Study of the gas composition ahead of the working face in a lignite seam from the Velenje basin

Raziskave sestave plina pred čelom delovišča v lignitni plasti iz Velenjskega bazena

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Abstract: The lignite seam in the Velenje basin has been exploited since 1875. During excavation of lignite in the Velenje coalmine, seam problems with gas outbursts occur. However, geochemical studies of the coalbed gases in the Velenje basin have been initiated only recently.

Mass spectrometric methods were used to determine the gas composition. Coalbed gases in the Velenje basin are highly variable in both their concentrations and stable isotope composition. Major gas components are CO_2 and methane. Their concentrations and isotopic studies revealed several genetic types of coalbed gases, including thermogenic methane, endogenic and thermogenic CO_2, CO_2 originating from carbonates, microbial methane and CO_2.

Most of the gases in the Velenje basin are the result of mixing of gases of different origin, caused by physicochemical processes.

Izvleček: Lignitno plast v Velenjskem bazenu raziskujejo že od leta 1875. Z začetkom izkopavanja lignita so se pojavili problemi s plinskimi izbruhi. Geokemične raziskave premogovega plina so pomembne za razumevanje mehanizma nastanka, preprečevanje in napovedovanje plinskih izbruhov. Te analize smo začeli izvajati v Velenjskem bazenu leta 1999.

Sestavo premogovnih plinov smo določili z metodami masne spektrometrije. Premogovni plini v Velenjskem bazenu se spreminjajo tako po koncentracijah kot tudi po izotopski sestavi. Glavni plinski komponenti sta: CO_2 in metan. Raziskave koncentracij in stabilnih izotopov oglljika premogovnih plinov kažejo različne vire: termogeni metan, endogeni in termogeni CO_2, CO_2, ki izhaja iz karbonatov, mikrobni metan in CO_2.

Večina plinov, ki se zadržujejo v lignitu so posledica mešanja plinov različnih virov. Fizikalno – kemijski procesi (migracija, difuzija, adsorbcija, desorbcija) lahko močno zabrišejo izvor premogovnih plinov in otežijo njihovo interpretacijo.

Key words: coalbed gases, carbon isotopes, gas origin, gas migration, Velenje basin
Ključne besede: premogovni plini, ogljikovi izotopi, nastanek plinov, migracija plinov, Velenjski bazen

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INTRODUCTION

The most trivial definition of coalbed gas is "gas from coal". Coalbed gas usually consist of hydrocarbons (mainly methane), CO_2 in concentrations from 0 to greater than 99 %, and occasionally small percentages of nitrogen (CLAYTON, 1998). Geochemical investigations are designed to help predict, prevent, and manage coal mine gas outbursts and to study their origin and mechanisms (FLORES, 1998).

Numerous models were developed to describe sources of hydrocarbon gases (SHOELL, 1983, KOTARBA, 1990, SCOTT, 1993, KOTARBA, 2001). Stable carbon isotope analyses of methane and CO_2 can be applied to identify the origin of coalbed gases, their migration pathways, and accumulation processes. Three main source categories for gas can be defined: abiogenic, biogenic and thermogenic (KOTARBA, 1991). In general, thermogenic gases are associated with high rank coal, whereas biogenic gases are thought to be produced in early stages of the coalification process. Large volumes of coalbed gases are generated during the coalification process, but gases produced by other processes may also occur in coal basins, i.e., endogenic CO_2, microbial methane, and abiogenic methane (RICE ET AL., 1989).

The aim of this study was to explain concentrations of coalbed gases at delivery and exit roadways ahead of the working face, and to extend possible interpretations of CO_2 and methane accumulating in the lignite seam in the Velenje basin.

METHODOLOGY

Sampling procedure

Sampling of coalbed gas was performed during 2000 – 2002 in the lignite seam of the Velenje basin with purpose of determining the concentrations and isotopic composition of carbon ($\delta^{13}C$) of methane and CO_2 from pillar coal. Coalbed gas samples from pillar coal at delivery and exit roadways ahead of

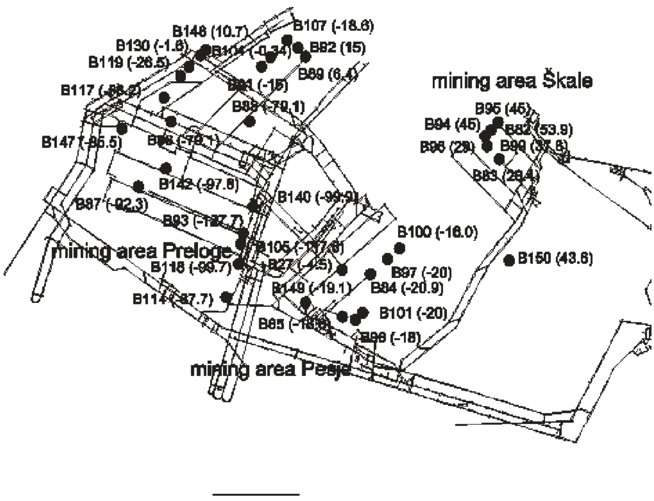

Figure 1. Map of gas sampling locations from the lignite strata of the Velenje basin

Slika 1. Karta vzorčnih mest odvzetega plina z lignitne plasti iz Velenjskega bazena the working face were taken from the mining areas Škale, Pesje and Preloge. A map of the sampling locations is shown on Figure 1. Depths of sampling locations are given on map of sampling locations. At each sampling location a 3 m deep borehole was drilled.

"Free" gas for geochemical analyses was collected from boreholes in evacuated ampoules using a metal capillary tube and plastic syringe. ‚Free" gas includes both the volatiles filling the pores and cracks within the coal structure and some gas degassed from the coal during drilling and sampling (Kotarba, 1990).

Analytical procedure

Determinations of the concentrations of methane, CO_2, nitrogen, oxygen and argon were performed using a homemade NIER mass spectrometer. The method of singular decomposition of the matrix was used to obtain simultaneous analysis of the gas component signals; the composition was calculated with the program MATH CAD). The precision of the method was ± 3 %.

The isotopic composition of methane and CO_2 was determined using an Europa 20-20 continuous flow isotope ratio mass spectrometer with an ANCA – TG preparation module. First water was removed and then CO_2 was directly analyzed for ^{13}C content. For methane measurements first CO_2 was removed and then methane was combusted over hot 10 % platinum covered CuO at 1000 °C. The methane completely converted to CO_2 was then directly analyzed for ^{13}C content. The stable carbon isotope composition is given in the δ – notation relative to the VPDB standard and expressed in ‰. The

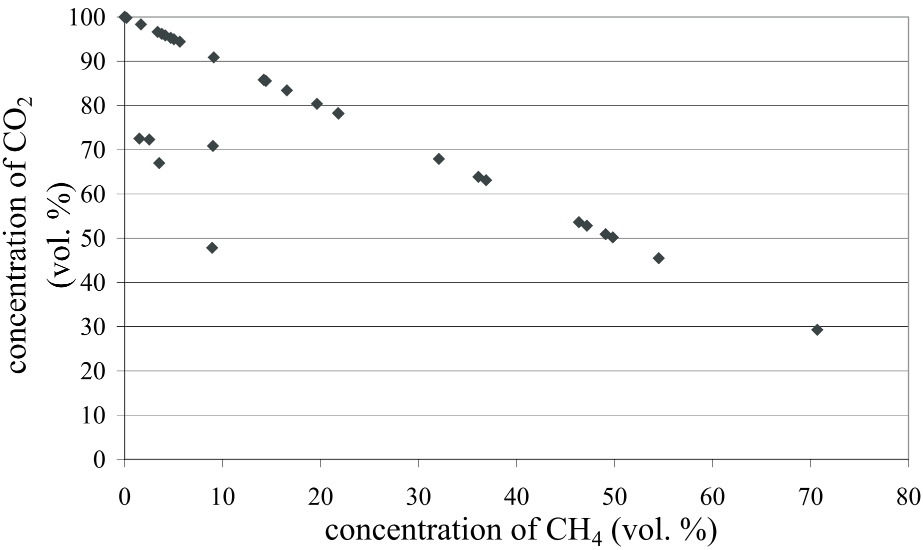

Figure 2. Concentration of CO_2 versus concentration of methane in the lignite seam ahead of the working face in the Velenje basin

Slika 2. Koncentracija CO_2 v odvisnosti od koncentracije metana v lignitni plasti pred čelom delovišča iz Velenjskega bazena analytical precision for carbon isotope composition is estimated to be ± 0.2 ‰.

RESULTS

"Free gases" accumulated within the lignite coal seam showed a considerable variability in concentrations and isotopic composition. To correct for to air contamination of the capillary system and evacuated ampoules, sample composition was were recalculated on an air - free basis. Major gas components were CO_2 and methane. Concentrations of CO_2 varied from 45.5 to 100 % and methane from 0 to 54.5 %. Geochemical index CDMI $((CO_2/(CO_2+CH_4)) \times 100\ \%)$ vary from 45.5 to 100 % and stable isotope ratios varied in the following ranges: $\delta^{13}C_{CO2}$ from -22.9 to -2.1 ‰ and $\delta^{13}C_{CH4}$ from -68.6 to -40 ‰.

A good regression (R = 0.72) was obtained between methane and CO_2 concentrations (Fig. 2) in the lignite seam at delivery and exit roadways ahead of the working face. Areas of high and low methane concentrations are due to the physicochemical properties of CO_2 and methane. Fissures generated by the advance of roadways enable migration of methane through lignite seam in surrounding strata or to the surface, while CO_2 remains adsorbed in the lignite seam.

Figure 2 a shows concentrations of CO_2 and methane in the Preloge mining area (B117 – 148) at the exit roadway ahead of the working face. Methane migrates faster than CO_2 with advance of the roadway, and therefore its concentration starts to increase before CO_2. Later, concentrations of methane decrease, while concentrations of CO_2 start to increase.

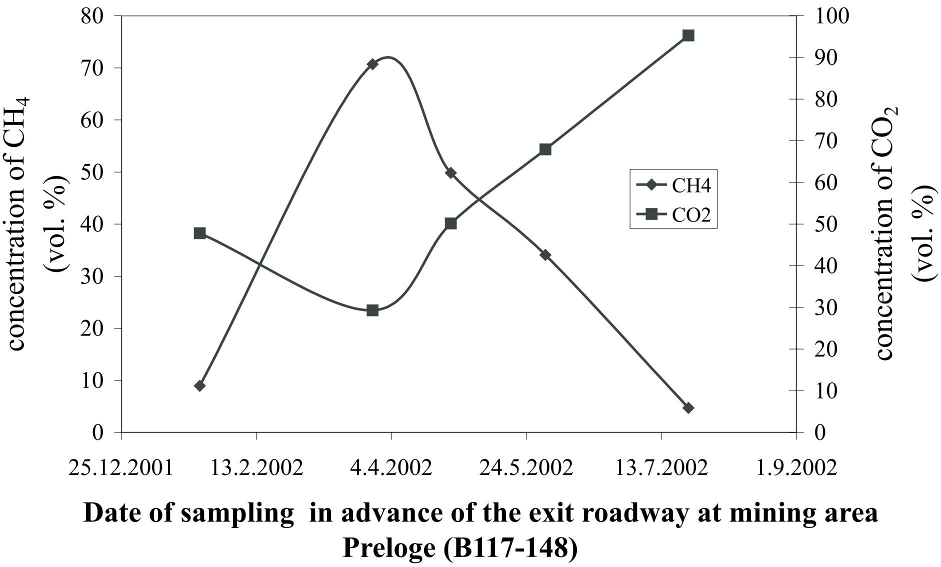

Figure 2 a. Concentration of methane versus date of sampling in advance of the exit roadway in the Preloge mining area (B117 – 148) ahead of the working face
Slika 2 a. Koncentracija metana v odvisnosti od časa vzorčevanja z napredovanjem odvozne proge pred čelom delovišča v Prelogah (B117 – 148)

The concentration of methane and CO_2 measured in the lignite seam at roadways mainly depends on the permeability and porosity of the seam ahead of the working face. When methane and CO_2 reach strata with low permeability such as fault zones, their concentrations start to increase, therefore high concentrations of methane and CO_2 might be expected in these areas. These areas might potentially have a high risk of gas outbursts. We applied diagrams of $\delta^{13}C_{CH4}$ versus $\delta^{13}C_{CO2}$ (Fig. 3) to explain the origin of methane and $\delta^{13}C_{CO2}$ versus CDMI index (Fig. 3, 4, KOTARBA, 2001). $\delta^{13}C_{CH4}$ (Fig. 3) in the Velenje basin indicates the successive origin of methane: thermogenic with $d^{13}C_{CH4}$ values from -40 to -50 ‰, microbial with $\delta^{13}C_{CH4}$ less than -50 ‰ and mixed origin between these two (CLAYTON, 1998).

The phenomenon of thermogenic methane in the Velenje basin could be explained in several ways: It could be generated in Oligocene marine clays, containing high concentrations of organic matter, which were overheated at a depth of over 2000 m and might have migrated through faults and fractures in the lignite strata at the time of formation of the basin. Thermogenic methane could also be explained by secondary processes, i.e., microbial oxidation of methane, which results in enrichment of residual methane with the ^{13}C isotope and depletion of ^{12}C in generated CO_2 (Fig. 3).

It is known that coalbed lignite strata were formed in the Pliocene in a calm sedimentary environment (MARKIČ AND SACHSENHOFER, 1997), but the proportion of

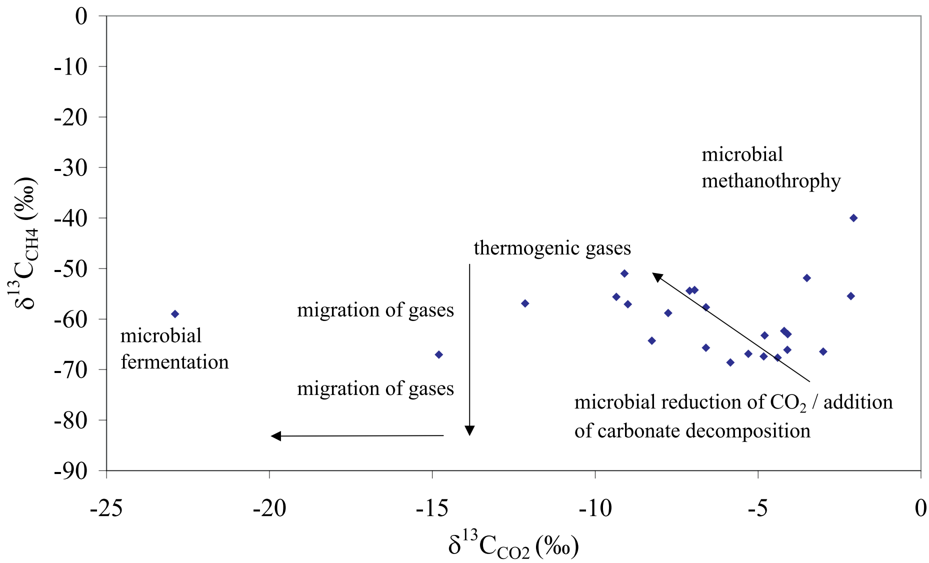

Figure 3. Interpretation of the origin of methane in the Velenje basin using $\delta^{13}C_{CH4}$ versus $\delta^{13}C_{CO2}$ in the lignite seam ahead of the working face

Slika 3. Interpretacija izvora metana v Velenjskem bazenu z uporabo diagrama $\delta^{13}C_{CH4}$ v odvisnosti od $\delta^{13}C_{CO2}$ v lignitni plasti pred čelom delovišča early stage microbial gas retained in the lignite structure (SMITH AND PALLASER, 1996) is difficult to estimate. Microbial methane in the Velenje basin was generated by microbial reduction and/or by microbial fermentation. Also recent microbial activity (methanogenic and methanotrophic bacteria) might generate microbial gas (KOTELNIKOVA, 2003). Methane and CO_2 were/are generated by a microbial fermentation process while methane was/is generated by a CO_2 reduction process. CO_2 generated by a fermentation process is characterized by $\delta^{13}C_{CO2}$ similar that of organic matter around -25 ‰ (SHOELL, 1983), while a microbial reduction process results in enrichment with the ^{13}C of residual CO_2 (Figs. 3 and 4).

The origin of CO_2 is interesting due to its relation to outbursts in coalmines. A plot of the CDMI index versus $\delta^{13}C_{CO2}$ (Fig. 4) was used to explain the origin of CO_2 (KOTARBA, 2001) and indicate endogenic CO_2, thermogenic CO_2, CO_2 originating from carbonates and CO_2 of microbial origin in relation to microbial methane discussed above.

Typical endogenic values of $\delta^{13}C_{CO2}$ are about -7 ‰ (KOTARBA, 2001) and the high CDMI indices found in our study are probably related to the tectonics of the Šoštanj and Smrekovec faults at the time of formation of the Velenje basin.

The values of $\delta^{13}C_{CO2}$ from -14.8 to -10 ‰ and the high CDMI index in the Velenje basin indicate thermogenic CO_2, which is characterized by an enrichment in ^{13}C in comparison to the organic matter from which it originates. Most thermogenic CO_2 is generated within a temperature interval of around 50°C with values more than -20 ‰ (CLAYTON, 1998). It could be derived from the coalification process, or might be related to

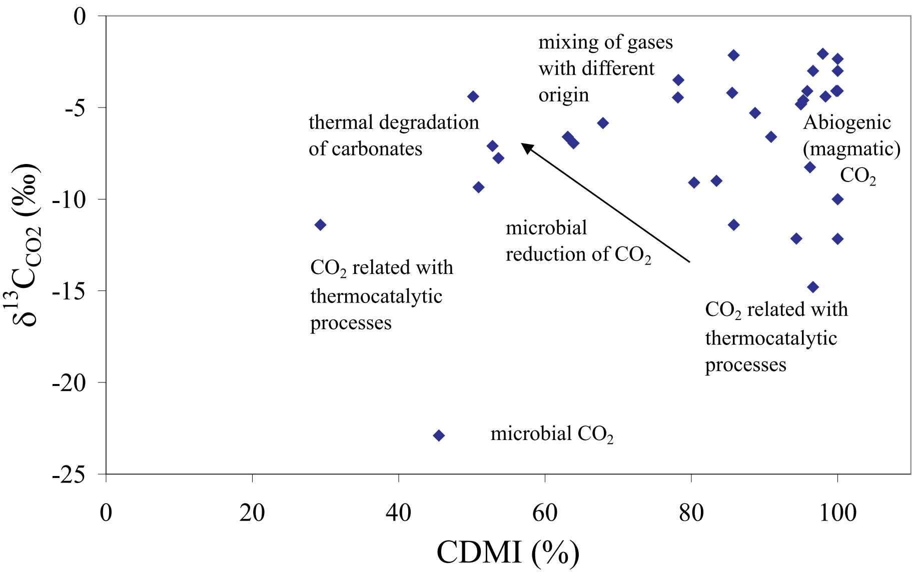

Figure 4. Interpretation of the origin of CO_2 in the Velenje basin using $\delta^{13}C_{CO2}$ versus CDMI index in the lignite seam ahead of the working face

Slika 4. Interepretacija izvora CO_2 v Velenjskem bazenu z uporabo diagrama $\delta^{13}C_{CO2}$ v odvisnosti od CDMI indeksa v lignitni plasti pred čelom delovišča

methanogenic CO_2 reduction activity (Fig. 4).
$\delta^{13}C_{CO2}$ derived from carbonates is dependent on $\delta^{13}C$ of the carbonates and the temperature of their degradation. Investigations in the western part of the Pannonian basin, located in the NE part of Slovenia (Pezdič et. al., 1995), indicate significant thermal decomposition of dolomite in the temperature range from 70 to 170 °C in the presence of metasiliceous acid and catalysts such as sulfates and organic matter. The resulting products are clay minerals and CO_2. The Triassic basement composed of carbonates and dolomites along the Šoštanj fault zone has not been bored through yet. Supposing that these dolomites underwent thermal decomposition and are located below the lignite seam along the Šoštanj fault zone, values of $\delta^{13}C_{CO2}$ from -2 to -6 ‰ might indicate CO_2 from thermal decomposition of dolomites.
Values of $\delta^{13}C_{CO2}$ from -10 to -6 ‰ indicating thermal degradation of carbonates might also be explained by microbial reduction of CO_2. Coalbed gases from the Velenje basin with a CDMI index from 60 – 85 % and $\delta^{13}C_{CO2}$ from -8 to -5 ‰ indicate mixing of gases of different origin. Migration of gases as a secondary process (Fig. 3) caused by reduction of pressure in the lignite seam causes enrichment in the light ^{12}C isotope in methane and in CO_2. During migration of coalbed gases, gases of different origin might be mixed together and complicate the interpretation of gas origin.

Conclusions

For coalminers gas outbursts remain one of the main problems in the Velenje coalmine, and therefore geochemical investigations are of utmost importance for the prediction of these gas outbursts.
Concentrations of methane and CO_2 change with advance of the delivery and exit roadways ahead of the working face. Areas with high CO_2 concentrations are characterized by low methane concentrations.
Knowledge of gas concentrations and stable isotope studies allow a possible interpretation of the origin of coalbed gas in the Velenje basin. Considering the results, it can be concluded that coalbed gas from the Velenje basin is of multiple origin. Secondary processes like migration, adsorption/desorption and mixing of gases of different origin complicate the interpretation of gas origin.
It can be concluded that a considerable fraction of the gas is of external origin, but the proportion of early stage biogenic gas in the Velenje basin is difficult to estimate.

Povzetek

Raziskave sestave plina pred čelom delovišča v lignitni plasti iz Velenjskega bazena

Lignitna plast v Velenjskem bazenu predstavlja rezervoar premogovnih plinov: CO_2 in metana. Poleg naštetih plinov štejemo med premogovne pline tudi višje ogljikovodike in N_2. Geokemične analize premogovnih plinov (koncentracije plinov in izotopske analize) izvajajo tudi drugod po svetu v še obratujočih premogovnikih z namenom (1) dobiti boljši vpogled v mehanizem nastanka plinskih izbruhov, (2) preprečevati plinske izbruhe, (3) napovedovati plinske izbruhe. Za raziskavo plinskih izbruhov so pomembne tudi sledeče raziskave: geološka zgradba, prepustnost, poroznost, sorbcijske lastnosti plinonosnih plasti, ki omogočajo zadrževanje in migracijo plinov.

V Premogovniku Velenje so se začeli pojavljati plinski izbruhi že leta 1887 z začetkom izkopavanja lignita, vendar smo začeli izvajati geokemične analize premogovnih plinov šele leta 1999. S pomočjo teh analiz lahko določimo izvor premogovnih plinov, njihove migracijske poti in akumulacijske procese.

Znano je, da večina premogovega plina (predvsem metana) nastane s koalifikacijskim procesom, vendar so znani tudi drugi procesi, ki lahko privedejo do akumulacij plinov kot so: endogeni CO_2, mikrobni metan in abiogeni metan.

Premogovne pline smo vzorčevali na pripravljalnih progah pred čelom delovišča v letih od 1999 – 2002. Po izvrtanju vrtin na pripravljalnih progah (odvozni/dovozni) smo s pomočjo bakrene kapilare in injekcije izčrpali premogovni plin v evakuirane ampule. Vzorčevali smo tako imenovan prosti plin. Prosti plin je plin, ki se sprosti v obliki proste plinaste faze po vrtanju in med vzorčevanjem in zapolnjuje pore in razpoke v lignitni plasti.

V prispevku so obdelani rezultati geokemičnih analiz CO_2 in metana na pripravljalnih delih pred čelom delovišča. Koncentracije plinov pred čelom delovišča so pomembni podatek in jih je potrebno spremljati na dovoznih in odvoznih progah, zaradi možnosti pojava plinskega izbruha z napredovanjem čela.

Rezultati analiz premogovnih plinov kažejo, da je sestava premogovnih plinov zelo spremenljiva. Glavni plinski komponenti sta CO_2 in metan. Koncentracije CO_2 se spreminjajo od 45,5 do 100 %. Koncentracije metana se spreminjajo od 0 do 54,5 %.

Metan in CO_2 se akumulirata na pripravljalnih progah pred čelom delovišča različno; vzrok temu so različne fizikalno – kemijske lastnosti (raztapljanje plinov v vodi, difuzija, adsorbcija, desorbcija na premogovno plast) obeh plinov, saj metan zaradi manjše molske mase napram CO_2 migrira hitreje, poleg tega je metan v vodi zelo slabo topen napram CO_2. Znano je, da se CO_2 tudi počasneje desorbira s premogove plasti. Ne glede na katerem mestu pripravljalne proge izmerimo koncentracije plinov, vedno dobimo podobno situacijo porazdelitve koncentracij plinov; pri povišanih koncentracijah metana, dobimo nižje koncentracije CO_2.

Geokemični indeks CDMI ((CO_2/CO_2 + CH_4) • 100 %), ki ga uporabljamo za interpretacijo premogovnega plina CO_2 se spreminja od 45,5 do 100 %. $\delta^{13}C_{CO2}$ se spreminja od -22,9 do -2,1 ‰, $\delta^{13}C_{CH4}$ se spreminja od -68,6 do -40 ‰. Vrednosti koncentracij CO_2, metana, $\delta^{13}C_{CO2}$, $\delta^{13}C_{CH4}$ kažejo na naslednji izvor premogovnih plinov: termogeni metan, endogeni in termogeni CO_2, CO_2, ki izhaja iz karbonatov, mikrobni metan in CO_2. Mešanje plinov različnega izvora povzročajo fizikalno – kemijski procesi, ki močno otežijo interpretacijo premogovnih plinov.

Na podlagi dosedanjih raziskav lahko zaključimo, da je večina premogovega plina, predvsem CO_2 iz Velenjskega bazena zunanjega vira, le - ta se je akumuliral v času tektonskih faz preko Šoštanjksega preloma iz večjih globin (termično pregrevanje karbonatov, endogeni CO_2). Termogeni metan lahko pojasnimo s pregrevanjem oligocenskih plasti bogatimi z organskimi komponentami v večjih globinah. Delež zgodnje diagenetskih biogenih plinov (CO_2 in metana) ne moremo oceniti, saj je sorbcija tega plina v lignitni plasti povezana z razvojem mikroporozne strukture in kompakcije sedimentov v času nastanka Velenjskega bazena. Poleg zgodnje diagenetskih plinov velja omeniti tudi možnost recentne biogene aktivnosti (mikrobna oksidacija metana, mikrobna redukcija CO_2), ki prav tako lahko vpliva na interpretacijo premogovnega plina.

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