**UDC: 550**

https://doi.org/10.59849/2409-4838.2024.3.52

# ABOUT THE SOURCE ROCK OF THERAPEUTIC OIL OF THE NAFTALAN FIELD

**Samir Gadir Zeinalov**
Institute of Geology and Geophysics, Baku, Azerbaijan
*zeynalov.samir.98@mail.ru
Received: 24.01.2024
Accepted: 15.07.2024

*The Naftalan field is a unique natural object not only because of the widely known healing properties of the oils, but also the variety of the composition of the oils available here. Thus, different types of oil at this field are spatially distributed, namely, therapeutic oil is strictly limited to the Upper horizons of the Maikop formation in the depth interval of 500-600 m, while the Lower horizons of this formation are saturated with fuel oil. Although there are many ideas about the source rock of naphthalene therapeutic oil, this issue remains open among researchers. In this study, we suggest that the source rock of Naftalan oil generated from Eocene deposits based on the biomarker analysis (the 18α (H) oleanane biomarker and the ratio of diasteranes to regular steranes) of the studied oil and the maturity indicators of the Eocene and the Maikop rock samples in the Middle Kura depression.*

***Keywords:*** *Naftalan oil, Maikop sediments,biomarker, oleanane, maturity.*

## INTRODUCTION

The use of Naftalan oil, distinguished by its unique balneological properties, dates back to ancient times. Even at the beginning of our millennium, many people came to this place in the vicinity of Ganja in camel caravans and transported Naftalan oil for treatment purposes.

It is known the presence of two types of oil different by its quality and biomarker-geochemical parameters in deposits of Maikop suite in Naftalan deposit: curative hard oil - in the upper horizons of the Upper Maikop (I, Marl and II horizons) and fuel light - in lower horizons of the Upper Maikop and Lower Maikop [10].

The Naftalan structure is located in the Ganja oil-gas region of the Middle Kura basin, which is the middle segment of the Kura Megadepression. The oil flows in the area of the Middle Kura depression were obtained from the Eocene, Maikop and Upper Cretaceous sediments [8].

The source rock of Naftalan oil remains a controversial and still open issue among researchers. In our research work, we will try to clarify this topic by taking into account the biomarker-geochemical properties of studied oil and the maturity potential of rocks in the structures of the Middle Kura basin.

## GEOLOGICAL SETTINGS

Geological section of Naftalan oil field was studied through numerous rock samples taken from structure-exploration and deep drilling wells, well logging diagrams, as well as rock outcrops. These data were then supplemented with new data from deep exploratory, appraisal and production wells drilled in 1959-1966 in order to more accurately base the calculation parameters for the calculation of therapeutic primary oil reserves [9].

Tertiary sediments are included in the geological section of the Naftalan deposit - Agcagilian layer (Upper Pliocene), Maikop formation (Oligocene-Lower Miocene) and foraminiferal layers (Eocene).

The Aghcagilian floor is widespread over the area and overlies Maikopian-aged sediments with a surface erosional unconformity.

In connection with the washing of the ceiling part of the Maikop formation in the Naftalan field, the cutting of the upper Maikop begins with clayey layers in one part of the bed and sandy layers in the other part. According to the general cross-section, the following divisions belong to the upper Maikop: the clayey section between the bottom of the Agcagilian and the ceiling of the I sandy horizon; I sandy horizon; clay section between I sandy and marl horizons; Marl horizon; ehe clayey section between the Marl and II sandy horizons. The cross-section of the Lower Maikop begins with the II sandy horizon and consists of the II, III, IV, V, VI, VII, VIII sandy horizons separated by different thick clay sections and the sandy-clay stratum (II Gazanbulag horizon) with a large thickness (889 m). The thickness of the Lower Maikop is 1672 m [9].

The forominiferal layers consist of alternating dense sandstones and clays. Sandstones are brown, dark brown, fine-grained and impermeable. The clays are dense, in some places limestone and mostly sandy. Small and large fragments of greenish marls with the fauna of the lower and upper divisions of the foraminiferal layers are found in the section of the indicated group. The thickness of the foraminiferal layers on the general section is 260 m [13].

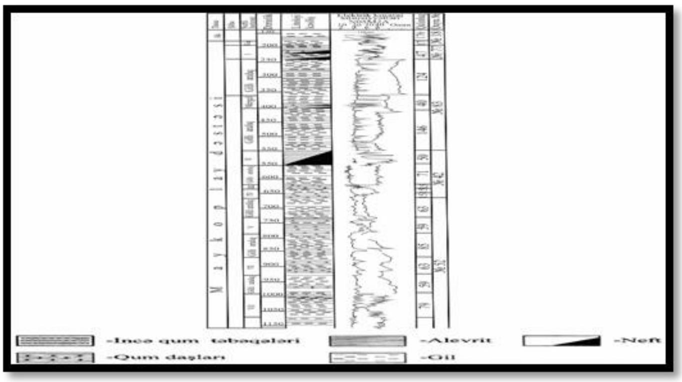


**Fig.1.** Lithological-stratigraphic section (based on Naftalan-18, 42, 52, 77, 83 wells) [1]

Numerous oil and gas flows were observed in the process of drilling structural, exploration and exploitation wells in the field. The Maikop formation, which is the main source of oil, is of greater importance. The thin sandy layers in the clay sections between I, marl, II, III, IV, V, VI, VII, VIII horizons are saturated with oil [13].

Therapeutic oils are mainly collected in I sandy, Marl and II horizons, and fuel oils, which differ from therapeutic oil in terms of their physical and chemical properties, are collected below them. Thus, the clay section between the II and III horizons can be considered as the boundary separating the therapeutic and fuel oils.

From the tectonic point of view individuality and uniqueness of Naftalan oil field are explained [10, 14] by its confinement to the deep fracture zone. The Naftalan structure is situated within Arpa-Samur fracture zone, which at all times from Paleozoic till now was the zone of active display of tectonic movements, conductor of magmatic melts, ore bearing solutions and seismicity. In the formation of the specific shape of oil the participation of the underlying fluids is possible, both as a result of interaction with the organic matter during its fossilization or at the stage of its transformation into the oil, and at the interaction of the mantle emanations with the already formed oil. At the same time, emanation of fluids into the paleobasin and formation of specific conditions of fermentation of initial organic matter at certain stages of sedimentogenesis, which in principle can explain the presence of different-type oils within the same field, seem to be quite probable. Based on the biomarker-geochemical indicators of Naftalan oils, in order to evaluate the Cretaceous and Eocene age sediments as potensial source rock, it is necessary to consider their lithological composition within the Middle Kura depression.

**Eocene** sediments have been studied through deep wells in almost all areas of the Middle Kura basin. It is mainly composed of sedimentary rocks.

The section of the Eocene is divided into three parts according to the characteristics of lithological and electric logging: sub-marl, middle-marl, and upper-marl. These layers are conventionally attributed to the Lower, Middle and Upper Eocene.

**The Lower Eocene** sediments are represented by clays, interbedded with sandstones, tuffaceous sandstones, gravelites, weak carbonate marls and argillites.

The sediments of the marl layer (**middle Eocene**) are characterized by high specific electrical resistance. The washing part of this layer is represented by the alternation of weakly carbonated clays and fine-grained sand interlayers. Marl series and marly clays with interlayers of fine-grained sand lie under it. Interlayers of limestone and dolomite are rarely encountered in the section. **Upper Eocene** (Upper Marl layer) is characterized by relatively low specific resistance. It was represented by alternation of marly-carbonate clays and clayey siltstones [8].

**Upper Cretaceous** sediments are represented by volcanogenic-sedimentary and sedimentary rocks. Cenomanian, Turonian, Coniacian, Santonian and Campanian-Maastrichtian layers are included in the stratigraphic units.

**Upper Cretaceous** sediments (Cenomanian-Maastrichtian) were found in several areas of the Muradkhanli field, in Sorsor (well No. 2) and Saatli (support well No. 1) wells. The exposed thickness of the Cenomanian in the Sorsor area is 300 m and consists of dolomite and limestone layers with volcanic-sedimentary layers (tuffaceous gravel and sands), and in the Saatli area 780 m thick limestones of different structural and genetic types alternate with effusive rocks (basalts).

**Lower Cretaceous**. These sediments consist of volcanic, volcanogenic-sedimentary and sedimentary rocks in all areas exposed by excavation. The sediments of the Hoteriv, Barrem and Apt floors are involved here.

It was opened in the Lower Cretaceous (Hoteriv-Apt) research region in the Carlı (wells Nos. 1, 4, 6, 10), Sorsor (wells Nos. 3 and 4) and Saatli No. 1 deep wells. The section consists of different genetic rock types and they are described as follows.

The exposed lower part of the section is 810 m thick (Saatli well No. 1) and consists of various tuffs, tuffaceous breccias, and tuffogenic-sedimentary assemblages (80 m) alternating with porphyrites. The rocks in this part of the section are composed mainly of Saatli area, sometimes basalts with layers of andesite and porphyrite. The upper part of the transect (Barrem) is represented by 290 m thick sedimentary formations consisting of dark gray argillites with marl, sandstone and siltstone beds. Aptian sediments are described in the lower part by volcanogenic-sedimentary (tuffaceous sands and gravels) and sedimentary assemblages (sandstones, siltstones). The thickness of these sediments is 100 m [8].

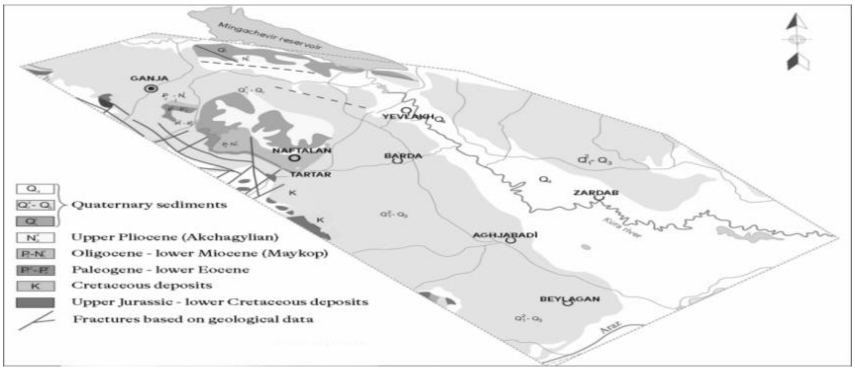

**Fig. 2.** Geological map of Evlakh-Agjabedi depression [1]

## MATERIAL AND METHODS

Biomarker analysis of medicinal Naftalan oil from oil base I-II horizon, filter 151-586 m was performed in this research study.

Biomarkers investigations were made by chromatography-mass spectrometry (GC-MS) on Perkin-Elmer Clarus 680 instrument having interface with high-efficiency mass-selective detector Clarus SQ8T. The chromatograph was equipped with a quartz capillary column of 100 m length, 0.25 mm diameter and impregnated with ZB-1 phase. The carrier gas is helium, with a flow rate of 1ml/min. Evaporator temperature 300 °C; programmed temperature ramp from 80 to 290 °C at a rate of 4 °C/min followed by an isotherm for 70 min. Ionizing source voltage 70 eV, source temperature 250°C. Methylene chloride was used as a solvent.

## RESULTS AND DISCUSSION

The geochemical parameters of Naftalan fuel and therapeutic oils have been reflected in articles as a result of numerous studies [2, 3].

Terpanes, steranes, hopanes and adamantanes were identified in oil sample. Here are given mass spectra plots for calculation of hopanes (m/z 191) and steranes (m/z 217) in sample of Naftalan oil (Fig.3, 4 and table 1, 2). Considering that Naftalan oil undergoes biodegradation that the maturity parameters and some other biomarker indicators probably do not correspond to real values. For this reason we will look through only some of the biomarkers that provide geological information about the age of source rock and its lithological composition.

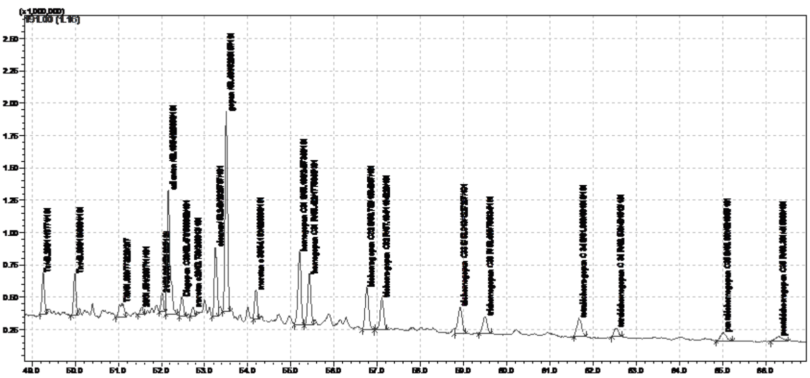

**Fig. 3.** Chromato-mass-spectrum section of hopanes (m/z 191) in Naftalan medicinal oil

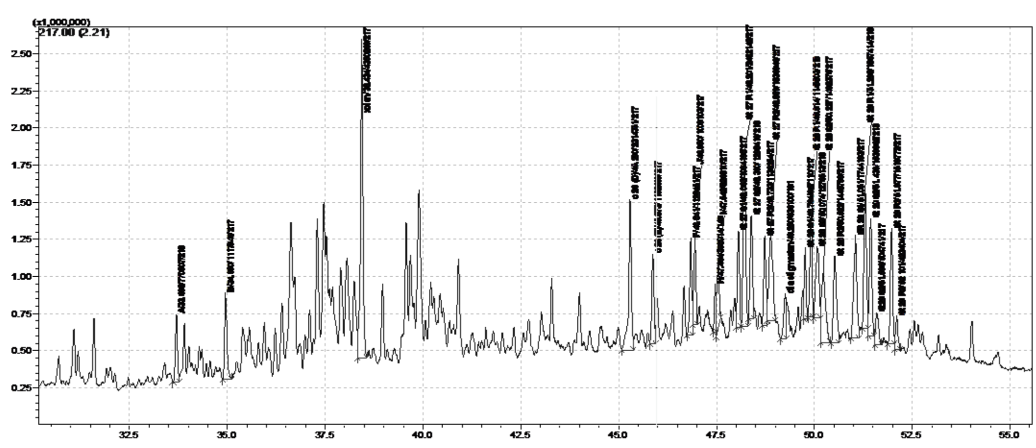

**Fig. 4.** Plot of the chromatography-mass spectrum of steranes (m/z 217) in Naftalan medicinal oil

**Table 1.**

Hopane content (m/z 191) in Naftalan oil

| Sample | Medicinal oil, % |
|---|---|
| Hopanes | 4.09 |
| Ts | 4.09 |
| Tm | 4.02 |
| $H_{28}$17αH,18αH,21βH bisnorhopane | 0.77 |
| $H_{29}$ Nor- 25- hopane | 1.96 |
| Adiantane | 14.84 |
| Diahopane $H_{30}$ | 2.2 |
| Moretane $H_{29}$ | 0.92 |
| Oleanane | 7.47 |
| Hopane $H_{30}$ | 19.19 |
| Moretane $H_{30}$ | 3.06 |
| Homohopane $Hh_{31}$ | 15.63 |
| Bis homohopane $H_{32}$ | 10.14 |
| Trishomohopane$Hh_{33}$ | 9.45 |
| Tetrakis homohopane $Hh_{34}$ | 4.8 |
| Pentakishomohopane $Hh_{35}$ | 3.35 |

One indicator of facies conditions of sedimentation is the ratio of diasteranes to regular steranes (dia/reg29). [4,12]. Increasing values of this coefficient indicate that the terrigenous complex dominates in source rocks of oil. Naftalan therapeutic oil has values such as 0.9, which allows us to conclude that the source rock is composed of a clayey rocks.

Terpanes in Naftalan oils are represented mainly by tricyclic $C_{19}$-$C_{20}$ (from 20.81 to 28.52) and pentacyclic triterpenoids (18α (H) oleanane (5-7% RH). This indicates the presence of continental and higher vegetation in the initial OM.

As already mentioned, oil in the Naftalan field is exploited from the Maikop formation. Taking into account the migration of hydrocarbons from the mature source rock (lower layers) to reservoirs (higher layers) via pores and fractures during the oil-gas field formation process, it is reasonable to suggest that the Naftalan oils were generated in the Upper Cretaceous, Eocene or Maikop deposits.

**Table 2.**

Stearanes content (m/z 217) in Naftalan oil

| Sample / Steranes % | Medicinal Naftalan oil |
|---|---|
| Diasterane | 19.41 |
| Sterane 27 | 22.31 |
| Sterane 28 | 17.14 |
| Sterane 29 | 21.6 |
| Diasterane/sterane 29 | 0.9 |

18α (H) Oleanane in oils is present in higher percentages in sediments of Cretaceous or younger age, coinciding with the evolution of angiosperms. Angiosperms are indicators of both source rock age and surface sediments both of which are useful biomarkers or molecular fossils in petroleum correlation studies and petroleum geochemistry in general. A higher oleanane to hopane ratio (oleanene index > 0.2) indicates that the oil is Paleogene or younger in age [11]. In Naftalan medicinal oil, this index is characterized by values of 0.4. This biomarker proves the Paleogene–Lower Miocene age of the studied oils.

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The source rock potential of Maikop sediments in the territory of Azerbaijan was determined as a result of pyrolytic studies conducted in the structures of the South Caspian basin [6]. However, although Maikop is a regional oil and gas stratigraphic unit in the area of the Middle Kura depression, as a result of research, it was found that Maikop is not mature enough as a source rock.

Final temperatures at Maikop in the Evlakh-Aghjabadi depression are about 112-116°C, which is favorable for the generation of mature oil. However, pyrolytic studies of Maikop Formation rocks show that these sediments are characterized by low maturity (Tmax values), rarely reaching Req 0.65%. This result is inconsistent with the maturity of the oils in the Cretaceous and Eocene formations. Oils from these layers are characterized by a greater maturity corresponding to the vitrinite reflectance equivalent Req=0.70-0.73% (calculated by the degree of sterane isomerization and isosteran/normal sterane ratio) [7].

The oil-gas potential of Cretaceous sediments in the area of the Middle Kura depression has already been determined in some structures by the deep drilling method (Muradkhanli, Zardab, etc.). Cretaceous sediments are suggested to be the possible source rock in Middle Kura depression, although absence of oil biomarker and pyrolysis data for Mesozoic deposits in Middle Kura depression. Considering all of this statements researchers suggest Eocene and Cretaceous (most probably Lower Cretaceous) deposits as a source rock in the Middle Kura depression [5].

## CONCLUSION

Biomarker analyzes of Naftalan oils give us some new information about the source rock of the oils. Thus, the ratio of diasteranes to normal steranes allows us to put forward the idea that the source rock of the oils consists of a clay complex. Also, the presence of enough oleanane biomarkers (5-7% RH) proves that the oil generated from Paleogene – Lower Miocene sratigraphic units. This result indicates that Cretaceous sediments, consisting of volcanic-sedimentary rocks in Middle Kura basin, do not contribute to the formation of Naftalan oil.

Although the Maikop deposits are the main stratigraphic unit in the area of the Middle Kura Depression, it is already known from pyrolytic studies that Maikop has a low degree of maturity (Req= 0.65%). This means that Naftalan oil was not generated from the Maikop source rocks. We believe that the Eocene deposits are the main source of Naftalan oil since they are composed predominantly of clay rocks in the Middle Kura basin and have a higher degree of maturity (Req = 0.70-0.73%) than Maikop.

All these indications allow us to say that Naftalan oil was generated in Eocene formation then migrated and accumlated in Maikop sediments.

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## NAFTALAN YATAĞININ MÜALİCƏVİ NEFTİNİN ANA SÜXURU HAQQINDA

**S.Q. Zeynalov**

Naftalan yatağı neftləri müalicəvi xüsusiyyətləri ilə yanaşı, həm də burada mövcud olan neftlərin tərkibinin müxtəlifliyinə görə unikal təbii obyektdir. Yataqda müxtəlif növ neftlər məkana görə paylanmışdır, belə ki müalicəvi neft 500-600 m dərinlik intervalında Maykop lay dəstəsinin yuxarı horizontları ilə əlaqəlidir, bu layın aşağı horizontları isə yanacaq nefti ilə doymuşdur. Naftalan müalicəvi neftinin ana süxuru haqqında çoxlu fikirlər olsa da, bu məsələ tədqiqatçılar arasında açıq olaraq qalır. Bu tədqiqat işində biz Naftalan neftinin biomarker analizi (18α (H) olean biomarker və diasteranların müntəzəm steranlara nisbəti) və Orta Kür çökəkliyi ərazisində Eosen və Maykop süxur nümunələrinin yetkinlik göstəricilərinə əsasən tədqiq olunan neftin Eosen çöküntülərində generasiya etdiyini irəli sürürük.

**Açar sözlər:** *Naftalan nefti,Maykop çöküntüləri, biomarker, oleanan, yetkinlik.*

## О МАТЕРИНСКАЯ ПОРОДЕ ЦЕЛЕБНОЙ НЕФТИ НАФТАЛАНСКОГО МЕСТОРОЖДЕНИЯ

**С.Г. Зейналов**

Нафталанское месторождение является уникальным природным объектом не только в связи с широко известными лечебными свойствами нефтей, но и из-за пестроты состава, имеющихся здесь нефтей. Вместе с тем разнотипные нефти на этом месторождении пространственно разобщены, а именно, лечебные нефти строго приурочены к верхним горизонтам майкопской свиты в интервале глубин 500-600м, тогда как топливной нефтью насыщены нижние горизонты этой свиты. Хотя существует множество представлений о нефтематеринской породе нафталиновой лечебной нефти, этот вопрос остается открытым среди исследователей. В данном исследовании мы предполагаем, что нефтематеринская порода Нафталанской нефти образовалась из эоценовых отложений на основании биомаркерного анализа (олеананового биомаркера 18α(H) и соотношения диастеранов к регулярным стеранам) исследуемой нефти и показателей зрелости образцы Эоценовых и Майкопских пород Средне-Курской впадины.

**Ключевые слова:** *Нафталанская нефть, Майкопские отложении, биомаркер, олеанан, зрелость*