

Hydrocarbon composition of bitumen from deeply buried terrestrial organic matter (*zone of apocatagenesis*)

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Abstract

We present new results on catagenetic alteration of dispersed organic matter (DOM) and individual hydrocarbon composition of bitumen extracts from the lower mesocatagenesis and apocatagenesis zone, based on the study of core samples from superdeep well SV-27 (Vilui syncline), which penetrated Permian and Upper Carboniferous coal-bearing strata. The vitrinite reflectance data show a progressive increase in the thermal maturity of DOM at a depth of ~4 km. The major biomarker indicators of the thermal history of DOM in the central part of the Vilui syncline appear to play only a minor role below this depth, thus reflecting the early stages of mesocatagenesis. The pristane/phytane ratios begin to invert at the same depth. Bitumen extracts from core samples collected from this depth contain new hydrocarbons in trace amounts, which increase with depth. The identified compounds include homologous series of alkenes, 2,4- and 2,7-dimethylalkanes, and alkylcyclohexanes with a prevalence of compounds with an odd carbon number predominance. Unusual differentiation of aliphatic and cyclic hydrocarbons with even and odd carbon-numbered chains occurs at the maximum depth (6458 m). Among aromatic hydrocarbons, four new diastereomers are identified: 17-desmethyl–23-methylmonoaromatic steroids C₂₇. Considerable variations in the composition of bitumen extracts from the apocatagenetically altered core samples appear to reflect the termination of hydrocarbon generation from kerogen and further thermolysis of residual bitumens, including their asphaltene components. This explains the low values of maturity biomarker indicators corresponding to the apocatagenesis grade, since in this case they reflect the composition of hydrocarbons generated during the early stages and later occluded and adsorbed by asphaltenes. “Deep-seated” microoil from Permian, Carboniferous, and Cambrian deposits did not participate in the formation of oil rims and major gas condensate pools in the Vilui petroleum area.

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Introduction

Our knowledge on the geochemistry of organic matter at a great depth (the zone of apocatagenesis) in sedimentary basin of East Siberia is still very scanty and sometimes quite schematic. The most interesting results are those reported from the analyses of core samples from the superdeep well SV-27 (Srednevilyuiskaya prospect within the Vilui syncline), which revealed a sequence of Mesozoic and Upper Paleozoic rocks down to a depth of 6519 m (Bodunov et al., 1990; Kontorovich et al., 1988). The present-day temperature recorded at the bottom of the borehole is 173 °C, although the

temperature was significantly higher at this depth before the formation of permafrost. The location of the borehole is shown in Fig. 1. The subdivision of Mesozoic and Cenozoic deposits in the central part of the Vilui syncline was discussed in previous studies (Golubeva et al., 1980; Grausman and Slastenov, 1978).

The previous study on lithification of the sediment and catagenesis of organic matter shows that transition from the zone of mesocatagenesis to the zone of apocatagenesis in the Vilui syncline occurs at a depth of 5090–5100 m. Variations in the composition of the soluble part of DOM (bitumen extracts) at the level of hydrocarbon groups and, to a lesser extent, individual constituents are demonstrated in this paper as well (Perozio et al., 1981).

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Fig. 1. Location of superdeep well SV-27 (Srednevelyuiskaya prospect).

Here we report the results of the analysis of catagenetic alteration of dispersed organic matter (DOM) and individual hydrocarbon composition of bitumen from the lower zone of mesocatagenesis and apocatagenesis. A total of 70 core samples of Upper Paleozoic (Permian–Upper Carboniferous) coal-bearing rocks were collected from well SV-27 at depths of 3370–6458 m. The vitrinite reflectance data show a progressive increase in the thermal maturity of DOM at a depth below 4 km (Fig. 2). Above this depth, the vitrinite reflectance increases only by 1 and is 2.5 times higher in the interval 2 km deeper. It should be noted that the major biomarker indicators of the thermal history of DOM in the central part of the Vilyui syncline appear to play only a minor role at a depth below 4 km, thus reflecting the early stages of mesocatagenesis (Fig. 2).

Methods

Core samples were extracted using chloroform. The maltene fraction of bitumen was separated after chromatographic fractionation of asphaltenes in the presence of an excess of petroleum ether into saturated and aromatic hydrocarbons, benzene and alcohol-benzene resins on a dual silica gel-alumina column. The saturated and aromatic hydrocarbon fractions were further analyzed by GC/mass spectrometry with the Agilent 6890/5973N gas chromatograph/mass selective detector system. Mass chromatograms were acquired in total ion current (TIC) and selective ion monitoring (SIM) modes. Peaks were identified by the search in the NIST-08 MS data library, comparison with the literature data, and structural reconstruction from electron impact fragmentation patterns.

Results

Figure 3 shows gas chromatograms of the saturated hydrocarbon fractions of the studied bitumen extracts from samples collected at 3387–6458 m. A distinctive feature of these gas chromatograms is the change with depth from a distribution of *n*-alkanes centered on C₂₃ to a distribution centered on C₁₉. Another characteristic is a decrease in the pristane/phytane ratio from 1.6 to 0.45. The pristane to phytane ratio close to unity is observed at depths of ~4 km and then decreases gradually to values typical of aquatic organic matter.

A series of previously unknown hydrocarbons were identified in bitumen from core samples collected at the same depth. Their concentration increases with depth. The largest variation in the hydrocarbon composition of extracted bitumen is observed in the last sample 6102 collected at a depth of 6458 m (Figs. 4–6). It should be noted that the hydrocarbon group composition of bitumen from samples collected at a depth of >5 km shows the absence of asphaltenes and a significant shift toward resins while hydrocarbons constitute 30–40% of the fraction.

Reconstruction of the *m/z* 69 + 97 mass fragmentogram (Figs. 4, 5) of the saturated fraction from sample 6102 allowed identification of two alkene homologous series containing a double bond at the C-1 and C-5 positions. These homologous series show a predominance of odd-numbered compounds in the first case and even-numbered compounds in the second case. This was quite unexpected but it was shown later that the differentiation into odd- and even-numbered homologues is also characteristic of other aliphatic and cyclic hydrocarbons from great depths, with the exception of normal alkanes. The identified compounds include 2,4-dimethylalkanes (*m/z* 85)

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