

Geostatistics. Throughout the geological history of karst, its morphological phenomena (doline, polja, sinkholes, obodine) were filled by sedimentation processes and hence conserved only to some extent in their particular development phases, subsequently being subjected to further morphological development in such conditions. Data on these phenomena were carefully collected for twenty years. As the number of studied elements exceeded 100000, the collected database is very large and these data are all the more significant because these morphological elements were accessible for observation and measurement only for a short time before being filled again. A geostatistical model of soil was developed using the variographic analysis on soil samples taken in three characteristic glacial areas. Scientifically established relations between the geomechanical model and parameters of geological origin were defined.

Shallow ground waters and the formation of carbonate soils in southeast Bulgaria – a study in progress

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Carbonate soils and indurate calcrete horizons are common in southeast Bulgaria. The carbonate accumulations are of variety of micro-structural and textural types. The calcrete usually forms lens or disk-like bodies on flat hills. The carbonate soils are observed on top of porous sediments but not on crystalline rocks. In the study area, where calcrete is common, the pH value of the agricultural land is usually above 7.5 and the surface, shallow ground and deep ground water is saturated with respect to calcium carbonate. Chemical analyses of indurate calcrete horizons, carbonate soils, rain water and ground water from southeast Bulgaria are commented in the text. It appears that competing processes of leaching and re-precipitation from waters oversaturated with respect to CaCO₃ are responsible for formation of transitional compounds - calcrete precursors, which further are transformed to calcrete. Because the rain water's acidity and ground water's degree of over-saturation, with respect to CaCO₃, vary with the season, it appears that seasonal variations in the water composition and the temperature control the net balance of soil carbonates.

Geochemical characteristics of organic matter from overcoal sediments and dump materials (Maritza-East Coal Basin, Bulgaria)

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The aims of the study were to characterize the geochemistry of organic matter from dump materials and overcoal sediments (Maritza-East Coal Basin, Bulgaria) as well as to try to find some differences among them from a chemical point of view. Three samples were studied: Sm. 1 – dump materials from “Iztok” Dump composed of a mixture of black clays and coals; Sm. 2 – gray schist-like clayey dump materials from “Staroseletz” Dump; Sm. 3 – overcoal massive black clayey sediments from “Trojanovo-3 mine”.

The samples were subsequently extracted by chloroform and ethanol-benzene (1:1, v/v). After asphaltene precipitation by *n*-hexane (1:50, v/v), the extracts were concentrated and subjected to Silicagel column chromatography separation. Solvents with increasing polarity were used for fractions preparation: *n*-hexane, for elution of alkanes/cycloalkanes (F. I); benzene for aromatic components (F. II); acetone for polar resins (F. III). Sulphur was removed from the first fraction by Cu grit treatment and thus cleaned F. I was studied by

GC/MS. By specific m/z fragment monitoring different homologue series were detected, i.e. *n*-alkanes, steranes, hopanes, tricyclic terpanes, *seco*-hopanes, diterpanes, etc. The relative content of *n*-alkanes as well as their patterns of distribution was determined. CPI values and ratios of the regular isoprenoids Pristine (Pr) and Phytane (Ph) were calculated.

The highest total, soluble and non-soluble organic matter (OM) content was obtained with dump materials from “Iztok” Dump (Sm. 1), lower values - were obtained with Sm. 2, and negligible ones - with Sm. 3. The same order kept the values for the yields of chloroform and ethanol-benzene bitumen A. Typical for all extracts is a domination of asphaltene over resins content. In Sm. 1 the aromatics content is higher compared to the alkane/cyclane fraction content. As for the other two samples - a reverse relation was established. For Sm. 1 and 2, short chain alkanes (nC_{15} - nC_{20}) content was lower than mid-chain alkanes (nC_{21} - nC_{25}) content, and the highest values were calculated for the sum of long chain homologues (nC_{26} - nC_{33}). For Sm. 3 - a reverse distribution pattern was observed, namely the lowest contents of long-chain alkanes was calculated. In all samples studied, the highest rel. % for *n*-alkanes was determined in the range nC_{23} - nC_{29} which is an indication for terrestrial input in OM formation. This observation was also supported by the high values for the CPI ratio. The low content of the regular isoprenoid, i.e. Pr and Ph, and the low Pr/Ph ratio (< 1) were a hint to assume reductive conditions by the primary sediments deposition.

Hopanes traced back by m/z 191 characteristic fragment show low (<2 rel. %) content. It should be emphasized that hopane distribution strongly differs for Sm. 1 and 3. In the first one (dump materials) “bio”- hopanes with $\beta\beta$ configuration and unsaturated hopanes dominate, and both feature to immature OM. For Sm. 3 (black clayey sediments) preponderant H27 β hopane and H29 $\beta\beta$ -H31 $\beta\beta$ hopanes series were accompanied by hopanes with $\alpha\beta$ configuration. In addition, in Sm. 3 only, tricyclic terpanes (6.6 rel. %) maximizing at C_{23} homologue were registered. In the same sample only, a tetracyclic terpane, 17,21-*seco*-hopane, C_{24} , M^+330 and steranes in the range of C_{27} - C_{29} were recognized.

In all samples studied the content of tetracyclic diterpenoid 16 α (H)-Phyllocladane, M^+274 (ca. 30 rel. %) is the highest among the diterpenoids. Simonellite ($C_{19}H_{24}$) was the other abundant (12.7 rel. %) tricyclic diterpenoid. The diterpenoids assemblage established could be interpreted as an indicator for gymnospermous *Cupressaceae/Taxodaceae* presence in the former mire as a predominant palaeocommunity.

Acknowledgements: The study is a part of project VU-11/06 financed by NSF, MES, Sofia, Bulgaria.

Organic matter composition and maturity of the Callovian (Middle Jurassic) sediments from Lithuania

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In both the terrigenous Papilė Formation (Lower Callovian) and shallow- to deeper-marine facies of the Papartinė and Skinija formations (Middle and Upper Callovian, respectively), terrestrial organic matter predominates. This is emphasized by the carbon preference values higher than 1 for all samples and in some cases higher than 2, as well as the occurrence of characteristic higher plants biomarkers like cadalene, dehydroabietane, simonellite and retene. Fragments of charcoal found in the samples of the Papilė Formation indicate wildfires that took place in the early Callovian of Lithuania. Unlike the Callovian of Western Europe, in the Middle Callovian of Lithuania there is no evidence of anoxic conditions occurring in the water column. Measured values of huminite reflectance (R_h) for selected samples are in the range of 0.21% to 0.31%, what is characteristic for immature OM. This indicates that investigated deposits during their whole diagenetic history laid nearly on the surface and the thickness of younger cover does not exceed 500 m. This is supported by biomarkers analysis. In the all Callovian samples less thermally stable $\beta\beta$ -hopanes significantly dominated what suggest immature character of the samples.