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Carbon Isotopic Composition of the Hydrocarbon Fluids of the South Caspian Megadepression

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Abstract—Carbon isotopic composition was studied in oils and hydrocarbon gases from different oil and gas fields and reservoirs hosted in the Upper Cretaceous to Upper Pliocene sequences of the South Caspian mega-depression. It was established that the carbon isotopic composition becomes gradually heavier in oils and lighter in hydrocarbon gases of reservoirs in accordance with decreasing age of the host sediments. Based on these revealed trends, the Pliocene reservoirs contain mixed oils generated by Paleogene–Lower Miocene and Diatomaceous (Middle–Upper Miocene) deposits, as well as oil produced within one stratigraphic complex. Using isotope tracers, the contributions of the Paleogene–Lower Miocene and Diatomaceous oils in the Pliocene reservoirs were estimated. The central part of the studied region is promising for the discovery of future hydrocarbon accumulations.

INTRODUCTION

The oil pools in the South Caspian megadepression (SCMD) are confined to the Upper Cretaceous to Upper Pliocene–Quaternary sedimentary rocks with an extremely large total thickness. Therefore, it is very difficult to estimate the contribution of each oil-generating complex in the hydrocarbon accumulations within the main oil-bearing horizon, the Productive Sequence (PS) of the Middle Pliocene. Some investigators believe that oil in the PS is primary, i.e., generated from organic matter of the PS itself (probably in its lower part), and then migrated laterally, vertically, or both laterally and vertically to the accumulation site from its source area located in the deeply subsided parts of the SCMD. Other investigators suggest that the oil originated from the lower Paleogene–Miocene and older deposits and migrated into the PS reservoirs along faults and fis-sures.

This and some other problems can be solved with complex investigations, including geochemical study of the oils, gases, and organic matter (OM) of the rocks. The previous chemical, gas chromatographic, and IR spectroscopic investigations of Azerbaijanian oil revealed some geochemical features of the oils and organic matter within the study area. However, these methods are not very capable of revealing genetic features of the OM, the paleoecology, and the facies–geochemical conditions of formation of the oil-generating sequences. We attempted to solve this question by studying variations in stable carbon isotopic composition and biomarkers in the oil and OM that reflect fluctuations in sedimentation and paleoclimatic conditions, the genetic type of the primary OM, the extent of oil maturation, etc. Our data on the carbon isotopic composition and biomarkers of the oils from practically all Azerbaijanian pools, together with previous geochemical data, allowed us to consider this problem more comprehensively and obtain results, which will be reported in a series of publications.

SAMPLES

The carbon isotopic compositions of the oils and their alkane and aromatic hydrocarbon fractions were studied in 152 samples (boreholes) from 38 deposits of the Apsheron, Evlakh–Agdzhabedin, Shemakha–Gobustan, and Nizhnaya Kura oil and gas fields of the Baku and Apsheron archipelagoes and the Kura–Gaby-ry watershed. The sampled reservoirs range in age from Upper Cretaceous to Upper Apsheronian (67 samples of crude oil and 85 samples of separate alkane and aromatic hydrocarbon fractions). The measured isotope ratios for the oil from all Upper Cretaceous–Upper Pliocene pools, from pools of a certain age, and each oil and gas field are plotted in the diagrams.

Some of the data on the carbon isotopic composition (CIC) of methane from gases of mud volcanoes and oil and gas pools were compiled from previous publications [8, 9].

RESULTS

The δ13C values in the studied samples of the SCMD range from −28.00 to −24.34‰ for oil and from −29.1 to −24.9‰ for its alkane fraction. The histograms demonstrate a distinctly bimodal distribution of the carbon isotope ratios for the alkane fraction and a polymodal distribution for the total oil content (Figs. 1a, 1b).
Fig. 1. Distribution of the carbon isotopic composition of oil and their alkane fractions in the Southern Caspian megadepression. (a, b) Oil from the Upper Cretaceous, Eocene, Maikopian, Diatomaceous, and Pliocene reservoirs: (a) all oil samples, (b) alkane fraction; (c, d) oil from the Upper Cretaceous, Eocene, Maikopian, and Chokrakian reservoirs: (c) bulk oil samples, (d) alkane fractions; (e) bulk oil samples from the Diatomaceous reservoirs; (f, g) oil from the Pliocene reservoirs: (f) bulk oil samples, (g) alkane fractions; (h) alkane fractions of the oils from the Pliocene reservoirs of the Baku and Apsheron archipelagoes; (i) alkane fractions of oils from the Pliocene reservoir of the Nizhnyaya Kura oil and gas field; (j) alkane fractions of oils from the Pliocene reservoir of the Apsheron Peninsula.

Based on these values, the SCMD oils can be divided into two groups: (1) isotopically light oils with $\delta^{13}C$ from $-28.0$ to $-27.0\%$ for bulk oil samples and from $-29.1$ to $-27.0\%$ for alkane fractions and (2) isotopically heavy oils with $\delta^{13}C$ from $-26.5$ to $-24.0\%$ for bulk oil samples and from $-26.5$ to $-24.5\%$ for alkane fractions. This confirms previous conclusions [1]. The SCMD mainly contains oil with heavy carbon (57.64–68.66%).
of the analyzed samples), whereas oil with light carbon accounts for 31.35–42.35%. The isotope ratios distinctly show regular variations along the stratigraphic section (Figs. 2a, 2b, 3). For example, the oil from the Upper Cretaceous reservoirs has the lowest δ¹³C values (−28.15; −28.0‰) (hereafter, the former value corresponds to δ¹³C of the alkane fraction and the latter value corresponds to that of the bulk oil samples), while the oil from the Eocene reservoir has δ¹³C values of −28.32 and −27.86‰. The oil from the Maikopian reservoir is characterized by δ¹³C values of −28.05 and −27.64‰, and the oil from the Chokrakian reservoir has δ¹³C values of −27.95 and −27.50‰. The δ¹³C values in the oil from the Diatomaceous Formation strongly increase (−26.45 and −26.13‰). The oil with the highest δ¹³C values are confined to the Middle Upper Pliocene reservoirs (−26.35 and −25.75‰). The intervals of δ¹³C values increase in the same direction. The isotopically light oils from the Upper Cretaceous, Eocene, Maikopian, and Chokrakian horizons range from −29.1 and −28.0 to −27.8 and −27.2‰ with differences of 0.1 and 0.5‰, whereas oil from the Diatomaceous reservoir vary from −27.5 and −27.79‰ to −25.4 and −25.19‰ with differences of 2.1 and 2.3‰. The oil from the Pliocene reservoirs show the greatest variations in carbon isotopic compositions, ranging from −27.70 and −27.67‰ to −24.80 and −24.38‰ with differences of 2.90 and 3.29‰. The histograms of the δ¹³C distribution for bulk oil samples and their alkane fractions clearly demonstrate the proportions of isotopically different oils in the Diatomaceous and Pliocene reservoirs. It is seen that oil from the Diatomaceous reservoir of the Apsheron oil and gas field (OGF) contains 40% isotopically light oils (−27.49 and −27.01‰) and 40% isotopically heavy oils (−25.67 and −25.19‰) (Fig. 1c).

Based on δ¹³C in the alkane fraction, the Pliocene reservoirs of the Apsheron, Shemakha–Gobustan, and Nizhnyaya Kura OGF, as well as of the Baku and Apsheron archipelagoes, contain 22.6% isotopically light oil
The carbon isotopic composition of methane from the atmosphere at that time and to the global decrease in CO2 content in the atmosphere at that time and to the

Fig. 3. Variations in carbon isotopic composition in the alkane and aromatic hydrocarbon fraction of oil from the South Caspian megadepression.

(a) Oils from reservoirs: (1) Pliocene, (2) Diatomaceous, (3) Maikopian and Chokrakian, (4) Eocene, (5) Upper Cretaceous complexes; (b) oils from reservoirs of the Pliocene complex of the (1) Apsheron Peninsula, (2) Apsheron Archipelago, (3) Baku Archipelago; (4) southeastern Gobustan; (5) Nizhnyaya Kura depression.

(‡) Continental OM

Marine OM

Continental OM

Marine OM

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(from −28.0 to −27.0‰) and 9.68% isotopically heavy oil (from −25.5 to −24.5‰). The oils with intermediate δ13C values (from −27.0 to −25.5‰) account for 67.7% (Fig. 1f). The same distribution is typical for the δ13C values in the bulk oil samples (Fig. 1g).

All oils of the SCMD are high in n-C15, n-C17, and n-C19 and low in n-C27, n-C29, n-C31 normal alkanes. They also have a low pristane/phytane ratio and sulfur content (up to 1.4 and 0.4%, respectively), which is typical of marine deltaic oil [2–5]. Their marine origin is also illustrated in the δ13C_{alk}–δ13C_{arom} diagram, where data points are plotted in the field of marine organic matter and form an ascending trend along the line distinguishing the continental and marine OM (Fig. 3a). This indicates an epigenetic origin of the oil with respect to the Pliocene reservoir (Fig. 3b), because, according to paleogeographic reconstructions, Pliocene sediments were formed from the terrigenous elastic material and continental organics in a closed brackish basin. This should affect the carbon isotopic composition of the generated oil. This is also supported by numerous data on biomarker parameters of the oils from the Pliocene reservoirs of all oil and gas fields.

The carbon isotopic composition of methane from the oil and gas pools and mud volcanoes ranges between −35 and −54‰ and between −35 and −60‰, respectively. The carbon isotope composition of methane from more than 70% of the mud volcano samples ranges from −35 to −45‰, while the composition in more than 80% of samples from the oil and gas pools ranges from −40 to −50‰. On average, the CIC of methane from mud volcanoes is 5‰ heavier. The gases of some mud volcanoes (Durovdag, Gainardzha, and others) and oil and gas pools contain methane with anomalously light carbon (from −50 to −60‰).

The carbon isotopic composition of ethane and pro-pane in the mud volcanoes ranges from −23.3 to −29.6‰ and from −25.8 to −25.9‰, respectively.

The δ13C of methane increases with increasing depth. This is consistent with experimental data on variations of the carbon isotopic composition with the degree of catagenetic transformation of organic matter [10–12]. Similar CIC variations are observed with stratigraphic depth. For example, the carbon isotopic composition of methane from the PS ranges from −43.8 to −49.3‰ (Nizhnyaya Kura depression), that of the Maikopian deposits ranges from −41.1 to −41.4‰, and that of the Upper Cretaceous deposits ranges from −34.3 to −38.6‰ (Ciscaspian–Ghubin area).

DISCUSSION

The isotopic and geochemical study of the oil and gas bearing provinces worldwide indicates that the carbon isotopic composition is highest in oil generated from Middle–Upper Miocene sediments. It is suggested that this is related to the global decrease in CO2 content in the atmosphere at that time and to the
respective decrease in CO₂ dissolved in marine water, which resulted in a less extensive extraction of C¹² by plankton during photosynthesis.

These facts explain the heavier average carbon isotopic composition of oil from the Diatomaceous and Pliocene reservoirs of the SCMD. Hence, the localization of isotopically light and isotopically heavy oil with δ¹³C intervals from 2.10–3.29‰ in the Diatomaceous–Pliocene reservoirs indicates at least two source rocks of various ages [6, 2]: pre-Diatomaceous (Cretaceous–Maikopian) and Diatomaceous (Karanaganian, Konkian, Sarmatian, Meotian).

There is a wide variation in δ¹³C values of the alkane fractions of oil from Pliocene reservoirs. Based on average values of this parameter, the oil and gas fields can be arranged into the following sequence: Nizhnyaya Kura (−26.8‰) Apsheron (−26.29‰) Shemakha–Gobustan (−26.1‰) Baku Archipelago (−26.04‰) Apsheron Archipelago (−25.87‰) (Fig. 2c). It is seen that oil from Pliocene reservoirs of the subaqueous part of the SCMD have a somewhat heavier carbon isotopic composition. This difference is more distinctly expressed in the δ¹³C value intervals. For example, the lowest and highest δ¹³C values of oil from the Nizhnyaya Kura field and the Apsheron Peninsula are −27.7 to −25.4‰ and −27.6 to −24.8‰ with differences of 2.3 and 2.8‰, respectively. Those of the Apsheron and Baku archipelagoes are −26.3 to −25.4‰ and −26.5 to −25.0‰ with differences of 0.9 and 1.9‰, respectively. This indicates that oil from Pliocene marine reservoirs is more uniform than that of reservoirs of the Nizhnyaya Kura field and the Apsheron Peninsula. The highest δ¹³C values of the alkane fraction of oil from the Diatomaceous and Pliocene reservoirs equal −25.4 and −24.8‰, respectively, while the highest δ¹³C values for the Upper Cretaceous–lower Middle Miocene (Chokrakian) oil are −27.5‰. Hence, the range from −25.1 ± 0.3‰ may be considered an indicator of the oil generated by the Diatomaceous complex. Oils with δ¹³C of the alkane fractions from −27.5‰ to −25.1 ± 0.3‰ represent a mixture of oils formed in the pre-Diatomaceous and Diatomaceous deposits. The δ¹³C values should vary depending on the proportions of these oils. This makes it possible to characterize and compare the homogeneity of the oil from the Pliocene reservoirs of the SCMD, as well as to quantitatively estimate the contribution of the Diatomaceous and underlying sediments in the generation of the oil and gas pools of the Pliocene complex and calculate the inferred hydrocarbon reserves.

The histograms of oil distribution with respect to the δ¹³C values of the alkane fractions for each oil and gas field illustrate the proportions of isotopically different oil (Figs. 1h, 1i, 1j). These plots indicate that the marine pools consist both of a mixture of the Paleogene–Lower Miocene–Diatomaceous oils and of the Diatomaceous oil itself. The mixed oil from the Apsheron Peninsula are lower in abundance due to an increase in mainly Paleogene–Lower Miocene oil at nearly the same amount of the oil with a Diatomaceous isotopic signature. The marine parts of the megadepression and Apsheron Peninsula show similar abundances (47.36 and 42.85%, respectively) of the modal values from −26.5 to −26.0‰. The Pliocene reservoir of the Nizhnyaya Kura OGF differs from the above-mentioned field in the absence of Diatomaceous oils and the higher proportion of Paleogene–Lower Miocene oils. This results in a different distribution of isotopic compositions: 30.77% of the oils range from −27.5 to −27.0‰ and 26.92% of the oils range from −27.0 to −26.5‰ (57.69% in total). Thus, the oils from the Pliocene reservoirs and the Nizhnyaya Kura OGF have a significantly higher percentage of the Paleogene–Lower Miocene oil.

The determination of δ¹³C values that are indicative of the pre-Diatomaceous and Diatomaceous oils allows us to quantitatively estimate the contribution of certain oil-generating complexes to the hydrocarbon accumulation within the Pliocene reservoirs of the SCMD as a whole, as well as in the individual pools.

The calculations based on the isotopic signatures of the oils show that the Apsheron Pliocene reservoir has a similar contribution from both the Paleogene–Lower Miocene and Diatomaceous oil and gas-generating complexes in the formation of oil deposits. This is also typical of the Pliocene reservoirs of the southeastern Gobustan and Baku Archipelagoes, although the Diatomaceous complex is slightly more dominant here. About 75% of the oil of the Nizhnyaya Kura OGF were formed in the Paleogene–Lower Miocene deposits, while 65% of the oil pools of the Apsheron Peninsula were derived from the Diatomaceous Formation.

The oil in the southeastern Gobustan and Baku Archipelagoes are similar in carbon isotopic compositions and contribution of various formations, thus confirming the previous tectonically based conclusion that the northern part of the Baku Archipelago represents a marine continuation of the Dzheirankechmes Depression of southeastern Gobustan. Seaward, the δ¹³C value of the oil increases owing to the contribution of younger deposits in the “oil window.” This is related to the fact that the young Pliocene–Quaternary deposits increase significantly in thickness seaward, while the underlying older deposits plunge to considerable depths.

A comparison of the carbon isotopic compositions of methane from mud volcanoes and pools from reservoirs of different ages shows that mud volcanoes of the Shemakha–Gobustan field with a heavier carbon isotopic composition of methane (from −36.3 to −44.0‰) are related to the older complexes (mainly Paleogene–Mesozoic). From the southern branches of the Great Caucasus toward the regional plunge of the deposits beneath the South Caspian Sea, the hydrocarbon gas
source is displaced to the younger (Neogene) sediments, which is confirmed by carbon isotopic data.

This conclusion may be verified by calculating the dependence between the carbon isotopic composition of gases and their catagenetic maturation (Ro) [12]. Based on this dependence and data on vitrinite reflectance (Ro), we may estimate the hypsometric depth of the studied gas source feeding a certain mud volcano. Data on the deep structure of the region make it possible to estimate the stratigraphic position of this source.

In order to determine the hypsometric and stratigraphic depths of the gas sources of mud volcanoes with this method, we used the dependence between the carbon isotopic composition of ethane and Ro [12]:

\[
\delta^{13}C_{C_2H_6} = 22.6 \log Ro - 32.2
\]

The relation between CIC of methane and Ro was not used in the calculations, because of possible mixing of the isotopes of thermocatalytic and biochemical methane.

Based on the calculations, the catagenetic maturation of ethane from the Charagan, Melik-Chobanly, Kyrylykh, Shikhzagirli, Perekyushkyul', Shorbulaq, Airantekyan, and Bakhar mud volcanoes ranges between 1.30–1.79% (Ro).

Using available Ro values for the South Caspian basin to a depth of 5300 m, we extrapolated the data for deep-seated horizons. Thus, we suggest that the ethane source of the mud volcanoes is located at a depth of 6.5–8.0 km.

The stratigraphic position of the ethane source for the Melik-Chobanly and Bakhar mud volcanoes was determined. The Melik-Chobanly mud volcano located at the southern branches of the Great Caucasus is confined to the Melik-Chobanly fold, whose arch contains the Paleogene–Miocene sediments. The Bakhar mud volcano is located at a considerable distance southeast of the Melik-Chobanly volcano, at the shore of the Caspian Sea. It is confined to the brachyanticline composed of younger Pliocene sediments.

Based on our calculations, the main gas source feeding the mud volcanoes changes from Mesozoic to Paleogene–Neogene rocks with the gradual plunging of the beds to the central part of the South Caspian mega-depression.

Calculations indicate that oil from the Pliocene reservoirs of the central part of the SCMD have equal proportions of Paleogene–Lower Miocene and Diatomaceous oils. The Oligocene–Lower Miocene sediments in this part of the megadepression are about two times thicker than those of the Diatomaceous Formation, but have similar average contents of organic carbon (0.68 and 0.63%, respectively) [7]. This indicates that Pliocene reservoirs contain no more than one-half of the realized hydrocarbon potential of the Diatomaceous Complex. Hence, at least 50% of the hydrocarbon reserves generated by Paleogene–Lower Miocene deposits remain undiscovered.

**CONCLUSIONS**

1. A statistically significant number of isotopic determinations reveal the spatial and temporal trends of isotopic and geochemical variations of the SCMD oils.

2. The existence of two major oil groups (isotopically light and isotopically heavy) is confirmed. It was established that isotopically light oils were formed by the Paleogene–Lower Miocene oil-generating complexes, while isotopically heavy oils were derived mainly from the Diatomaceous Formation. A contribution from the Productive Sequence, mainly its lower portion, in oil generation is also possible. However, this contribution is insignificant, because of the low oil-generating potential of this sequence. This assumption requires additional investigations and source rock–oil correlation.

3. The oil of the Pliocene reservoir represents a mixture of oils that were derived from different complexes playing different roles in each geological situation, both on the regional scale and within individual oil and gas fields.

4. The revealed trends made it possible to estimate the contribution of various oil-generating complexes to the formation of oil pools in various oil and gas fields.

5. The general lateral CIC variations in the carbon isotopic composition of methane in the mud volcanoes is consistent with those of the oil.

6. Unlike the oil, the carbon isotopic composition of methane becomes gradually heavier with increasing stratigraphic depth.

**REFERENCES**


5. Peters, K.E., Moldowan, J.M., Shoel, M., and Henghkins, W.B., Petroleum Isotopic and Biomarker Composition Related to Source Rock Organic Matter and Dep-


iskikh otlozhenii Azerbaidzhana* (Oil-Generating Potential of Meso–Cenozoic Sedimentary Rocks of Azer-
baijan), Baku: Elm, 1975.


12. Faber, E.Z., *Isotopengeochemich Gasformiger Kohlen-