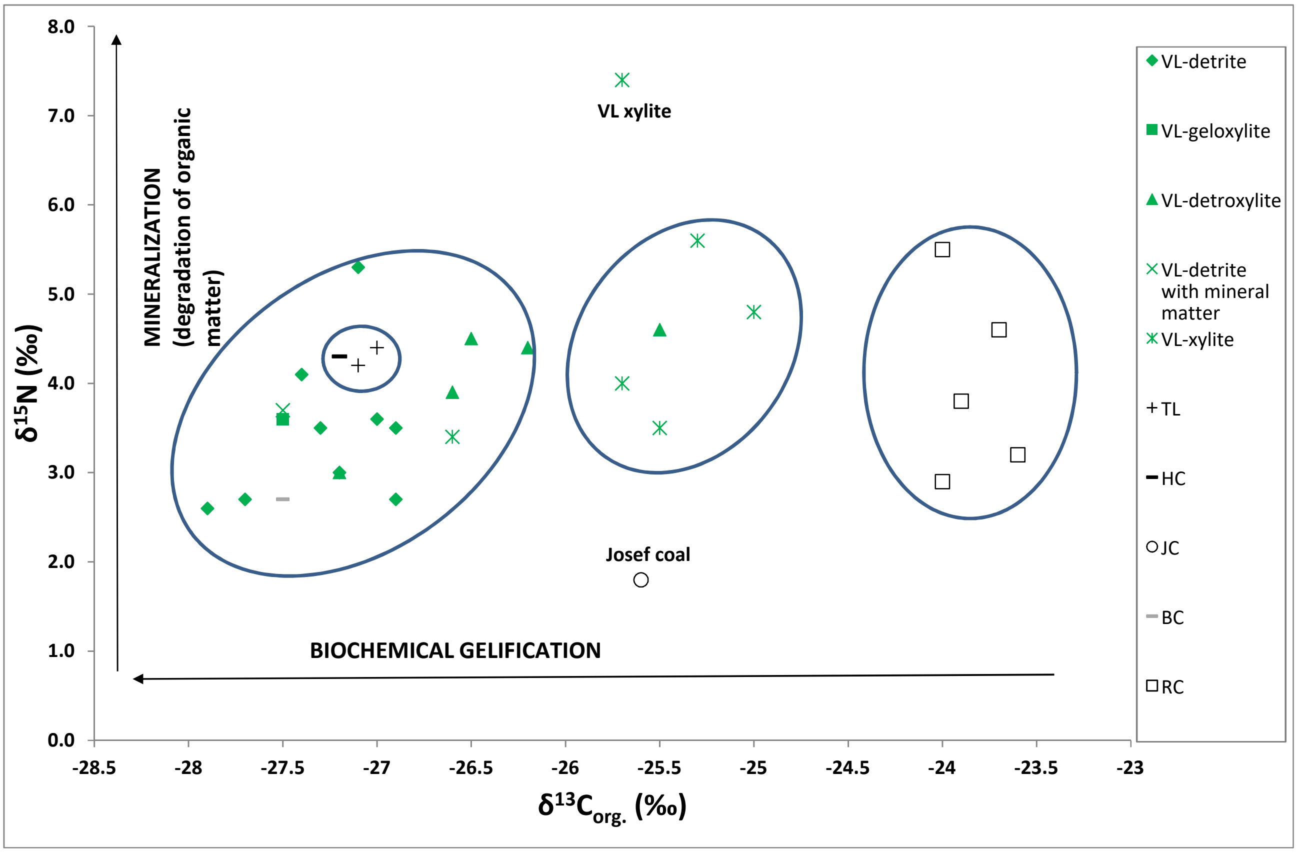



Fig. 12. $\delta^{15}$N vs $\delta^{13}C_{org}$ for Velenje lignite – VL, Raša coal – RC, Hrastnik coal - HC, Jožef coal - JC, Barito coal - BC and Terbegovci lignite - TL. *Degradation of organic matter* enriches coal samples with $^{13}$C and $^{15}$N isotopes; different degrees of biochemical *gelification* (weak, moderate, strong) enriches lignite with $^{12}$C and is the most expressed in Velenje lignite samples.

the light $^{12}$C isotope) are best expressed in the Velenje lignite samples (Table 2a, Fig. 12). The lower $\delta^{13}C_{org}$ values (≤-27.9 ‰) in the Velenje ortho-lignite indicate a high degree of gelification and are common in fine-detrital matrix. In comparison, the $\delta^{15}$N values (≤7.4 ‰) indicate intense mineralization. The $\delta^{15}$N value for liptinite is commonly more positive than that for vitrinite, followed by inertinite (Rimmer et al., 2006). Fine organic terrestrial detritus (giving fine detrital lignite) was accumulated in open-water environments of the inner and upper parts of the initial peatland, whereas higher bush and forest vegetation (giving xylite-rich lignite) occupied the periphery (Markič & Sachsenhofer, 2010).

Several groups indicating one or both processes (mineralization and biochemical gelification) can be distinguished (Fig. 12): lower values of $\delta^{13}C_{org}$ (<-26.9 ‰) are characteristic for the freshwater fine-detrital Velenje ortho-lignite formed in topogeneous mire, as well as for meta-lignite from Terbegovci and Hrastnik, and sub-bituminous coal from Barito formed in a raised swamp.

The lowest $\delta^{13}C_{org}$ values (Fig. 12) are observed in the fine-detrital lignite, which is more affected by the gelification process than the xylite fragments, especially in an alkaline environment where there is significant anaerobic bacterial activity, as in Velenje (Pliocene), Hrastnik (Zasavje Basin - Oligocene) and Terbegovci (Mura-Zala Basin – upper Pannonian). Environments with strong gelification are also characterized by low mineralization, as indicated by low $\delta^{13}$C values. However, as the proportion of xylite components increases, $\delta^{13}C_{org}$ and $\delta^{15}$N values increase due to weaker effects of biochemical gelification and stronger effects of mineralization (Fig. 12). This can be explained by the presence of more aerobic conditions, the subdued oxidation of organic components, and the activity of aerobic bacteria, which result in a relative loss of organic matter and an increase in mineral content. A distinctly notable pattern with a $\delta^{15}$N value of 7.4 ‰ is observed in Velenje xylite (Fig. 12), which is attributed to the highest degree of mineralization. The lowest $\delta^{15}$N value (1.8 ‰) was analyzed in the meta-lignite/sub-bituminous coal from the Josef seam (Oligocene) in the Sokolov Basin. The coal from the Josef seam is a predominantly “detritus-rich,” even “sapropelic-rich,” coal formed from accumulated organic matter in a low drained swamp environment (“peat bog”) with occasional input of tuffaceous material (Rojík, P. in Pešek et al., 2014, p.101). Such an environment is characterized by negligible mineralization and low gelification, most likely due to a relatively acidic paleoenvironment.

A different isotopic composition occurs in the ortho-bituminous (black) coal from Raša (Istrian Basin - Paleocene). This coal formed in a paralic environment with a carbonate hinterland and the probable influence of brackish or marine waters. It shows a narrow range of relatively higher $\delta^{13}C_{org}$ values, from -24.0 to -23.6 ‰, and a broader range of $\delta^{15}N$ values, from 2.9 to 5.5 ‰. Higher $\delta^{13}C_{org}$ values, from -24.0 to -23.6 ‰, could be attributed to the contribution of organic matter of marine origin. A fluctuating water table (alternating transgressions and regressions) in a paralic carbonate platform environment (e.g., tidal flats, lagoons, deltas, mixing of nonmarine and marine sediments) most probably caused by significant changes in mineralization, is evidenced by a wide range of $\delta^{15}N$ values. Bacterial activity was also likely present in the brackish paralic carbonate-rich environment. However, they did not lead to intense gelification of the organic matter; instead, bacterial degradation led to different mineralization.

The lowest $\delta^{15}N$ value (1.8 ‰) was measured in the meta-lignite/sub-bituminous coal from the Sokolov basin, indicating the lowest mineralization of organic matter among all the samples examined and a low degree of bacterial activity. The highest measured $\delta^{15}N$ value (7.4 ‰) of "pure" xylite (i.e., < 5 % ash yield, Table 2a) in the Velenje ortho-lignite indicates pronounced mineralization (Fig.12). Microscopic inspection did not prove the effect of fuzinitization (Fig. 13a). However, cell lumena of textinites are empty implying exposure to air and thus the degradation (mineralization) of organic matter primarily filling cell lumena. The volume content of the textinite (highly prevailing), texto-ulminite and ulminite macerals (Fig. 13a) together is 75 %, corresponding to the of macro-petrographic estimates (X 85 %, Table 2a).

The Velenje fine-detrital ortho-lignite (VL) composed of >90 % of the fD component (Table 2a)

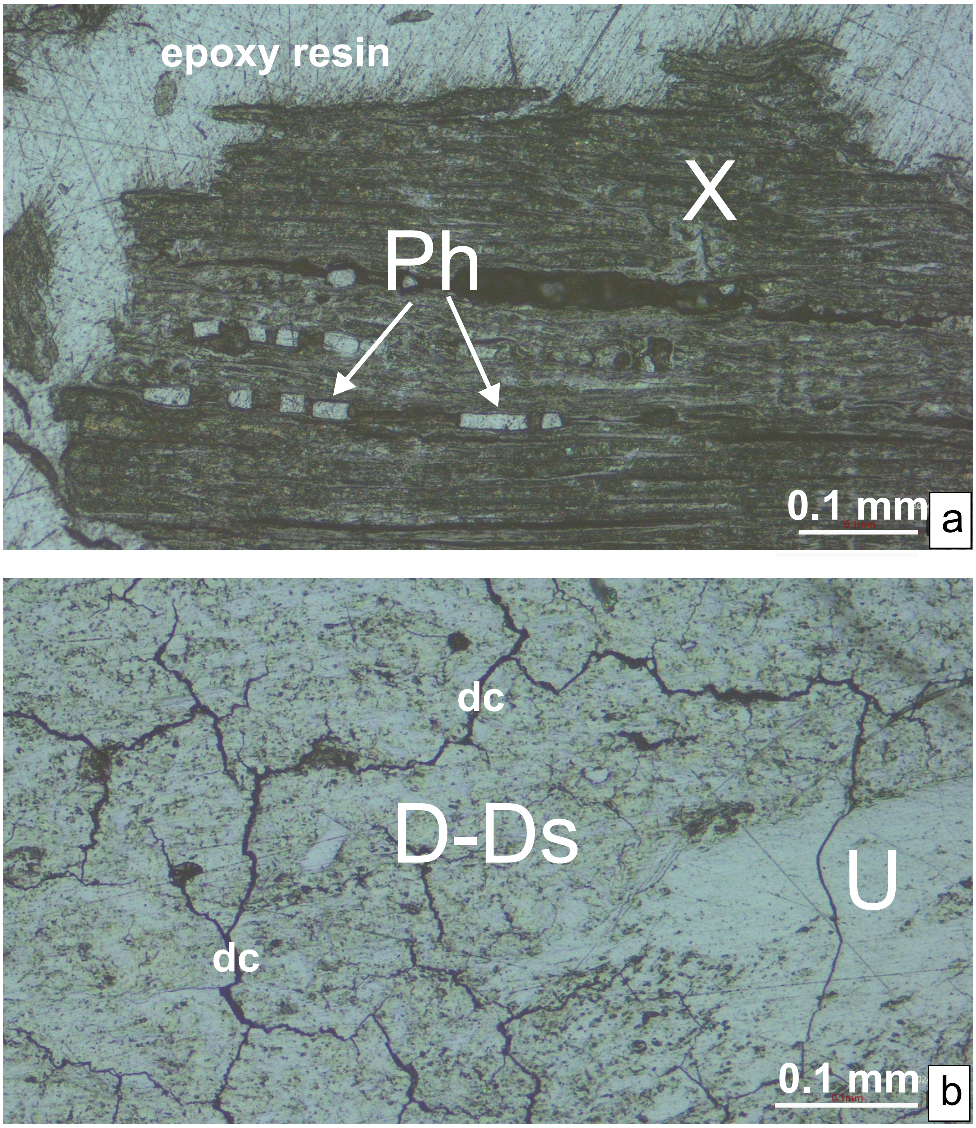



Fig. 13. Micro-petrographic appearance of two contrast lithotypes of Velenje lignite: a) sample VL-3 - Xylinite (X) with phlobaphynite (Ph) highly prevails in xylite-rich ortho-lignite; analyzed ash yield is <5 wt. % and b) sample VL-5 – Ditrinite to densinite (D-DS) highly prevails in fine detrital ortho-lignite; analysed ash yield is <10 wt. %.

U is ulminite; dc are desiccation cracks.

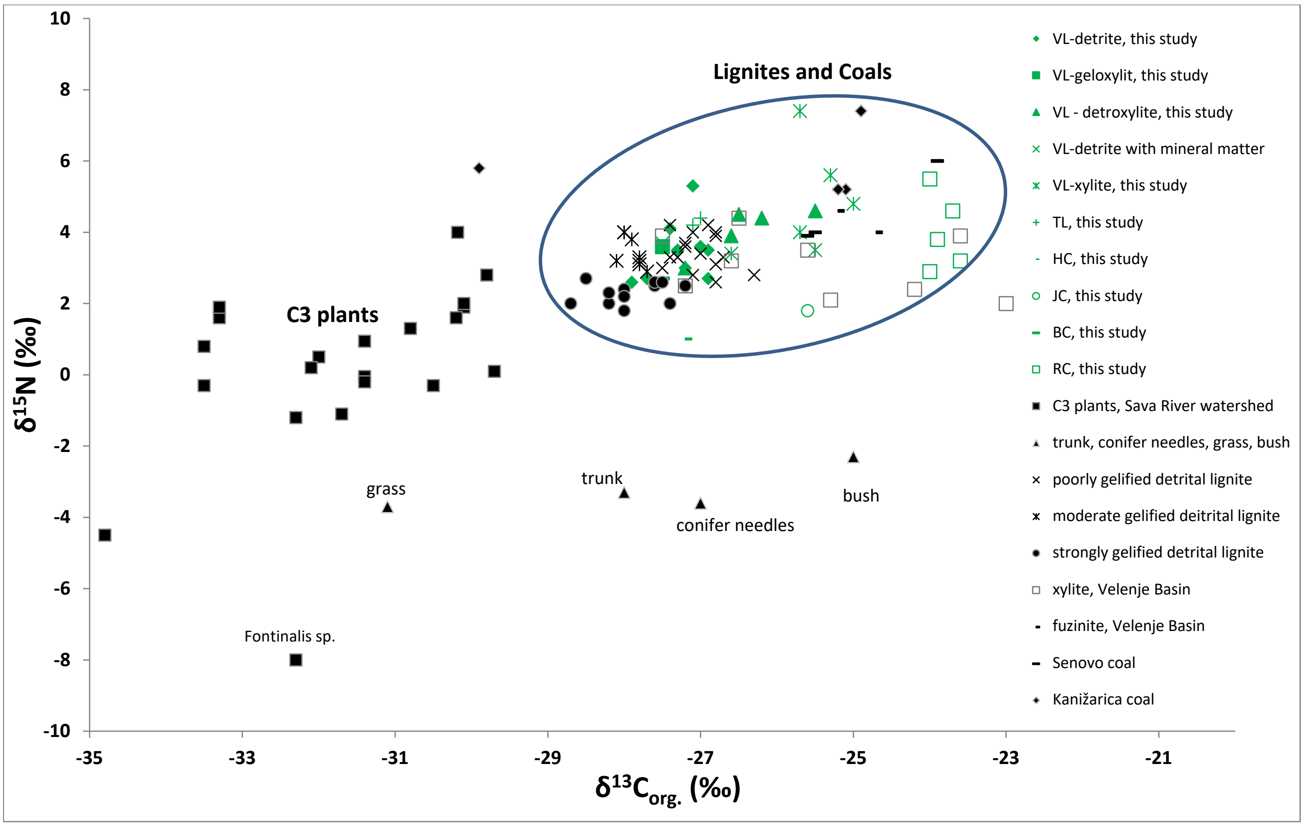



Fig. 14. $\delta^{15}$N versus $\delta^{13}C_{org.}$: plants (terrestrial and aquatic) (Kanduč et al., 2005; Kanduč et al., 2007), and lignites and coals from this and previous studies (Šlejkovec & Kanduč, 2005; Kanduč et al., 2005, Kanduč et al., 2018).

has $\delta^{13}C_{org}$ from -27.9 to -26.9 ‰ (avg.: -27.3 ‰) and $\delta^{15}$N mostly from 2.6 to 3.5 ‰ (extremes: 4.1 ‰ and 5.3 ‰, respectively) (avg.: 3.5 ‰), both indicating considerable gelification (Table 2a and Figs. 12 and 13b). Strongly gelified samples from previous studies (excavation field -50/C, Velenje Basin) had $\delta^{13}$C around -28.0 ‰ with the lowest $\delta^{13}C_{org}$ value of even -28.7 ‰, (Fig. 14) (strong gelification) and $\delta^{15}$N of 2 ‰, which indicates low mineralization (Kanduč et al., 2018; Kanduč et al., 2023).

Considering $\delta^{13}$C values, the precursor plants are C3 plants with values from -33 ‰ to -22 ‰ in all investigated coals (Figs. 12 and 14).

Recent plants collected around the Velenje Basin (Kanduč et al., 2005; Kanduč et al., 2012; Kanduč et al., 2023), such as trunks ($\delta^{13}$C = -28.0 ‰, $\delta^{15}$N = -3.3 ‰), conifer needles ($\delta^{13}$C = -27.0 ‰, $\delta^{15}$N = -3.6 ‰), grass ($\delta^{13}$C = -31.1 ‰, $\delta^{15}$N = -3.7 ‰), and bushes ($\delta^{13}$C = -25.0 ‰, $\delta^{15}$N = -2.3 ‰), exhibit more negative $\delta^{15}$N values compared to lignites and coals (Fig. 14). Recent plants in the Sava River Basin, Slovenia, have on average $\delta^{13}$C values of -31.6 ‰ and $\delta^{15}$N values of 0.2 ‰ (Kanduč et al., 2007; Kanduč et al., 2023). The $\delta^{13}$C and $\delta^{15}$N values of parent organic matter and coalification processes depend on the source of organic matter (bushes, grass, trunks, and conifer needles) and local meteorological conditions (Liu et al., 2020).

## Calculated $\delta^{13}$C values of atmospheric $CO_2$ ($\delta^{13}C_{CO2}$)

The variation in $\delta^{13}$C of the plants is primarily controlled by the atmospheric $CO_2$ isotopic composition ($\delta^{13}C_{CO2}$) rather than the concentration of $CO_2$ in the atmosphere (Arens et al., 2000). Therefore, the $\delta^{13}$C values of coal can be used to estimate the ancient $\delta^{13}C_{CO2}$ values (Arens et al., 2000; Gröcke, 2002). The Eqs. (2) and (3) proposed by (Arens et al.,2000) and (Gröcke, 2002), respectively, have been used for estimating ancient $\delta^{13}C_{CO2}$ using the carbon isotopic composition of organic matter ($\delta^{13}C_{plant}$). This estimation assumes that the carbon isotopic fractionation of plants with atmospheric $CO_2$ is a single-step process (Gröcke, 2002). Enrichment with $^{13}$C in atmospheric $CO_2$ could be related to the burial of more terrestrial plant debris due to rising sea levels (Xu et al., 2020). Diessel (2010) also demonstrated that the late Carboniferous-early Permian was characterized by low $pCO_2$ and more positive $\delta^{13}C_{air}$ values, followed by an increasing atmospheric oxygen content in the mid-early Permian.

In this study from selected coals, the $\delta^{13}C_{CO2}$ value ranges from -3.4 to -8.4 ‰ (Tables 2a, b) based on Eqs. (2) and (3) for all selected coal locations. The calculated $\delta^{13}C_{CO2}$ of coals in our study are in the broader range of values published by Panda et al. (2022) for coals of Permian age (-5.6 to -2.3 ‰). Interestingly, Raša coals of Paleogene age have $\delta^{13}C_{CO2}$ ranging from -4.8 to -3.4 ‰, while a broader range is observed in geologically the youngest Pliocene Velenje lignite (from -5.8 to -8.4 ‰ after (Arens et al., 2000). The global average $\delta^{13}C_{CO2}$ value of modern atmospheric $CO_2$ was reported as -8.4 ‰ in 2015 (Graven et al., 2020). Results from one year of monitoring (January 2011 to November 2011) from nine locations in the Velenje basin around thermo power plant Šoštanj indicate $\delta^{13}C_{CO2}$ of atmospheric $CO_2$ in the range from -18.0 to -6.4 ‰ with an average value of -11.7 ‰ (Kanduč, 2015). This average value shows enrichment with $^{12}C$ compared to $\delta^{13}C_{air}$ from the Pliocene Velenje lignite formation. The pre-industrial global average was estimated for 1850 at -6.6 ‰ (Graven et al., 2020).

Table 3. The $\delta^{13}C$ values of peat (Alaska), lignites and coals from this study and of different world coals.

| Country | Age | $\delta^{13}C$ (‰) | Rank | Reference |
|---|---|---|---|---|
| **Alaska** | Late galicial-E. Holocene | from -28 to -34 | Peat | Panda et al., 2022 and references therein |
| **China** | Pliocene | from -28.4 to -25.4 | Lignite | Panda et al., 2022 and references therein |
| **Velenje, Slovenia** | Pliocene | from -25.3 to -27.0 | Lignite | Panda et al., 2022 and references therein |
| **Austria** | Miocene | from -27.4 to -23.8 | Lignite | Panda et al., 2022 and references therein |
| **Poland** | Miocene | from -27.2 to -24.6 | Lignite | Panda et al., 2022 and references therein |
| **Germany** | Miocene | from -27.3 to -24.6 | Lignite | Panda et al., 2022 and references therein |
| **Australia** | Miocene | from -27.8 to -24.9 | Lignite | Panda et al., 2022 and references therein |
| **Australia** | Oligocene | from -26.4 to -24.2 | | Panda et al., 2022 and references therein |
| **Australia** | Eocene | from -26.4 to -23.6 | | Panda et al., 2022 and references therein |
| **India** | Eocene | from -28.7 to -25.3 | Lignite | Panda et al., 2022 and references therein |
| **India** | Palaeocene | from -30.7 to -25.5 | Lignite | Panda et al., 2022 and references therein |
| **Mongolia** | L. Cretaceous | from -23.5 to -21.3 | Lignite | Panda et al., 2022 and references therein |
| **Australia** | Jurassic | from -25.2 to -20.9 | Sub-bituminous | Panda et al., 2022 and references therein |
| **South-Africa** | Permian | from -25.0 to -23.2 | Bituminous | Panda et al., 2022 and references therein |
| **North China** | Permian | from -25.3 to -22.7 | Sub-bituminous to bituminous | Panda et al., 2022 and references therein |
| **Australia** | Permian | from -26.6 to -21.9 | | Panda et al., 2022 and references therein |
| **India** | Permian | from -24.2 to -21.0 | Bituminous | Panda et al., 2022 and references therein |
| **China** | Late Carboniferous | from -24.3 to -23.1 | Bituminous | Panda et al., 2022 and references therein |
| **USA** | Carboniferous | from -25.1 to -23.5 | Bituminous | Panda et al., 2022 and references therein |
| **India** | Permian | from -23.8 to -21.7 | Sub-bituminous to bituminous | Panda et al., 2022 and references therein |
| **Velenje, Slovenia** | Pliocene | from -27.4 to -22.6 | Ortho - lignite | Pezdič et al., 1998 |
| **Velenje, Slovenia** | Pliocene | from -28.7 to -23.0 | Ortho - lignite | Kanduč et al., 2005, Kanduč et al., 2018 Kanduč et al., 2023 |
| **Kanižarica** | Miocene | from -29.9 to -24.9 | Brown coal | Kanduč et al., 2018 |
| **Senovo** | Oligocene | from -25.6 to -23.9 | Brown coal | Kanduč et al., 2018 |
| **Velenje, Slovenia** | Pliocene | from -27.9 to -25.0 | Ortho - lignite | This study |
| **Hrastnik** | Oligocene | -27.2 | Bitumnious coal – durain | This study |
| **TER-1/03, NE Slovenia** | Upper Pannonian | from -27.0 to -27.1 | Meta-lignite-durain | This study |
| **Raša, Croatia** | Paleocene | from -24.0 to -23.6 | Bituminous–vitrain | This study |
| **Sokolov, Czeck Republic** | Oligocene | -25.6 | Brown coal | This study |
| **Pasir mine, Indonesia** | Miocene | -27.5 | Humic, high-grade meta–lignite | This study |

Table 4. The $\delta^{15}N$ values of lignites and coals from this study and from different world coals.

| Country | $\delta^{15}N$ (‰) | Rank | Reference |
|---|---|---|---|
| **China** | from -6 to -10 | Lignite to antracite | Panda et al., 2022 and references therein |
| **Canada** | from -0.2 to 1.4 | NA | Panda et al., 2022 and references therein |
| **Russia** | from 1.86 to 4.35 | NA | Panda et al., 2022 and references therein |
| **SE-Asia (Indonesia, Malaysia, Phillippines)** | from 0.38 to 2.32 | NA | Panda et al., 2022 and references therein |
| **Europe** | from 3.5 to 6.3 | Lignite to anthracite | Panda et al., 2022 and references therein |
| **Australia** | from 0.3 to 3.7 | Lignite to semi-anthracite | Panda et al., 2022 and references therein |
| **USA** | from 2.1 to 5.35 | Bituminous to anthracite | Panda et al., 2022 and references therein |
| **Germany** | from 2.7 to 3.72 | Anthracite | Panda et al., 2022 and references therein |
| **India** | from 1.07 to 3.44 | Bituminous to anthracite | Panda et al., 2022 and references therein |
| **India** | from 0.6 to 3.4 | Sub-bituminous to high volatile bituminous | Panda et al., 2022 and references therein |
| **Velenje, Slovenia** | from 1.8 to 4.6 | Ortho – lignite | Kanduč et al., 2005, Kanduč et al., 2018 |
| **Kanižarica** | from 5.2 to 7.4 | Brown coal | Kanduč et al., 2018 |
| **Senovo** | from 3.9 to 6.0 | Brown coal | Kanduč et al., 2018 |
| **Velenje, Slovenia** | from 2.6 to 7.4 | Ortho – lignite | This study |
| **Hrastnik, Slovenia** | 4.3 | Bitumnious coal-vitrain | This study |
| **TER-1/03, NE Slovenia** | from 4.2 to 4.4 | Meta-lignite-durain | This study |
| **Raša, Croatia** | from 2.9 to 5.5 | Meta-lignite-durain | This study |
| **Sokolov, Czech Republic** | 1.8 | Brown coal | This study |
| **Pasir mine, Indonesia** | 2.7 | Humic, high-grade meta-lignite | This study |

## Isotopic data in this study gathered with worldwide coals

The $\delta^{13}C$ and $\delta^{15}N$ values in coals analyzed in this study and previous studies and those for worldwide coals are presented in Tables 3 and 4. Data from the coalfields analyzed in our study fall within the range of isotopic values of coals worldwide, i.e., from -30.7 to -20.9 ‰. Characteristic $\delta^{13}C$ values for Paleozoic coals range from -25.7 to -20.2 ‰ (Panda et al., 2022 and references therein). Higher $\delta^{13}C$ values (up to -23.6 ‰) are also observed for Raša coals of Miocene age (Table 3).

The $\delta^{13}C_{org}$ values of Velenje lignites fall within the characteristic range for worldwide lignite, while a broader range (up to 7.4 ‰) is observed for $\delta^{15}N$ (Table 2a). The carbon isotopic composition ($\delta^{13}C_{coal}$, VPDB) of coal samples from the Taiyuan and Shanxi formations of Quinshi and North China-Boloiwan basins ranges from -25.3 ‰ to -22.7 ‰, with an average of -23.7 ‰. The average $\delta^{13}C_{coal}$ value is -23.6 ‰ in the late Carboniferous, -23.4 ‰ in the early Permian, and -20.5 ‰ in the mid-early Permian (Xu et al., 2020). Early Permian coals in the southern North China-Boloiwan Basin to the east were isotopically significantly more negative, with a $\delta^{13}C_{org}$ value of -25.2 ‰ (Table 3), likely due to regional aridity changes. Geologically younger lignites (Paleocene to Pliocene age) have more negative $\delta^{13}C$ compared to geologically older higher rank coals (Late Carboniferous – Late Cretaceous) (Table 3).

There is also disagreement regarding the relationship between $\delta^{15}N$ and coal rank, with several authors reporting a positive correlation between $\delta^{15}N$ and coal rank (Zheng et al., 2015), while others suggest that $\delta^{15}N$ values are largely independent of maturation (Boudou et al., 2008). The $\delta^{15}N$ of the examined peats range from -1.4 to 1.6 ‰, while lignites exhibit values from -1.4 to 1.8 ‰ and coals from India show values from -2.8 to 5.0 ‰. These values indicate that each material preserves its unique organic matter source signature. Moreover, the highest $\delta^{15}N$ values found in Cenozoic lignites compared to Cenozoic sub-bituminous coal suggest regional climatic variation. Furthermore, Gondwana anthracites display elevated $\delta^{15}N$ values from 1.3 to 5.0 ‰, attributed to the tectonic influence of the Himalayan orogeny (Ganguly et al., 2023). In addition, our study observes no relationship between coal rank and $\delta^{15}N$ values; Pliocene lignites from the Velenje Basin can also be enriched with $^{15}N$ with $\delta^{15}N$ up to 7.4 ‰ (Table 4).

## Conclusion

This study examined various ortho-lignite samples from the Velenje Basin, having homogeneous fine-detrital and heterogeneous xylite-rich lithotypes. We also analyzed higher-rank coals for comparison, such as meta-lignites, meta-lignites/sub-bituminous coals, sub-bituminous coals and ortho-bituminous coals. The coals under study were formed in different paleoenvironments and deposited in environments influenced by seawater, as seen in the case of the Raša ortho-bituminous coal and Barito sub-bituminous coal. They were also found in freshwater lake environments, as exemplified by the Velenje ortho-lignite, Hrastnik, and Josef seam meta-lignite/sub-bituminous coals, as well as the Terbegovci meta-lignite and span different geological ages, including the Paleocene (RC), Upper Oligocene (HC, JC), Upper Miocene (JC), upper Pannonian (TL) and Pliocene (VL).

During the processes of peatification and coalification, bacterial activity differed in oxic and anoxic conditions across all the investigated sedimentary coal basins. Moreover, the coals were deposited in open waters, bush moors, and forest swamps. These variations are reflected in the $\delta^{13}C_{org}$ and $\delta^{15}N$ of coals we investigated. The wide range of $\delta^{13}C_{org}$ (from -27.9 to -23.6 ‰) and $\delta^{15}N$ (from 1.8 to 7.4 ‰) values observed in the six different coals indicates different intensities of biogeochemical processes and depositional conditions, including the source of vegetation, humification, bacterial activity, and redox conditions. Gelification, which leads to enrichment with $^{12}C$ and mineralization, which leads to enrichment in $^{15}N$, are most evident in the Velenje ortho-lignite samples.

The detrital lignite sample exhibited the lowest $\delta^{13}C$ value of -27.9 ‰, whereas the highest value of -23.6 ‰ was measured in Raša coal. The $\delta^{15}N$ values of the coal samples also fall within the typical worldwide range, which is between -6.0 to 5.4 ‰. Only the Raša sample with a value of 5.5 ‰ and two xylite samples with $\delta^{15}N$ values of 5.5 ‰ and 7.4 ‰ from Velenje deviate from the worldwide values, indicating higher mineralization. In previous studies, the highest microbial degradation, indicating high activity, was observed in the Raša coal (Paleocene) and the Velenje xylite samples (Pliocene), with the highest $\delta^{13}C$ values of -23.6 ‰. Among all the analyzed samples, gelification was characteristic of Velenje lignite samples, with $\delta^{13}C_{org}$ ranging up to -27.9 ‰ and the lowest (-29.9 ‰) in the Kanižarica sample in previous studies. Similar $\delta^{13}C$ and $\delta^{15}N$ values were only detected in Hrastnik coal (durain maceral type) and Terbegovci lignite samples, suggesting they were deposited in freshwater environments (open water) with similar precursor plants. Both the $\delta^{13}C$ and $\delta^{15}N$ parameters indicate that C3 plants are the precursor plants in all the investigated coal locations. The precursor plant material and microbial degradation played crucial roles during peatification and coalification, influencing both $\delta^{13}C$ and $\delta^{15}N$ values.

The calculated $\delta^{13}C_{CO2}$ values range from -8.4 ‰ to -3.4 ‰, which is more positive in all the coal sedimentary basins compared to the $\delta^{13}C_{CO2}$ of modern atmospheric $CO_2$, reported for the year 2015 (-8.4 ‰, global average). In our study, we can conclude that biogeochemical processes in the coal basin mask the paleoclimate. However, further systematic studies based on macropetrological and microscopic analysis and using elemental ratios and biomarkers combined with $\delta^{13}C_{org}$ and $\delta^{15}N$ data are needed to understand better the biogeochemical processes involved in coalification.

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**Declaration of generative AI and AI-assisted technologies in the writing process.**

While preparing this work, the author(s) used Chat GPT v3.5 for minor language editing and statistical processing. After using this tool/service, the authors reviewed and edited the content as needed and takes full responsibility for the content of the publication.

## References

Arens, N.C., Jahren, A.H. & Amundson, R. 2000: Can C3 plants faithfully record the carbon isotopic composition of atmospheric carbon dioxide? Paleobiology, 26: 137–164. https://doi.org/10.1666/0094-8373(2000)026<0137:CCPFRT>2.0.CO;2

Bangjun, L., Vrabec, M., Markič, M. & Pűttman, W. 2019: Reconstruction of paleobotanical and paleo-environmental changes in the Pliocene Velenje Basin, Slovenia by molecular and stable isotope analyses of lignite. International Journal of Coal Geology, 206: 31–5. https://doi.org/10.1016/j.coal.2019.03.006

Bechtel, A., Sachsenhofer, R.F., Markič, M., Gratzer, R., Lücke, A. & Püttmann, W. 2003: Paleo-environmental implications from biomarker and stable isotope investigations on the Pliocene Velenje lignite seam (Slovenia). Organic Geochemistry, 34/9: 1277–1298. https://doi.org/10.1016/S0146-6380(03)00114-1

Bechtel, A., Markič, M., Sachsenhofer, R.F., Jelen, B., Gratzer, R., Lücke, A. & Püttman, W. 2004: Paleoenvironment of the upper Oligocene Trbovlje coal seam (Slovenia). International Journal of Coal Geology, 57: 23–48. https://doi.org/10.1016/j.coal.2003.08.005

Bechtel, A., Gratzer, R., Sachsenhofer, R.F., Gusterhuber, J., Lücke, A. & Pütman, W. 2008: Biomarker and carbon isotope variations in coal and fossil wood of Central Europe through the Cenozoic. Palaeogeography, Palaeoclimatology, Palaeoecology, 262/3-4: 166–175. https://doi.org/10.1016/j.palaeo.2008.03.005

Boudou, J.P., Schimmelmann, A., Ader, M., Mastelerz, M., Sebilo, M. & Gengenbre, L. 2008: Organic nitrogen chemistry during low-grade metamorphism. Geochimica Cosmoshim Acta, 72/4: 1199–1221. https://doi.org/10.1016/j.gca.2007.12.004

Brand, W.A., Coplen, T.B., & Vogl J., Rosner, M & Prohaska, T. 2014: Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). Pure Applied Chemistry, 86/3: 425–467. https://doi.org/10.1515/pac-2013-1023

Brezigar, A. 1985: Coal seam of the Velenje coal mine. Geologija, 28/29: 319–336 (in Slovene with English summary).

Brezigar, A., Kosi, G., Vrhovšek, D. & Velkovrh, F. 1985: Paleontološke raziskave pliokvartarne skladovnice velenjske udorine = Paleontological investigations of the Plio-Quaternary beds of the Velenje depression. Geologija, 28/29: 93–119.

Buser, S. 1978: Osnovna geološka karta SFRJ 1:100.000. List Celje. Zvezni Geološki zavod, Beograd.

Choi, B.H., Ryn, C.H., Deb, D., Jung, Y.B. & Jeong, J.H. 2013: Case study of establishing a safe blasting criterion for the pit slopes of an open-pit coal mine. International Journal of Rock Mechanics and Mining Sciences, 57: 1–10. https://doi.org/10.1016/j.ijrmms.2012.07.014

Coplen, T.B. 1996: New guidelines for reporting stable hydrogen, carbon and oxygen isotopes ratio data. Geochimica et Cosmochimica Acta, 60: 390–3360. https://doi.org/10.1016/0016-7037(96)00263-3

Diessel, C.F.K. 1992: Coal-Bearing Depositional Systems. Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong: 721 p.

Diessel, C.F.K. 2010: The stratigraphic distribution of inertinite. International Journal of Coal Geology 81/4: 251–268. https://doi.org/10.1016/j.coal.2009.04.004

Ding, D.S., Liu, G.J. & Fu, B. 2019: Influence of carbon type on carbon isotopic composition of coal from the perspective of solid-state $^{13}C$ NMR. Fuel, 245: 174–80. https://doi.org/10.1016/j.fuel.2019.02.072

ECE-UN, 1998: ECE-UN, Economic Commission for Europe, Committeee on sustainable energy. International Classification of in seam coals, 1998/19 documents United Nations, Geneva: 14 p.

Flores, R.M. 2014: Coal and Coalbed Gas. Elsevier, 697 p.

Ganguly, M., Kumar, das S., Ekblad, A. & Behera, P.K. 2023: Variation of $\delta^{15}N$ in Indian coal, lignite and peat. Geochemistry, 83: 126013. https://doi.org/10.1016/j.chemer.2023.126013

Graven, H., Keeling, R.F. & Rogelj, J. 2020: Changes to carbon isotopes in atmospheric $CO_2$ over the industrial Era and Into the Future. Global biogeochemical cycles, 34: e2019GB006170. https://doi.org/10.1029/2019GB006170

Gröcke, D.R. 2002: The carbon isotope composition of ancient $CO_2$ based on higher plant organic matter. Philosophical Transactions A, Mathematical, Physical, and Engineering Sciences, 360/1793: 633–658. https://doi.org/10.1098/rsta.2001.0965

Hamrla, M. 1959: O pogojih nastanka premogišč na krasu = On the conditions of origin of the coal beds in the karst region. Geologija, 5: 180–264.

Hamrla, M. 1960: K razvoju in stratigrafiji produktivnih liburnijskih plasti Primorskega krasa. Rudarsko Metalurški zbornik, 3: 203–2016.

Hamrla, M. 1985: Optična odsevnost nekaterih slovenskih premogov = Light reflectance of some Slovenian coals. Geologija, 28/29: 293-317.

Hann, D., Žarn, J. & Markič, M. 2020: Properties of $CO_2$ adsorption for petrographically diverse ortho-lignites and some higher rank coals. Acta Montanistica Slovaca, 25/3: 324–336. https://doi.org/10.46544/AMS.v25i3.6

Hariana, Prismatoko A., Putra, H.P., Nuryadi, A.P., Sugiarto, Enjang & Nielsen, C. 2021: Characteristics of low-rank and medium–rank Indonesian coal using the TG-DSC method. International Seminar on Mineral and Coal Technology IOP Conf. Series: Earth and Envi-

ronmental Sciences, 882: 012031, https://doi.org/10.1088/1755-1315/882/1/012031
Hoefs, J. 1987: Stable isotope geochemistry. Springer-Verlag, Heidelberg: 241 p.
ICCP-International Committee for Coal Petrology, 1993: International Handbook of Coal Petrography, 3rd Supplement to 2nd Edition. University of Newcastle upon Tyne, England.
Kanduč, T., Markič, M. & Pezdič, J. 2005: Stable isotope geochemistry of different lithotypes of the Velenje lignite (Slovenia). Geologija, 48/1: 83–95. https://doi.org/10.5474/geologija.2005.008
Kanduč, T., Ogrinc, N. & Mrak, T. 2007: Characteristics of suspended matter in the River Sava watershed, Slovenia. Isotopes in environmental and health studies, 43/4: 369–386. https://doi.org/10.1080/10256010701705112
Kanduč, T., Markič, M., Zavšek, S. & McIntosh, J. 2012: Carbon cycling in the Pliocene Velenje Coal Basin, Slovenia, inferred from stable carbon isotopes. International Journal of Coal Geology, 89: 70–83. https://doi.org/10.1016/j.coal.2011.08.008
Kanduč, T. 2015: Isotopic composition of carbon in atmospheric air; use of a diffusion model at the water/atmosphere interface in Velenje Basin. Geologija, 58/1: 35–46. https://doi.org/10.5474/geologija.2015.002
Kanduč, T., Vreča, P., Gregorin, Š., Vrabec, Mi., Vrabec, Ma. & Grassa, F. 2018: Authigenic mineralization in low-rank coals from the Velenje Basin, Slovenia. Journal of sedimentary research, 88/2: 201–2013. https://doi.org/10.2110/jsr.2018.7
Kanduč, T., Markič, M., Žigon, S. & Novak, R. 2023: Data set on petrological and isotopic composition of some selected lignites, sub-bituminous and ortho-bituminous coals. Mendeley Data, https://doi.org/10.17632/ydc964pbdm.2
Kirby, B.M., Vengadajellum, C.J., Burton, S.G. & Cowan, D.A. 2010: Coal, Coal Mines and Spoil Heaps. Handbook of Hydrocarbon and Lipid Microbiology, 2277–2292. https://doi.org/10.1007/978-3-540-77587-4_166
Kuščer, D. 1967: Zagorski terciar (Tertiary formations of Zagorje). Geologija, 10: 5–85.
Lin, Y., Wang, S., Schobert, H. H., Guo, Q. & Li, X. 2022: Sulfur and nitrogen isotopic composition of Late Permian bark coals: source identification and associated environmental assessment. Organic geochemistry, 164: 104369. https://doi.org/10.1016/j.orggeochem.2022.104369
Li, J., Wang, Y., Nguyen, X., Zhuang, X., Li J., Querol, X., Li B., Moreno, N., Hoang, V., Cordoba, P. & Do, V. 2022: First insights into mineralogy, geochemistry and isotopic signatures of the Upper Triassic high-sulphur coals from the Thai Nguyen Coal Field NE Vietnam. International Journal of Coal Geology, 261: 104097. https://doi.org/10.1016/j.coal.2022.104097
Liu, B., Vrabec, M., Markič, M. & Püttman, W. 2019: Reconstruction of paleobotanical and palaeoenvironmental changes in the Pliocene Velenje basin, Slovenia by molecular and stable isotope analysis of lignites. International Journal of Coal Geology, 206: 31–45. https://doi.org/10.1016/j.coal.2019.03.006
Liu, J., Dai, S., Hower, J.C., Moore, T.A., Moroeng, O.M., Nechoer, V.P., Petrenko, T.I., French, D., Graham, I.T. & Song, X. 2020: Stable isotopes of organic carbon, palynology, and petrography of a thick low-rank Miocene coal within the Mile Basin, Yunnan Province, China: implications for paleoclimate and sedimentary conditions. Organic geochemistry, 149: 104103. https://doi.org/10.1016/j.orggeochem.2020.104103
Markič, M. & Sachsenhofer, R.F. 1997: Petrographic composition and depositional environments of the Pliocene Velenje lignite seam (Slovenia). International Journal of Coal Geology, 33/3: 229–254. https://doi.org/10.1016/S0166-5162(96)00043-2
Markič, M., Zavšek, S., Pezdič, J., Skaberne, D. & Kočevar, M. 2001: Macropetrographic characterization of the Velenje lignite (Slovenia). Acta Uniiversitaties Carolinae Geologica, 45: 81–97.
Markič, M. & Sachsenhofer, R.F. 2010: The Velenje lignite: its petrology and genesis. Geološki zavod Slovenije, Ljubljana: 218 p.
Markič, M., Turk, V., Kruk, B. & Šolar, S.V. 2011: Premog v Murski formaciji (pontij) med Lendavo in Murskim središčem ter v širšem prostoru SV Slovenije = Coal in the Mura Formation (Pontian) between Lendava (Slovenia) and Mursko Središče (Croatia), and in the wide area of NE Slovenia. Geologija, 54/1: 97–120. https://doi.org/10.5474/geologija.2011.008
Markič, M. & Brenčič, M. 2014: High arsenic (As) content in the upper Miocene coal matter from TER-1/03 borehole. Geologija, 57/1: 015–026. https://doi.org/10.5474/geologija.2014.002
Masood, N., Zafar, T., Hudson-Edwards, K.A., Rehman, H. U. & Farooqi, A. 2022: Trace element geochemistry and stable isotopic ($\delta^{13}$C and $\delta^{15}$N) records of the Paleocene Coals, Salt Range, Punjab, Pakistan. International Journal of Mining Science and Technology, 32: 551–561. https://doi.org/10.1016/j.ijmst.2022.03.007

Medunić, G., Rađenović, A., Bajramović, M., Švec, M. & Tomac, M. 2016: Once grand, now forgotten: what do we know about the superhigh – organic-sulphur Raša coal? The Mining Geology Petroleum Engineering Bulletin, 27–45. https://doi.org/10.17794/rgn.2016.3.3

O'Leary, M.H. 1988: Carbon isotopes in photosynthesis. Bioscience, 38: 328–336. https://doi.org/10.2307/1310735

Panda, M., Equeemuddin, Sk., Md. & Mohanty, D. 2022: Organic petrography and stable isotopic characteristics of Permian Talcher coal, India: Implications on depositional environment. International Journal of Coal Geology, 264: 104130. https://doi.org/10.1016/j.coal.2022.104130

Papež, D. 2019: Elaborat o klasifikaciji in kategorizaciji izračunanih zalog in virov premoga v Premogovniku Velenje s stanjem 31.12.2018. Premogovnik Velenje (in Slovene).

Pešek, J. et al. (23 co-authors), 2014: Tertiary basins and lignite deposits of the Czech Republic. Czech Geological Survey: 283 p.

Peterson, B.J. & Fry, B. 1987: Stable isotopes in ecosystem studies. Annual Review of Ecology, Evolution and Systematics, 18/1: 293–320.

Pezdič, J., Markič, M., Lojen, S., Čermelj, B., Ulrich, M. & Zavšek, S. 1998: Carbon isotope composition in the Velenje lignite mine – its role in soft brown coal genesis. Materials and geoenvironment, 45: 149–153.

Placer, L. 1998: Structural meaning of the Sava folds. Geologija, 41/1: 191–221. https://doi.org/10.5474/geologija.1998.012

Premru, U. 1983: Osnovna geološka karta SFRJ 1:100.000. List Ljubljana. List Ljubljana. Zvezni geološki zavod, Beograd.

Rađenović, 2006: Inorganic constituents in coal. Kemija u industriji, 55: 65–71.

RCMWRA, (Republic Commission for Mineral and Water Reserves Assessment) 2002: Annual Balance of Mineral Raw Material Reserves and Resources in Slovenia – I Energy raw materials. Ministry of Economic Affairs: Ljubljana.

Rimmer, S.M., Rowe, D., Toulbee, D.N. & Hower, J.C. 2006: Influence of maceral content on $\delta^{13}$C and $\delta^{15}$N in a Middle Pennsylvanian coal. Chemical Geology, 225: 77–90.

Rojík, P. 2004: New stratigraphic subdivision of the Tertiary in the Sokolov basin in Northwestern Bohemia. Journal of Czech Geological Society, 49/3–4: 173–185.

Rojík, P., Dašková, J., Kvaček, Z., Pešek, J., Skorov Rojík, P., Dašková, J., Kvacêk, Z., Pesêk, J., Sýkorová, I. & Teodoridis, V. 2014: The Sokolov Basin. In: Pesêk, J. (ed.): Tertiary basins and lignite deposits of the Czech Republic. Czech Geol Survey, Prague: 90–142.

RTH d.o.o. 2013: Elaborat o klasifikaciji in kategorizaciji izračunanih zalog in virov rjavega premoga na pridobivalnem prostoru Rudnika Trbovlje – Hrastnik s stanjem 31.12.2012 = Elaborate on the classification and categorization of the calculated reserves and resources of lignite in the extraction area of the Trbovlje-Hrastnik mine with the status of 31.12.2012 (in Slovene).

Shafiee, S. & Topol, E. 2009: When will fossil fuel reserves be diminished? Energy Policy, 37: 181–189.

Speight, J.G. 2013: Coal-Fired Power Generation Handbook. Scrivener Publishing LLC, Salem, 8–21.

Stach, E., Mackowski, M.-Th., Teichmüler, M., Taylor, G.H., Chandra, D. & Teichmüler, R. 1982: Stach's Textbook of Coal petroogy (Third Edition). Gebrüder Borntraeger, Berlin: 535 p.

Supandi & Hartono, H.G. 2020: Geomechanic properties and provenance analysis of quartz, sandstone from the Warukin formation. International Journal of GEOMATE, 18/66: 140–149. https://doi.org/10.21660/2020.66.50081

Šturm, M., Lojen, S., Markič, M. & Pezdič, J. 2009: Speciation and isotopic composition of sulphur in low rank coals from four Slovenian Coal Seams. Acta Chimica Slovenica, 56: 989-996.

Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R. & Robert, P. 1998: Organic Petrology. Gebrüder Borntraeger, Berlin: 704 p.

Thomas, L. 1992: Handbook of practical coal geology. John Wiley and Sons, Chichester: 338 p.

Veber, I. & Dervarič, E. 2004: Reserves presentation for Velenje colliery according to United Nations framework classification. First session of the ad hoc group of experts on classification of energy reserves and resources; Geneva, http://www.unece.org/ie/se/pdfs/adclass/day2/Subelj Veber_UNFC.pdf

Velić, J., Malvić, T., Cvetković, M. & Velić, I. 2015: Stratigraphy and petroleum geology of the Croatian part of the Adriatic basin. Journal of Petroleum Geology, 38/3: 281–300.

Vrabec, M., 1999: Style of postsedimentary deformation in the Plio-Quaternary Velenje basin, Slovenia. N. Jb. Geol. Paläont. Mh.: 449–463.

Xu, Z., Hamilton, S.K., Rodrigues, S., Baublys, K. A., Esterle, J. S., Liu, Q. & Golding, S.D. 2020: Palaeoenvironment and palaeoclimate during the late Carboniferous – early Permian in northern China from carbon and nitrogen isotopes of coals. Palaeogeography, Palaeoclimatology, Palaeoecology, 539: 109490. https://doi.org/10.1016/j.palaeo.2019.109490

Zheng, Q., Liu, Q., Huang, B. & Zhao, W. 2015: Isotopic composition and content of organic nitrogen in the coals of Quinshui coalfield, North China. Journal of Geochemical Exploration, 149: 120–126. https://doi.org/10.1016/j.gexplo.2014.12.002

Electronic sources:

Internet 1: https://www.statista.com/statistics/544848/distribution-of-thermal-coal-exporting-countries-worldwide/ (accessed in 15 December 2023)

Internet 2: https://www.gem.wiki/Pasir-coal_mine (accessed on 15 November 2023)

Appendix to Figure 10