*Technical paper*

# Speciation and Isotopic Composition of Sulphur in Low-rank Coals from Four Slovenian Coal Seams

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## Abstract

The abundance, distribution and isotopic composition of sulphur in low-rank coals from four Slovenian coal seams are presented. Samples were characterised as medium (1–3 wt%) or as high sulphur coals (>3 wt%), with the majority of sulphur occurring in the organic form. The isotopic composition of sulphur in coals in Slovenia was determined for the first time. It was found that $\delta^{34}S$ varies between different coal seams, as well as between different lithotypes inside particular coal seams. This can be explained by different $SO_4^{2-}$ and $Fe^{2+}$ availability and microbial activity inside the coal forming basin.

**Keywords:** Coal, sulphur, stable isotopes, lignite

## 1. Introduction

A knowledge of the abundance and nature of sulphur (S) in coal is important in coal utilization because sulphur oxides released during coal combustion can be a major source of acid rain.[1] Sulphur can be present in coal as iron sulphides (mostly as pyrite and marcasite, seldom as sphalerite, galenite, or halcopyrite), as sulphates (mostly as gypsum or barite, sometimes as iron sulphate, formed by oxidation of sulphides, i.e. coquimbite, szomolnokite), as elemental sulphur or as organically bound sulphur. Variation in the sulphur content of coal is controlled mainly by geological conditions,[2] such as the acidity of the peat and by the sulphate content of waters within the peat.[3] Coals have been graded according to their sulphur content into low-sulphur coals that contain less than 1 wt% total sulphur, medium-sulphur coals that contain 1–3 wt% total sulphur and high-sulphur coal that contain more than 3 wt% total sulphur.[4] It is well known that marine-influenced peats generally have higher sulphur contents than freshwater-influenced ones[3] and high sulphur contents in coal seams cannot be accounted for by the original plant sulphur. Therefore, some sulphur must have been incorporated into the peat after the plants died and were buried.[2] Sulphur available during plant growth is the principal source of sulphur in low-sulphur coals. In contrast, in medium and high-sulphur coals overlain by a marine roof, most of the sulphur is derived from seawater sulphate.[1,2,5] Many researchers[5,6,7] emphasized that freshwater coals deposited in calcium-rich environments have similar sulphur contents as brackish-marine coals.

Sulphur isotopes can be used to interpret the origin of sulphur and provide important information on processes within peat-forming depositional environments. In general, the $^{34}S/^{32}S$ ratios in medium and high sulphur coals are variable, suggesting microbiological isotopic fractionation,[2] which favours the incorporation of $^{32}S$ into the reaction products. Where sulphate concentrations remain low and limited during early diagenesis, such as in non-marine environments, near-quantitative bacterial reduction of all the available sulphate results in the addition of comparatively $^{34}S$-rich sulphur species to the coal.[2]

Bacterial reduction of sulphate produces hydrogen sulphide ($H_2S$), which reacts either with $Fe^{2+}$ or organic matter during early diagenesis to form sulphides or organosulphur compounds.[2] The $Fe^{2+}$ source comprises two pools: detrital $Fe^{2+}$ within the peat and $Fe^{2+}$ diffusing from underlying sediments.[8] It is well known that $Fe^{2+}$ has a

greater affinity for $H_2S$ than organic material does.[2,9] Under conditions where $SO_4^{2-}$ is abundant and bacterial activity is constant, organic matter and $H_2S$ can react to produce organic sulphur. However, in closed system conditions under limited $^{32}SO_4^{2-}$ availability, both organic matter and $Fe^{2+}$ incorporate $H_2S$ enriched in $^{34}S$, producing pyrite and organic sulphur with higher $\delta^{34}S$ values.[2]

In the presented work sulphur abundance, speciation and for the first time the isotopic composition of low-rank coals from four coal seams in Slovenia were studied.

## 2. Experimental

Eleven low-rank coal samples from four different Slovenian coal seams were taken (with the number of samples and sampling description in parentheses), as follows. The Velenje lignite seam (5; 4 different lithotypes, taken afresh) (Fig. 1); the Kanižarica coal seam (4; samples already taken for previous studies) (Fig. 2); the Trbovlje-Hrastnik coal seam, Ojstro coal pit (1; taken afresh) (Fig. 3) and the Senovo coal seam (1; taken from the coal mine collection) (Fig. 4). Samples were stored in sealed plastic vials or plastic bags. The abundance and isotopic composition of sulphur, carbon and nitrogen were determined for all samples. The macroscopic description of the lignite samples in terms of lithotypes was determined following the criteria for lithotype classification for soft brown coals (lignites) of the International Committee for Coal Petrology (ICCP, 1993).[10] The microscopic description was determined by optical reflection microscopy following the criteria for classification of macerals of soft brown coals – lignites after ICCP (1971, 1975).[11] Microscopic analysis was performed only qualitatively to estimate the concentration of sulphide (pyrite and/or marcasite) grains.

In the laboratory, samples were pulverized to a fine powder using an agate mortar and pestle and homogenized before subsamples were taken for further analyses. The samples were dried at 40 °C to constant weight prior

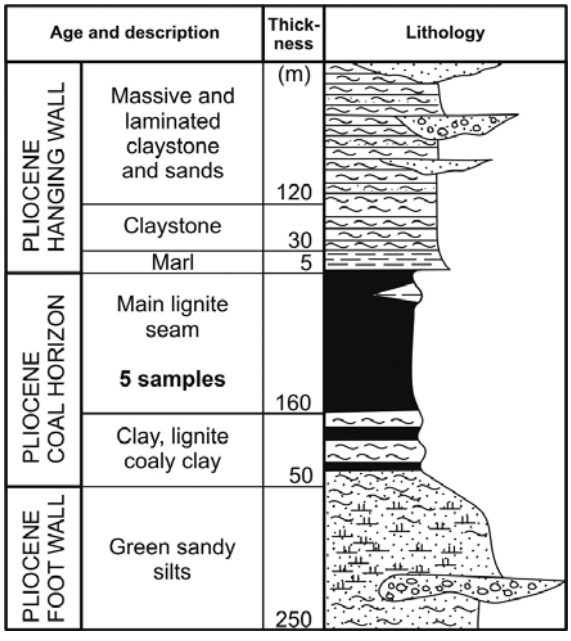


**Figure 1:** A sector from the general lithological column of the Velenje (after[12]).

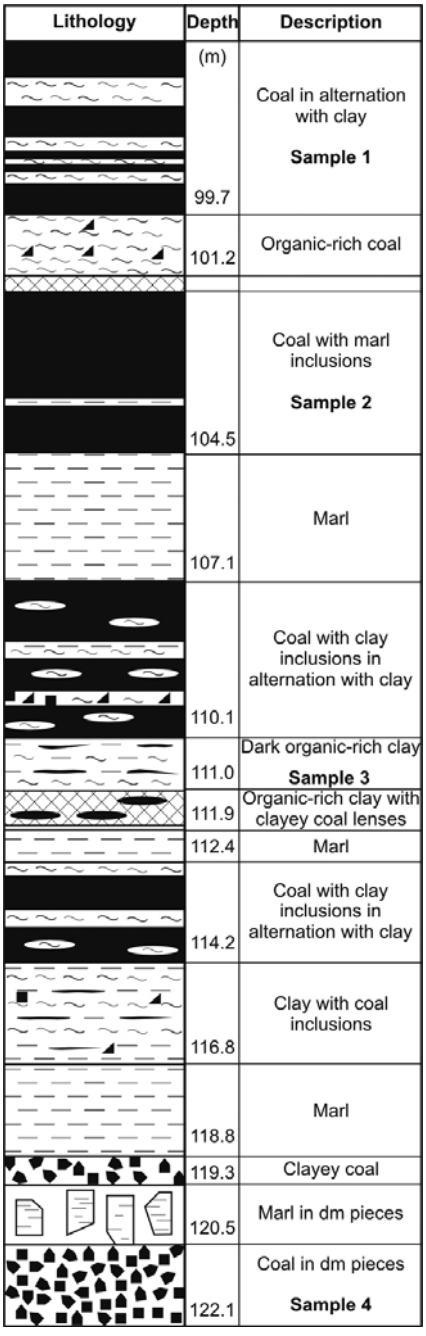


**Figure 2:** Coal-bearing interval from the V53/89 borehole of the Kanižarica coal seam (after[13]).

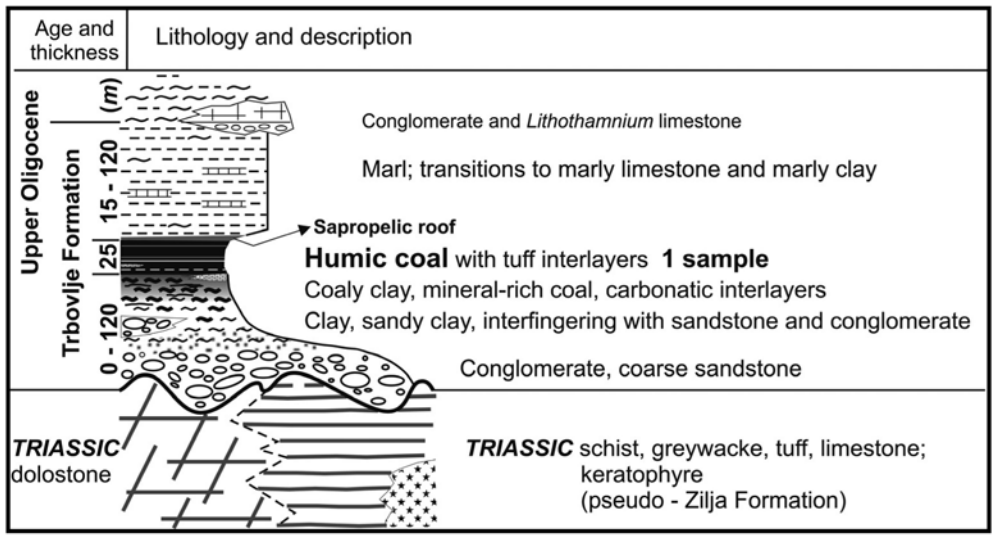


**Figure 3:** Lithological column of the Trbovlje coal-bearing formation of Oligocene age (based on[14]; from[15]).

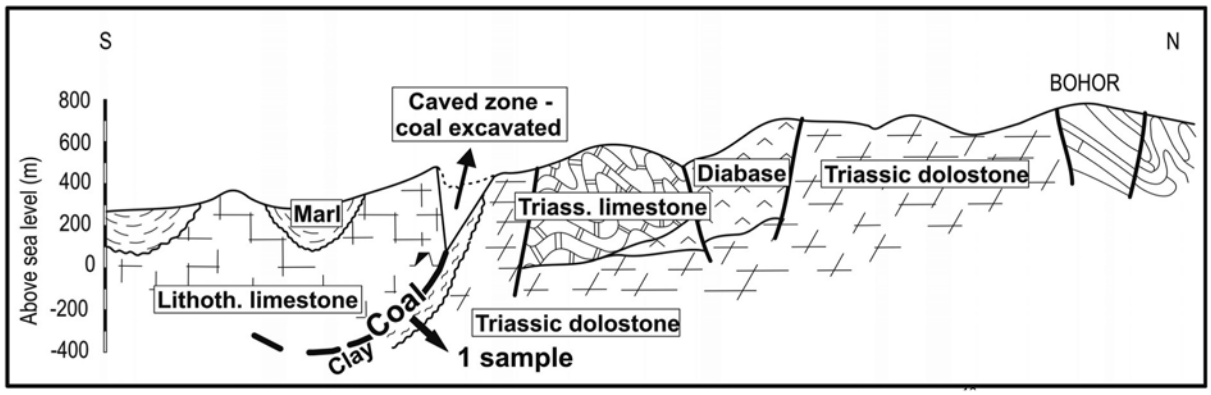


**Figure 4:** Geological profile of the Senovo coal deposit in N–S direction (from[16]).

to the sequential analysis of sulphate (SULPH), monosulphides estimated as acid volatile sulphides (AVS), sulphides estimated as total chromium reducible sulphur (CRS), and bulk insoluble organic (ORG) sulphur which was than determined gravimetrically with a limit of detection of 0.01 mg. Total (TOT) sulphur content was determined as the sum of the separate species. The above sequential extraction of sulphur species was made following the procedure described in references.[17,18]

The reproducibility and yield of the method were determined during optimisation of the procedure on organic-rich sediment samples (1) by replicate analyses of the same samples, (2) by comparing the concentrations of separate sulphur species to the total S as determined by elemental analysis, and (3) by the analysis of pure calcite and silica powder mixtures with known concentrations of added S-species (sphalerite, pyrite and Ca sulphate as substitutes for AVS, CRS, and sulphate, respectively). The average yield was better than 96%, and repeatable within 10%. Most important, differences in reaction yield did not significantly affect the isotopic composition of the precipitates, as the measured δ values of parallel samples were within 1 ‰, which is negligible compared to the isotope separation between different S species.

The concentration and isotopic composition of sulphur was determined for each sulphur fraction separately, as well as for total nitrogen ($N_{TOT}$) and organic carbon ($C_{ORG}$). Prior to sulphur isotope analyses, $Ag_2S$ was mixed with an equal amount of $V_2O_5$, whereas sulphate was mixed with equal amounts of $V_2O_5$ and $SiO_2$ to facilitate the combustion of samples in the elemental analyser. Homogenised sample mixtures were put into tin capsules. Samples for carbon analysis were pulverized, homogenized and soaked with 3 M HCl overnight to remove carbonates, rinsed with deionised water and dried prior to analysis, whereas pulverized samples untreated with HCl were analysed for determination of the N isotope composition.

The concentration (C, N) and isotopic composition (C, N, S) of the samples were determined simultaneously using an Europa 20–20 continuous flow isotope ratio mass spectrometer with an ANCA-SL preparation module (PDZ Europa Ltd., U.K.), connected to an elemental analyser. The $^{34}S/^{32}S$, $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios are reported in delta notation (δ) indicating parts per thousand (‰) as deviations from default reference materials: Vienna Canyon Diablo Troilite (VCDT), Vienna Pee Dee Belemnite (VPDB) and AIR, respectively, as follows:

$$\delta S = \frac{R_S - R_{RM}}{R_{RM}} \cdot 1000 \quad [‰] \qquad (1)$$

where R is the ratio between the heavier and lighter stable isotope of a particular element, S is sample and RM is the reference material. Positive δ values mean that the sample contains more heavier isotope than the reference material, and negative δ values that it contains less.[19]

The analytical precision of the determination of carbon and nitrogen contents was estimated to be ±6%, and for isotopic measurements ±0.2‰ for $\delta^{13}C$ and $\delta^{15}N_{tot}$, and ±0.4‰ for $\delta^{34}S$, based on replicate measurements of reference materials and samples. The following reference materials were used: NBS 23, NBS-127, IAEA-S-1, IAEA-S-2, IAEA S-3, IAEA-S-4, IAEA-SO-5 for sulphur, IAEA-CH-7, USG-24 for carbon and IAEA-N-1, IAEA-N-2 for nitrogen isotope measurements.

# 3. Results and Discussion

## 3. 1. Elemental Composition

The total sulphur, nitrogen and total organic carbon contents of the samples analysed (Tab. 1) varied among different coal seams, as well as among different lithotypes inside particular coal seams. With regard to total S, two samples from the Velenje lignite coal seam were characterized as high-sulphur coal with more than 3 wt% total sulphur (fine detritial lignite and gelified fine detritial lignite), and three as medium-sulphur coal, with 1–3 wt% total sulphur (xylite, fusite and gelified fine detritial lignite taken ahead of a working face). All coal samples from the Kanižarica lignite coal seam, as well as coal samples from the Trbovlje-Hrastnik and the Senovo coal seams were characterized as medium-sulphur coals.

Acid volatile sulphides (AVS) were below the detection limit. In all samples, with the exception of the sample from the Trbovlje-Hrastnik coal seam and Kanižarica 3 (organic-rich clay), organic sulphur predominated (Tab. 1, Fig. 5). Considering the fact that $Fe^{2+}$ has a higher affinity to $H_2S$ than organic material,[2,9] the higher organic sulphur contents compared to CRS could be explained by a lack of reactive iron. This, however, was not the case in the Trbovlje-Hrastnik coal seam and Kanižarica 3, where CRS was more abundant than organic sulphur. In the samples analysed, sulphate sulphur was mostly present in very low abundances (≤0.1 wt%), with the exception of two samples from Kanižarica with 0.7 and 1.0 wt%, where the first sample was coal in alteration with clay and the second sample not coal but organic-rich clay. Since the isotopic composition of sulphate S was lower compared to sulphides (see Section 3.2), the presence of sulphate sulphur could be explained by the reoxidation of sulphides, where lighter isotopes are preferentially oxidized, leaving the remaining sulphide enriched with the heavier isotope.

Total nitrogen and total organic carbon in samples from the Velenje lignite coal seam varied from 0.4 to 1.8 wt% and from 42 to 59 wt%, respectively. Microbial degradation of organic matter during early diagenesis affects the variation in C/N ratio,[20,21] where higher microbial activity results in lower C/N ratio.[22] This phenomenon was also observed in Velenje lignite samples (Tab. 1), with the C/N ratio decreasing from xylite, with a C/N

**Table 1:** Elemental composition and C/N weight ratios of the coals studied.

| Coal minefv | Macroscopic description | Elemental composition (wt%; dry basis) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $C_{ORG}$ | $N_{TOT}$ | $S_{TOT}$ | $S_{CRS}$ | $S_{ORG}$ | $S_{SULPH}$ | C/N |
| Velenje 1 | Xylite | 50 | 0.4 | 2.7 | 0.1 | 2.6 | 0.1 | 125 |
| Velenje 2 | Fusite | 59 | 0.6 | 1.4 | 0.3 | 1.2 | <LOD | 98 |
| Velenje 3 | Fine detritial lignite | 54 | ND | 3.4 | 1.3 | 2.0 | 0.1 | ND |
| Velenje 4 | Gelified fine detritial lignite | 42 | 1.2 | 3.9 | 1.2 | 2.6 | <LOD | 35 |
| Velenje 5 | Gelified fine detritial lignite, working face | 57 | 1.8 | 1.4 | 0.1 | 1.3 | <LOD | 32 |
| Trbovlje | Hard brown coal | 54 | ND | 2.3 | 1.6 | 0.7 | <0.1 | ND |
| Senovo | Brown coal | 82 | 1.5 | 1.9 | 0.8 | 1.1 | <LOD | 55 |
| Kanižarica 1 | Lignite | 42 | 0.7 | 2.2 | 0.2 | 1.4 | 0.7 | 60 |
| Kanižarica 2 | Lignite | 40 | 0.8 | 1.6 | 0.1 | 1.3 | <LOD | 50 |
| Kanižarica 3 | Org.-rich clay | 16 | 0.3 | 1.6 | 0.1 | 0.6 | 1.0 | 53 |
| Kanižarica 4 | Lignite | 42 | 1.2 | 1.7 | 0.6 | 1.3 | <LOD | 35 |

ND – not determined, <LOD – below limit of detection (<0.01 mg); TOT – total, ORG-organic, CRS-chromium reducible sulphur, SULPH-sulphate.

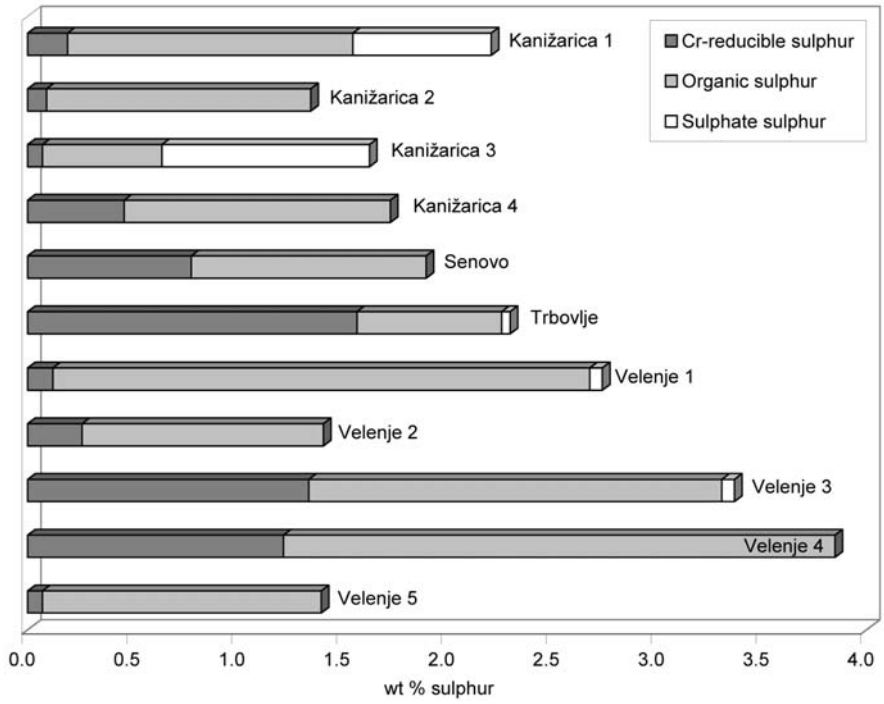


**Figure 5:** Composition of different sulphur species of the studied coals.

weight ratio of 125 (lower microbial activity), towards gelified detrital samples (higher microbial activity), with a C/N ratio of 32. As emphasised by Diessel,[5] a high proportion of nitrogen in peat is widely regarded as an indicator of extensive microbial reworking of the peat forming vegetation.

## 3. 2. Isotopic Composition

Isotopic fractionation of sulphur may indicate the source of sulphur species.[23] It occurs during the bacterial reduction of sulphate to monosulphide, the reduced sulphide being enriched in $^{32}S$.[23,24] Very low $^{34}S/^{32}S$ ratios can be obtained in the sulphide fraction if there is an unlimited source of sulphate.[23] The residual sulphate becomes increasingly enriched in $^{34}S$ if the sulphate reservoir is restricted, in which case the $^{34}S/^{32}S$ ratio for sulphide increases as the sulphate reservoir is restricted.[23] Results of the stable isotope analyses of $N_{TOT}$, $C_{ORG}$ and S species in coal samples are presented in Tab. 2 and Fig. 6.

It is generally believed that the isotopic composition of pyritic sulphur is more variable than that of organic sulphur.[2,25] This phenomenon was observed in the three characteristic lithotypes of Velenje lignite (xylite, fusite

**Table 2:** Isotopic composition of $C_{ORG}$, $N_{TOT}$ and $S_{CRS}$, $S_{ORG}$ and $S_{SULPH}$ of the studied coals.

| Coal seam | Macroscopic description | Isotopic composition | | | | |
|---|---|---|---|---|---|---|
| | | $\delta^{13}C_{ORG}$ | $\delta^{15}N_{TOT}$ | $\delta^{34}S_{CRS}$ | $\delta^{34}S_{ORG}$ | $\delta^{34}S_{SULPH}$ |
| Velenje 1 | Xylite | –26.0 | 5.5 | 1.3 | 15.4 | 10.8 |
| Velenje 2 | Fusite | –26.0 | 2.2 | 7.8 | 15.5 | <LOD |
| Velenje 3 | Fine detritial lignite | –26.0 | 3.0 | 10.0 | 14.5 | 9.6 |
| Velenje 4 | Gelified fine detritial lignite | –27.1 | 3.0 | 10.0 | 14.1 | <LOD |
| Velenje 5 | Gelified fine detritial lignite, working foce | –27.5 | 2.9 | 10.6 | 13.2 | <LOD |
| Trbovlje | Hard brown coal | –27.3 | 5.1 | 20.8 | 22.7 | 16.5 |
| Senovo | Brown coal | –26.6 | 5.1 | 3.3 | 10.9 | <LOD |
| Kanižarica 1 | Lignite | –25.3 | 6.9 | –2.3 | 3.0 | –7.6 |
| Kanižarica 2 | Lignite | –25.8 | 7.3 | 3.3 | 4.4 | <LOD |
| Kanižarica 3 | Organic rich clay | –25.3 | 7.3 | –3.3 | –3.2 | –5.1 |
| Kanižarica 4 | Lignite | –26.4 | 7.2 | 13.1 | 4.1 | <LOD |

<LOD – below limit of detection. 200–300 μg of S is needed for the determination of $\delta^{34}S$.

and fine detritial lignite). The highly variable isotopic composition of pyritic sulphur in high-sulphur coals indicates that there are probably several generations of pyrite.[2] Microscopic analyses showed several forms of pyrite in the Velenje lignite samples studied, i.e. framboidal pyrite, euhedral pyrite, and anhedral pyrite, but the isotopic composition of separate grains of pyrite was not determined up to now since the isotopical analyses were performed on pulverized samples. It can be presumed that isolated microenvironments existed in the peat and these microenvironments might have given rise to an inhomogeneous distribution of sulphate-reducing bacteria and contributed to the complexity of pyrite formation.[2,4] A study[26] of the texture of pyrite in pyritiferous carbonate concretions in ancient sedimentary rocks showed that the texture of pyrite depends on the relative rates of $H_2S$ generation and $Fe^{2+}$ supply. Disulfide generation is determined by the rate of $SO_4^{2-}$ reduction, and $Fe^{2+}$ supply by the in situ availability of reactive iron.[18,26] In these concretions, framboidal pyrite apparently formed during early stages of diagenesis. During later stages of diagenesis, euhedral pyrite with higher $^{34}S/^{32}S$ isotope signatures formed because in situ $Fe^{2+}$ sources and pore-water $SO_4^{2-}$ became depleted, and the $SO_4^{2-}$ reduction rate decreased.[26]

In our study, a linear relationship was found between $\delta^{34}S$ in CRS and in organic sulphur. Lower $\delta^{34}S$ values for CRS compared to organic sulphur can be explained by preferential formation of sulphides, due to the higher affinity of $Fe^{2+}$ towards $H_2S$.[2,9] Researchers[2] who studied the distribution, isotopic variation and origin of sulphur in coals from the Wuda coalfield (Inner Mongolia, China) reported a linear relationship between the $\delta^{34}S$ values of pyritic and organic sulphur and a negative relationship between $\delta^{34}S$ values for organic and pyritic sulphur, and the total sulphur content. In our study, the latter relationship is not expressed.

With the exception of xylite, $\delta^{34}S$ was lower for sulphate sulphur compared to CRS, which could be explained by the oxidation and weathering of pyrite, where $^{32}S$ is preferentially oxidized, leaving the remaining pyrite enriched in $^{34}S$.

Variation in the maceral composition of a coal, which may reflect differences in plant assemblages, depositional environments at the time of peat accumulation and early diagenetic processes of coal formation, especially biochemical ones, is the primary influence on $\delta^{13}C$, $\delta^{15}N$, and C/N compostion.[27] $\delta^{15}N$ and $\delta^{13}C$ values of different lithotypes of the Velenje lignite samples analysed varied from +2.2‰ to +5.5‰ and from –26.0‰ to –27.5‰, respectively. The results are consistent with the results of a previous study[28] of the isotopic composition of nitrogen and carbon in 47 samples of different lithotypes of Velenje lignite, in which the authors found that $\delta^{15}N$ varied from +1.8‰ to +4.6‰ and $\delta^{13}C$ from –28.7‰ to –23.0‰. Many studies[15,28,29] report that $\delta^{13}C$ values decrease from xylites toward detrital and gelified detrital lignite, which was also observed in this study. We found low $\delta^{13}C_{org}$ and $\delta^{15}N$ values as well as low C/N ratios in gelified lignite samples from Velenje. This was interpreted by different authors[15,28,30] by bacterial activity which affects fine detrital organic matter more easily than resistant wood (xylite) pieces and/or by the presence of considerable amounts of isotopically light organic matter from leafs, resins and bark in fine detrital coal matrices.

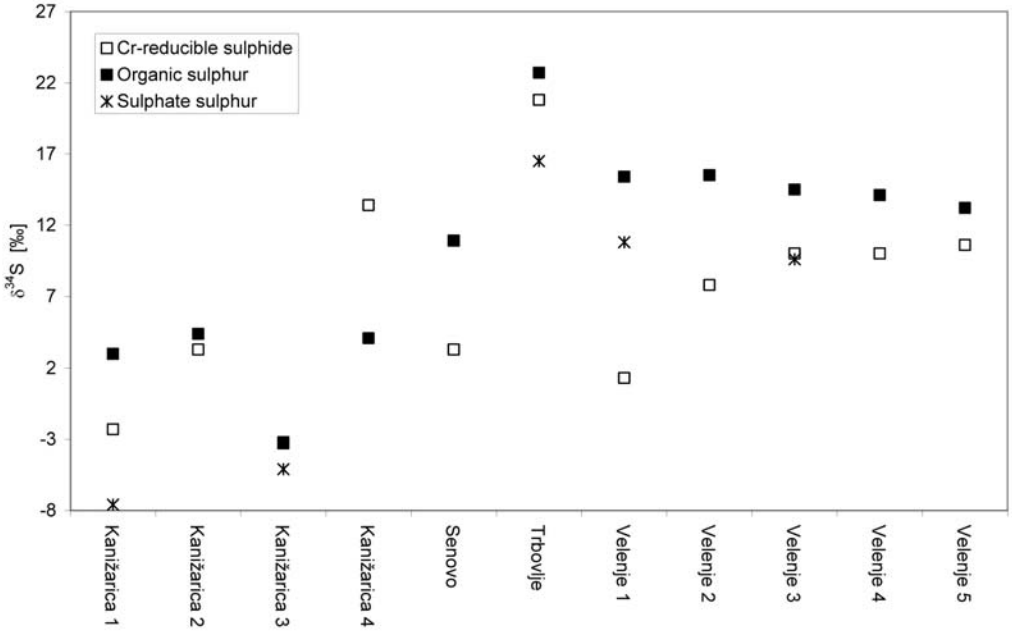


**Figure 6:** $\delta^{34}S$ of different sulphur species of the studied coals.

Kanduč et al.[28] found that $\delta^{13}C$ and $\delta^{15}N$ values of different lignite lithotypes from the Velenje coal seam were influenced by the original isotopic heterogeneity of the source plant components and by biogeochemical processes (gelification, mineralization of organic matter) at the early stage of biomass accumulation and its early diagenesis.

## 4. Conclusions

The previous discussion can be summed up in the following conclusions:

- The isotopic composition of sulphur in low-rank coals from four coal seams in Slovenia is presented for the first time.
- Regarding the total sulphur content, samples are characterized as medium sulphur coal, with 1–3 wt% sulphur, or as high sulphur coal, containing more than 3 wt% total sulphur.
- The C/N ratio of different lithotypes from the Velenje coal seam decreases with increasing microbial degradation of organic matter from xylite towards gelified varieties, which is in agreement with the previous study of Kanduč et al..[28]
- With the exception of hard brown coal sample from the Trbolje-Hrastnik coal seam and one sample from Kanižarica (org. rich clay), the organic sulphur content predominates over CRS, indicating low iron availability inside the coal forming basin, considering the higher affinity of $Fe^{2+}$ towards $H_2S$ compared to organic matter.
- $\delta^{34}S$ values of the samples analysed vary between different coal seams, as well as between different lithotypes inside particular coal seams.
- According to the literature,[2,23] $\delta^{34}S$ of different species is mostly affected by $SO_4^{2-}$ and $Fe^{2+}$ availability and microbial activity inside the coal forming basin, which can also explain the considerable isotopic fractionation between different sulphur species observed in our study.
- The linear relationship between $\delta^{34}S_{CRS}$ and $\delta^{34}S_{ORG}$ indicates preferential formation of sulphides, which are hence enriched with $^{32}S$ compared to organic sulphur.
- The higher variability of $\delta^{34}S_{CRS}$ compared to $\delta^{34}S_{ORG}$ among lignite samples from the Velenje coal seam is explained by the presence of different forms of pyrite, as found by optical reflection microscopy.
- In addition, $\delta^{13}C$ and $\delta^{15}N$ values of the studied coal samples were determined and the results are in good agreement with the results of the previous study of Kanduč et al.,[28] who found that $\delta^{13}C$ and $\delta^{15}N$ values of different lignite lithotypes from the Velenje coal seam were influenced by the original isotopic heterogeneity of the source plant components and by biogeochemical processes at the early stage of biomass accumulation and its early diagenesis.
- The present study has a preliminary character; in future it should be extended on a greater number of samples.

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## Povzetek

Vzorcem premoga iz štirih slovenskih premogovnikov smo določili vsebnost in prvič tudi izotopsko sestavo sulfidnega, organskega in sulfatnega žvepla. Analizirane premoge smo uvrstili med premoge s srednjo oziroma visoko vsebnostjo žvepla, pri katerih, z izjemo trboveljskega vzorca in vzorca Kanižarica 3, prevladuje organsko vezano žveplo. Rezultati kažejo, da se izotopska sestava posameznih zvrsti žvepla spreminja tako med posameznimi premogovnimi plastmi, kot med različnimi litotipi znotraj posameznih plasti premoga. Odvisna je predvsem od razpoložljivosti $SO_4^{2-}$ in $Fe^{2+}$ ionov ter mikrobne aktivnosti v času zgodnje diageneze premoga.