The kerogen composition of the Upper Devonian Domanik carbonaceous deposit of the Timan-Pechora basin

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Summary

The organic matter of carbonaceous Domanik strata of Upper Devonian Timan-Pechora basin deposits were studied by wide analytical technique range. It was shown that accumulation of high concentrations of C_{org} took place in anoxic basin, lipid components of initial organic matter were subject to diagenetic sulphurization but carbohydrates are not sulphurized. The main molecular units of kerogen network are long n-alkyl chains and aromatic groups. The part of oxygen bridges is relatively low. Sulphur bridges are spread widely and mainly connect long n-alkyl chains but not sugar remains.

Domanic strata as a carbonaceous deposits

The Upper Devonian domanik deposits of the Timan-Pechora basin are known as the rock mass with high C_{org} content. Outcrop samples were taken from Domanik, Chut and Lya-El rivers (near Ukhta city). Totally 71 samples were investigated, the results of Corg determination shows 0.17 – 18.1% values with the average C_{org} content of 4-6%. The rocks are characterized by high bitumen content that riches 1-2%. The opinion about domanik strata as a main oil source rock of the Pechora basin is widely known.

The bitumen biomarker composition

According to a number of biomarker hydrocarbon ratios the maturity level of the bitumen could be classified as the beginning of oil window, i.e. equivalent to 0.5-0.7% R_{oil}. Thus 22S/22S+R ratio of C_{31} $\alpha\beta$ hopanes changes from 0.54 to 0.59, the 20S/20S+R ratio of C_{29} $\alpha\alpha\alpha$ steranes is equal to 0.25-0.46. The C_{30} moretan/hopan ratio is not least that 0.10. The biomarker analysis of bitumen extracts show two types of sterane hydrocarbons distribution. The C_{29} steranes content is higher in the samples collected on the Chut and Lya-El (C_{27}:C_{28}:C_{29} as 31:19:50) rivers outcrops compared to Domanik river (C_{27}:C_{28}:C_{29} as 36:22:42). We suppose high C_{29} steranes content is not a terrestrial input marker but is a marker of cyanobacterial input (fig. 1). The bitumen extracted from Domanik river samples is usually characterized by n-alkanes absent, that is typical for the biodegraded oils and bitumen. The GC-MS analysis of an aromatic bitumen fractions shows that arylcarotenoid derivatives are typical compound of domanik bitumen. The isorenieraten derivatives present there is usually considered as sedimentation anoxic environment condition indicator (Koopmans et al., 1996).

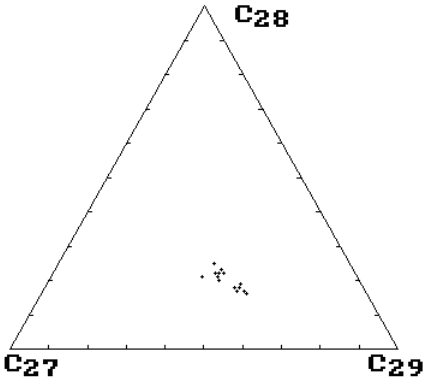

Fig. 1. The αββ steranes distribution in the domanik deposits bitumen.

The kerogen analysis

Kerogen concentrates were isolated by the HCl/HF asid demineralization of debitumenized rock samples. To study kerogen structure we used a number of following techniques: elemental analysis, pyr-GC, off-line pyrolysis with the GC-MS analysis of the aromatic and aliphatic fraction isolated, ^{13}C NMR spectra were also studied for the selected samples.

The H/C and O/C atomic ratios of the studded kerogen sample set allow us to identify the domanik kerogen as type II (fig. 2). The S_{org} content is not high, and kerogen could not be classified as II-S type. Kerogen is relatively enriched in nitrogen (N/C ratio is equal to 0.03-0.04) which is the possible zooplankton source indicator, it is well known that chitin are abundant in Upper Devonian deposits under study.

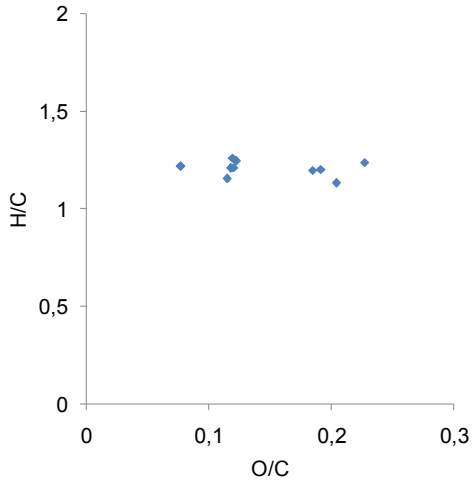

Fig. 2. The elemental analysis of the domanik kerogen samples on the Van Krevelen diagram.

Two samples of Domanik kerogen were used to obtain solid state ^{13}C NMR spectra. Their spectra contain two main signals regions 10-60 ppm, including 30 ppm band and 100-160 ppm (fig. 3, Bushnev et al., 2010). The band in the 100-160 ppm area is believed to aromatic,

geteroaromatic and phenolic carbon atoms. The wide area in 10-60 region could be associate with different kind of aliphatic carbons and single bound to sulphur carbon atoms. The narrow band at 30 ppm is belonging to carbons of aliphatic chains. The analysis of ^{13}C NMR data allow suggesting that aliphatic carbons attached to oxygen by a single bond are not typical for the domanik deposits kerogen (Bushnev et al., 2010).

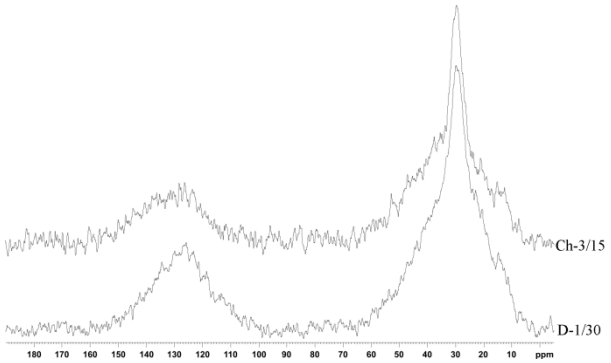

Fig. 3. ^{13}C NMR spectra of Domanik kerogen from Chut (Ch-3/15) and Domanik (D-1/30) rivers (Bushnev et al., 2010).

The GC-MS analysis of the off-line pyrolysis products shows that main components of aliphatic fractions are n-alkanes/n-alkenes-1. Their yield is varying from 2.73 to 8.27 mg/g C_{ker}, indicating relative enrichment of the domanik kerogen by aliphatic chains. The detail GC-MS investigations of aromatic pyrolysis products shows that main components of this fraction are: *n*-alkyl benzene, *n*-alkyltoluene, *n*-alkylnaphthalene, *n*-alkylthiophene, and alkylated derivatives of benzothiophene, all of which are typical of many kerogens. The arylcarotenoids derivatives were also identified. The presence of large amount of long chain n-alkyl containing thiophenes and benzothiphenes is a sign of sulphur bridges between n-alkyl chains in the kerogen structure. Therefore a diagenetic sulphurization played a role in lipid conservation process.

Pyr-GC results show hydrocarbons of aromatic and aliphatic nature are the main products of thermal kerogen decomposition. The concentration of sulphur containing compounds is not high. Thus the thiophene ratio (TR, Eglinton et al., 1990) does not exceed that complies to S/C values of kerogens. As it was shown above, TR decreases with increasing C_{org} in the rock of the Domanik sample set. This trend is not typical of immature sediments of anoxic basins. It is possible in particular that the initially sulfurous kerogen of higher carbonaceous domanik deposits lost most of the relatively labile sulfurous compounds during insignificant transformation at the early catagenetic stage (Bushnev, 2009). The analysis of C2 thiophenes distribution in domanik kerogen pyrolysate shows that the 2,5-DMT/(2-ET+2,3-DMT+2,4-DMT) ratio believed (Van Kaam-Peters et al., 1998) to be measure of sulphurized carbohydrates negatively depends by C_{org} concentrations in the rock. Thus we could suggest that early diagenetic sulphurization of carbohydrates did not play an important role in domanik organic matter accumulation.

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