Geochemical Evidence of Deep Source Rocks—Adamantanes in Oils from the Absheron Archipelago, South Caspian Basin, Azerbaijan

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Abstract

Oil samples taken from various depths and stratigraphic formations of the fields in the Absheron archipelago were analyzed to evaluate the composition of adamantane hydrocarbons, its derivatives, and other biomarkers using gas-chromatography and gas-chromatography-mass-spectrometry. Reservoirs in the study area are Middle Pliocene age stacked fluvial-deltaic sandstone units that contain hydrocarbons generated by organic-rich shales of deep-water Oligocene–Miocene and Diatom formations. s organic matter matures, the total amount of the biomarkers in the hydrocarbons decreases. It happens due to the thermodynamic equilibrium that builds between certain types of biomarkers, suggesting that in the case of highly mature oils, it is more beneficial and diagnostic to apply thermally highly resistant structures, such as adamantanes. Adamantanes and their homologs have been identified in the oil samples analyzed. The number of adamantanes and their methyl substitution compounds are present in the sequence of increasing their thermodynamic resistances. This indicates the formation of the adamantine as a result of thermal transformations of normal alkanes. It is known that the amount of adamantane hydrocarbons in oils depends on the oil's chemical nature. Data clearly show a direct relationship between the number of naphthenic hydrocarbons and adamantanes in oils. It indicates that the degree of transformation of the polycyclic hydrocarbons into adamantanes and their isomers is much higher in the naphthenic type of oils. Unique geological setting–rapid sedimentation and low to moderate geothermal gradients suggest the presence of deeper source rock that can support geochemical features, which we observe in the oil samples analyzed, including a high abundance of adamantanes hydrocarbons.

Keywords

South Caspian Basin • Hydrocarbons • Biomarkers • Adamantanes • Source rock

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1 Introduction

South Caspian Basin is one of the wealthiest hydrocarbon provinces in the world, with more than 100 years of oil and gas production history. It contains more than 20 km of Mesozoic and Tertiary sediments deposited on oceanic or thinned continental crust. The primary production in the basin is from the Pliocene productive series of fluvial-lacustrine, deltaic sandstones deposited after the Miocene base level fall that caused the isolation from the global ocean. Principal source rocks for the oil and gas fields are organic-rich Oligocene–Miocene Maykop and Diatomaceous shales deposited in deep water environments. Raw data on source rocks predominantly come from the onshore well penetrations and natural outcrops. This work aims to share preliminary results from the geochemical work done on the oil samples collected from the various oil fields in the Absheron archipelago. The focus was on the composition and distribution of adamatanes, their homologs, and other biomarkers, as well as evaluating the role of adamantanes in hydrocarbon formation. Adamantane is the chemical name for "diamond-type hydrocarbons." It is a bridged hydrocarbon of the $C_{10}H_{16}$ composition, consisting of three cyclohexane rings in the "armchair" conformation. An essential feature of adamantane hydrocarbons is their thermodynamic stability, which helps a lot in the case of studying highly mature or biodegraded oils.

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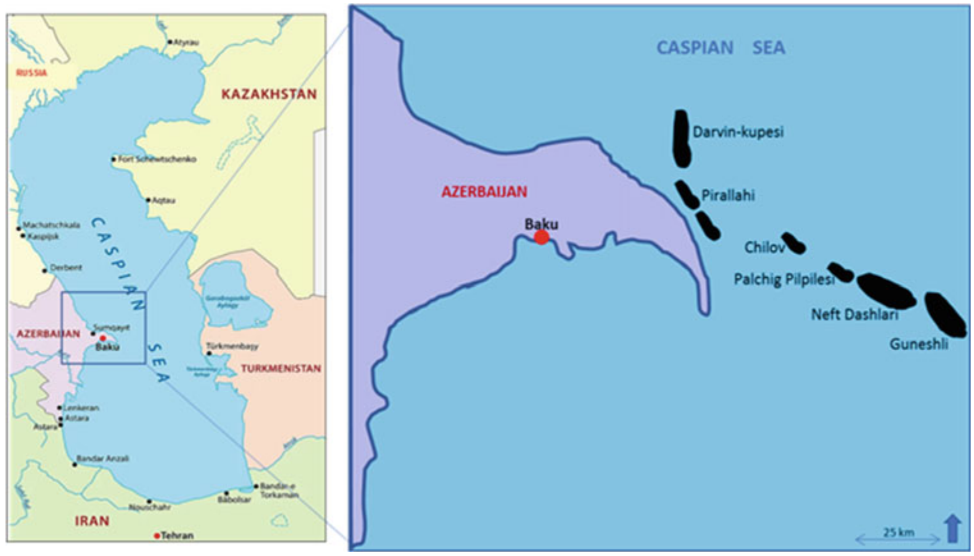
Fig. 1 Study area location map



Oil samples from various depths and stratigraphic formations of the fields in the Absheron archipelago, such as Darvin-kupesi, Pirallahi, Palchig Pilpilesi, Neft Dashlari, Guneshli, Chilov, and Sangachal-Deniz fields are the subjects of the current study (Fig. 1).

2 Materials and Methods

Gas-chromatography-mass-spectrometry (Perkin-Elmer Clarus 680) was used to analyze the oil samples selected: carrier gas—helium, 60 m capillary column/0.25 mm diameter. Temperature programming steps 2 °C/min from 80 to 300 °C, and source temperature is 250 °C. Chromatograms of hydrocarbons were obtained by total ion current (TIC) and specific ion fragments (SIR). The individual hydrocarbons were identified through a computer search of the National Institute of Standards NIST-08 library (more than 130,000 mass-spectrums of organic compounds), according to published data and based on the reconstruction of ion fragments that have been identified. Adamantane hydrocarbons were detected by scanning fragmented ions m/z 136, 135, 149, and 163.

3 Results

More than 250 individual hydrocarbons have been identified in the oil samples analyzed. The important ones are the biomarkers—terpenes, steranes, hopanes, and adamantanes (Peters & Moldowan, 1993). In addition to adamantanes, their homologs with C_{11}–C_{15} composition have also been identified in the oil samples. It should be noted that the samples analyzed represent oils of different stratigraphic ages. The distribution of adamantanes in the oil samples from the Guneshli field is given as an example in Table 1.

The distribution of adamantanes C_{10}–C_{13} in oils from the Guneshli and Neft Dashlari fields shows that the highest amount of alkyl-adamantanes corresponds to its dimethyl-transitioned homologs. In contrast, the concentration of the adamantanes that have not been transformed is the lowest. We also observe high content of 2-monomethyl-adamantanes (2-MAd) in C_{12}. Generally, there is the following trend in the distribution of adamantane hydrocarbons in oils analyzed: 2-MAd > 1-MAd > 3-MAd > Ad., i.e., we see a higher concentration of thermodynamically stable adamantanes.

4 Discussion

It is known that the amount of adamantanes in oils directly depends on their chemical composition. The highest content of adamantane is typical for the naphthenic type of oils. Our data clearly show a direct relationship between the concentration of the naphthenic hydrocarbons and adamantanes in oils, i.e., naphthenic oils have a higher amount of adamantanes. It indicates that the degree of transformation of the polycyclic hydrocarbons into adamantanes and their isomers is much higher in a naphthenic type of oil. A high concentration of adamantanes in some of the samples could be due to intensive transformations due to thermal destructions or biodegradation. The correlation of the distributions of adamantane hydrocarbons and their isomers from various oil samples shows a good relationship between individual isomers that could suggest common mechanisms for forming adamantanes in the study area. As per the formation of adamantanes, there could be different mechanisms to

Table 1 Biomarkers in oils—guneshli field, absheron archipelago

Well #	Adamantanes, % C10:C11:C12:C13	C11/C10	C12/C11	C13/C12	C11/C13	C12/C13
135	10:35:40:25	3.6	1.14	0.63	1.4	1.6
250	7:31:36:27	4.43	1.16	0.75	1.15	1.33
136	5:27:40:27	5.4	1.48	0.67	1	1.48
293	23:29:30:17	1.26	1.03	0.56	1.7	1.76
244	5:37:25:33	7.4	0.68	1.32	1.12	0.76
212	3:19:37:37	6.3	1.94	1	0.51	1

consider here, including thermal cracking of n-alkanes, saturated hydrocarbons, and polar components (Chen et al., 1996; Giruts & Gordadze, 2007; Giruts et al., 2014; Goodwin et al., 2020). This will require high temperatures and thus deep-buried source rocks in the cold South Caspian Basin case. The formation of adamantanes could occur during the migration of hydrocarbon fluids from the deeper strata due to chemical transformations and isomerization processes. The presence of acid catalysts (clays) is an important criterion here. This subject requires further analytical work and modeling.

5 Conclusions

- Adamantanes and their homologs have been identified in soil samples from various depths, stratigraphic ages, and locations in the Absheron archipelago and South Caspian Basin fields.
- Chromato-mass spectrometry data show the following distribution of the adamantane and its methyl substitutions: 2–MAd > 1-MAd > 3-MAd > Ad. The such distribution suggests the formation of adamantanes due to thermal transformations of normal alkanes.
- A high amount of adamantanes, low geothermal gradients, and potential formation mechanisms of adamantanes described above suggest the presence of deeper buried source rocks (deeper than 8 km in the case of the cold South Caspian Basin) to support temperatures enough to form mature source rocks that generate hydrocarbon fluids accumulated in the study area.

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