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Full Length Article

Genesis of the asphaltite of the Ivanovskoe field in the Orenburg region, Russia

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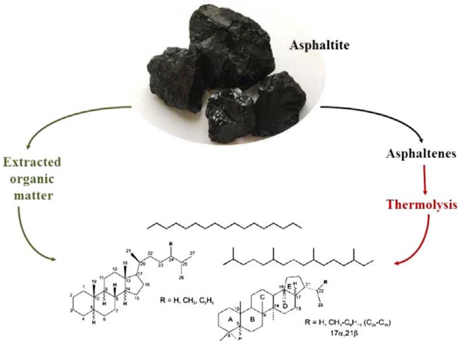
GRAPHICAL ABSTRACT



1. Introduction

Nowadays the reserves of light and medium-density oils are depleted and there is an increasing interest in the search for unconventional sources of hydrocarbons (malts, asphalts and asphaltites). These raw materials have geological reserves several times higher than conventional oil reserves.

Asphaltites are unique natural raw material characterized by high heteroatoms and metals content. Asphaltites are one of the groups of solid natural bitumens. Gasification of the asphaltites leads to production of gaseous or liquid fuels, hydrogen, raw materials for chemical industry and adsorbents [1,2]. If the environmental requirements are met for combustion products asphaltite is an important raw material for the production of energy in thermal power plants because of its high-calorie structure [3,4].

It is considered that asphaltites are oil derivatives formed as a result of oil transformation on a ground surface or in shallow depths. However, conditions of asphaltites deposits formation are still not fully studied. Despite of the variety of proposed schemes for natural bitumen deposits formation there are still some questions to be understood. In this regard, the interest of scientists is directed to the determination of sources of asphaltite deposits and paths of their formation [5–15].

Large asphaltite deposits are located in Australia, Sweden, Turkey, Argentina, Trinidad and Tobago, Russia are described in literature [1–3,6–12]. One of the interesting representatives of asphaltites is the aspaltite of the Ivanovskoe field found in the Orenburg region (deposited in Permian rocks at 400 m depth). Reserves of the asphaltite of the Ivanovskoe field are estimated to be 10 million tons. The special feature of this asphaltite is an absence of mineral particles in it. So it could be supposed that not an impregnation of fluids into empty space of a reservoir took place but a rupture of rocks followed by an intrusion of hydrocarbons [16,17].

First attempts to determine the source and the conditions for the formation of the asphaltite of the Ivanovskoe field (the asphaltite) were made in [17,18]. Authors of this works proposed that the source of the asphaltite was oil from the Lower Carboniferous terrigenous deposits. At that time there were no possibility for the analysis of the hydrocarbons composition at a molecular level. That is why this conclusion was based on elemental compositions and group compositions of narrow fractions of the asphaltite, an acid value and a saponification value, compositions of gases desorbed from the asphaltite samples, a polynological (spore-pollen) analysis of the asphaltite. It is well

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understood that on a base of this parameters it is hardly possible to determine the asphaltite source.

Later in [16] distributions of hydrocarbon biomarkers, heteroatomic compounds as well as functional and group compositions of the investigated asphaltite were studied in details. Based on the data obtained the authors concluded that the asphaltite was formed from oil generated by marine carbonates on the stage of catagenesis corresponding to the beginning of the «oil window». They also concluded that sedimentation and diagenesis of organic matter was carried out in coastal-marine conditions in anoxic environment in a zone of hydrogen sulfide contamination. They refuted the conclusions of [17,18] that the source of the asphaltite was oil from the Lower Carboniferous terrigenous deposits. Authors of [16] claimed that the source of the asphaltite was Permian oil located in the same deposits where the asphaltite was found.

However, in our opinion, it is impossible to reestablish a geochemical history relying only on the analysis of hydrocarbon composition of asphaltites (or petroleum in general). The reason is that the relative concentration of the hydrocarbons in oil changes with time because of biodegradation, weathering, dissolution in reservoir water, migration etc.

In order to define the genesis of the asphaltite more accurately in addition to investigation of the regularities of the hydrocarbon biomarkers distribution in the asphaltite we carried out a thermolysis of asphaltenes separated from the asphaltite. The detailed analysis of regularities of the biomarkers distribution in thermolysis products of the asphaltenes compared to the same distribution in the asphaltite's oil fraction makes it possible to discover the geochemical history of the asphaltite. Such approach was developed by authors and successfully performed for petroleum [19,20]. In this work, the same approach was applied for the asphaltite for the first time. The studies based on this approach did not confirm the conclusions of [17,18] and do not completely coincide with the conclusions of [16] as will be shown later.

2. Material and methods

The asphaltite was taken from the Ivanovskoe field located in the Volga-Ural Petroleum and Gas Province on the southeast of the Russian platform within the framework of the Malikilensky system of deflections. An almost horizontal monolithic formation body (vein) with a thickness of 1.4–7.2 m lies at a depth of 400–420 m in Upper Permian sediments (P_{2kz}) (Fig. 1). The asphaltite contacts mainly with a thick (54.0–54.5 m) bed of a rock salt and, locally, an anhydrite at the bottom or with the anhydrite and the rock salt interlayers at the roof. Mineral impurities are barely found. The asphaltite contains 69% of asphaltenes, 18% of oil and 13% of resins [16].

The asphaltenes of the asphaltite (the asphaltenes) were precipitated from benzene solution (5 ml/g) of the asphaltite by n-pentane in relation of 40 ml/g [16]. The oil fraction was obtained using column chromatography on activated silica gel with n-hexane as eluent.

Thermolysis of the asphaltenes was carried out in a sealed glass ampoule at 330 °C for 6 h in a thermostat. The weight of the asphaltenes was ~300 mg. The n-hexane was used for products extraction.

The saturated hydrocarbon biomarkers in the oil fraction and in the asphaltenes thermolysis products were subjected to gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

The analysis of n-alkanes and isoprenanes distributions was performed by capillary GC on Bruker 430-GC instrument with FID. The temperature was programmed from 80 to 320 °C at a heating rate of 4/min. Hydrogen was the carrier gas. The hydrocarbons were separated on a HP-1 25 m × 0.25 mm × 0.5 μm capillary columns.

Steranes and terpanes distributions were analyzed by GC-MS. The GC–MS analysis was performed using Agilent 6890N/5975C instrument equipped with computer data acquisition and processing system, in the SIM mode with recording ions at *m/z* 217, 218 for tetra- and *m/z* 191, 177 for tri- and pentacyclic terpanes. The temperature was programmed from 70 to 290 °C at a heating rate of 4°/min. Helium was the carrier gas. Separation of hydrocarbons was performed on a similar HP-1MS 25 m × 0.25 mm × 0.5 μm capillary column with a silicone phase. All spectra were recorded at ionization energy of 70 eV and accelerating voltage of 3500 V. The temperature in the ionization chamber was 250 °C. Compounds were identified by adding authentic reference compounds to the test samples and using NIST mass spectrum library.

3. Thermolysis of Petroleum asphaltenes as a method for establishing their geochemical history

It is well known that the regularities of qualitative and quantitative distributions of the biomarkers are used for correlations in oil–oil, oil–extractable organic matter (EOM) (oil–potential source rocks)

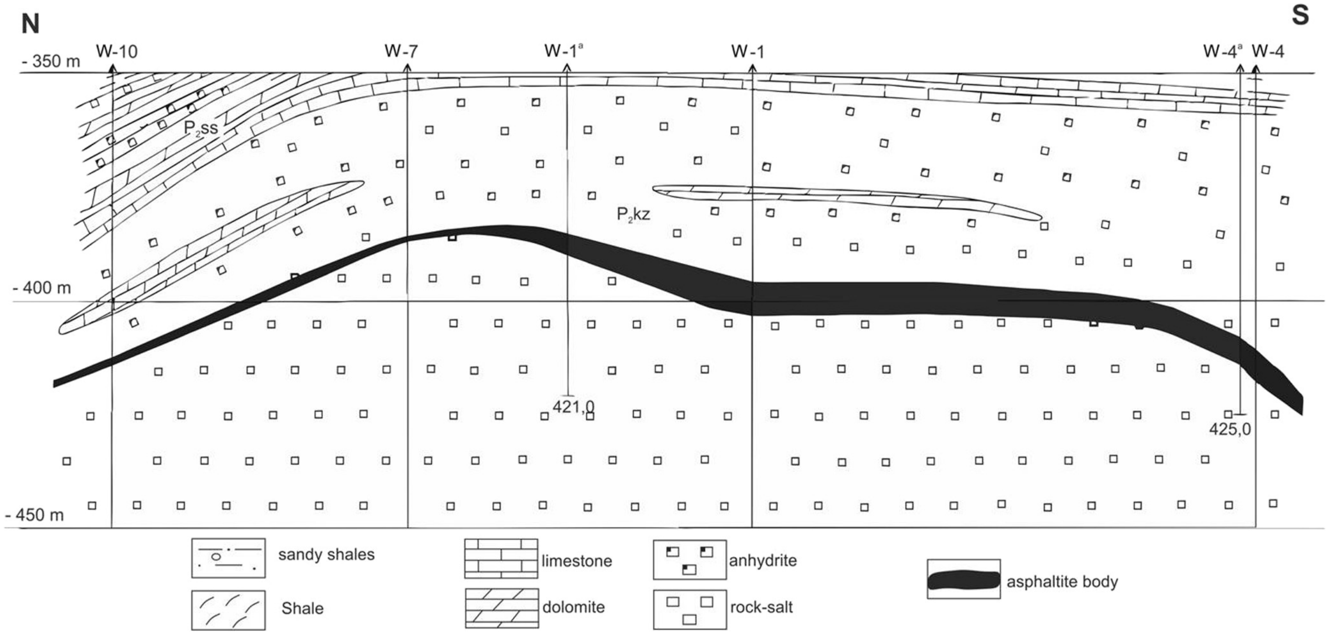

Fig. 1. Geological section of the asphaltite location (the Ivanovskoe field) (W – well).