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Bioconversion of Coal: Hydrologic indicators of the extent of coal biodegradation under different redox conditions and coal maturity, Velenje Basin case study, Slovenia

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Underground mining of coal and coal combustion for energy has significant environmental impacts. In order to reduce greenhouse gas emissions, other lower –carbon energy sources must be utilized. Coalbed methane (CBM) is an important source of relatively low-carbon energy. Approximately 20% of world's coalbed methane is microbial in origin (Bates et al., 2011). Interest in microbial CBM has increased recently due to the possibility of stimulating methanogenesis. Despite increasing interest, the hydrogeochemical conditions and mechanisms for biodegradation of coal and microbial methane production are poorly understood. This project aims to examine geochemical characteristics of coalbed groundwater and coalbed gases in order to constrain biogeochemical processes to better understand the entire process of coal biodegradation of coal to coalbed gases. A better understanding of geochemical processes in CBM areas may potentially lead to sustainable stimulation of microbial methanogenesis at economical rates. Natural analogue studies of carbon dioxide occurring in the subsurface have the potential to yield insights into mechanisms of carbon dioxide storage over geological time scales (Li et al., 2013). In order to explore redox processes related to methanogenesis and determine ideal conditions under which microbial degradation of coal is likely to occur, this study utilizes groundwater and coalbed gas samples from Velenje Basin. Determination of the concentrations of methane, carbondioxide, nitrogen, oxygen, argon was performed with homemade NIER mass spectrometer. Isotopic composition of carbon dioxide, isotopic composition of methane, isotopic composition of deuterium in methane was determined with Europa-Scientific IRMS with an ANCA-TG preparation module and Thermo Delta XP GC-TC/CF-IRMS coupled to a TRACE GC analyzer. Total alkalinity of groundwater was measured by Gran titration. Major cations were analyzed by ICP-OES and anions by IC method. Isotopic composition of dissolved inorganic carbon was determined by MultiflowBio preparation module. The stable isotope composition of sulphur was determined with a Europa Scientific 20-20 continuous flow IRMS ANCA-SL preparation module. Concentrations of tritium were determined with the electrolytic enrichment method. PHREEQC for Windows was used to perform thermodynamic modelling. The average coalbed gas composition in the coalbed seam is approximately carbon dioxide: methane > 2:1, where a high proportion of CO_2 is adsorbed on the lignite structure, while methane is present free in coal fractures. It can be concluded that isotopic composition of carbon in methane from -70.4‰ to -50.0‰ is generated via acetate fermentation and via reduction of carbon dioxide, while isotopic composition of carbon in methane values range from -50.0‰ to -18.8‰ thermogenic methane can be explained by secondary processes, causing enrichment of residual methane with the heavier carbon isotope. Isotopic composition of deuterium in methane range from -343.9‰ to -223.1‰İsotopic composition of carbon in carbon dioxide values at excavation fields range from -11.0‰ to +5‰ and are endogenic and microbial in origin. The major ion chemistry, redox conditions, stable isotopes and tritium measured in groundwater from the Velenje Basin, suggest that the Pliocene and Triassic aquifers contain distinct water bodies. Groundwater in the Triassic aquifer is dominated by hydrogen carbonate, calcium, magnesium and isotopic composition of dissolved inorganic carbon indicating degradation of soil organic matter and dissolution of carbonate minerals, similar to surface waters. In addition, groundwater in the Triassic aquifer has isotopic composition of oxygen and isotopic composition of deuterium values which plot near surface waters on the local and global meteoric water lines and detectable tritium reflects recent recharge. In contrast, groundwater in the Pliocene aquifers is enriched in magnesium, sodium, calcium, potassium, and silica and has alkalinity and isotopic composition of dissolved inorganic carbon values with low sulphate and nitrate concentrations. These waters have likely been influenced by sulfate reduction and microbial methanogenesis associated with coal seams and dissolution of feldspars and magnesium-rich clay minerals. Pliocene aquifer waters are also depleted in heavier oxygen isotope and heavier deuterium isotope and have tritium concentrations near the detection limit, suggesting

these waters are older.

References

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