Source potential of the Mesozoic-Cenozoic rocks in the South Caspian Basin and their role in forming the oil accumulations in the Lower Pliocene reservoirs

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Geochemical Characteristics of Organic Matter from Maikop Rocks of Eastern Azerbaijan

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Abstract—Based on investigation of more than 170 samples taken from natural outcrops of the Maikop Formation (Oligocene–Lower Miocene) in eastern Azerbaijan, the genetic hydrocarbon potential and the organic matter (OM) maturity of these rocks were estimated. In the study region, sedimentary rocks of this formation were deposited under reductive or weakly oxidative conditions. Possessing a relatively high (1.9%, on the average) content of organic matter of a mixed (continental–marine) OM, these rocks are able to generate both liquid and gaseous hydrocarbons under favorable conditions. Contributions of both the continental and marine components to the total organic carbon (TOC) varied in time and space. The upper and lower subformations of the Maikop Formation differ in the qualitative and quantitative compositions of OM. Oligocene rocks have a relatively lower OM content and are characterized by better oil-generating properties, as compared to lower Miocene rocks.

The South Caspian Depression is filled with sedimentary rocks widely ranging in age from the mid-Jurassic to Quaternary. Depression zones in Azerbaijan incorporate a thick sequence of Oligocene–Lower Miocene rocks known as the Maikop Formation that is predominantly composed of clayey and sandy–clayey lithofacies. The Maikop Formation is divided into two subformations. The lower subformation corresponds to the Oligocene section, while the upper one embraces the lowermost Miocene. On the land, within eastern Azerbaijan, these deposits vary in thickness from 200 to 1200 m (Salaev, 1961). The thickness of the Maikop Formation increases from the southeastern slope of the Greater Caucasus to the deep-water sector of the southern Caspian Sea, where the seismic sounding revealed that the thickness is 2500 m or more. A marine transgression, which reached the maximum during the accumulation of Maikopian sediments, led to the formation of reductive or strongly reductive geochemical conditions favorable for the accumulation and transformation of initial OM. This is suggested by a wide distribution of pyrite and siderite in this rock sequence (Ali-Zade *et al.*, 1975). According to previous investigations, the TOC content in these rocks reaches 3–4%, while the chloroform bitumenoid content is 0.1–0.3%.

In the principal oil- and gas-bearing districts of eastern Azerbaijan, the Maikop Formation occurs at depths technically inaccessible for drilling. However, there are numerous natural outcrops of Maikop rocks on the southeastern slope of the Greater Caucasus and within the Talysh Mountains (Fig. 1), which were objects for geochemical investigations by numerous researchers during several decades (Ali-Zade *et al.*, 1975, 1985; Guliyev *et al.*, 1999; Korchagina *et al.*, 1988; Zhabrev and Mekhtiev, 1959).

This study is based on data obtained using modern laboratory methods of investigation of the OM composition, oil- and gas-generating properties, and maturity.

METHODS

The geochemical characteristics of OM is based on the investigation of a collection of clayey rocks sampled from 14 geological sections with both subformations of the Maikop Formation. Thus, all the known Maikop reference sections were studied. A total of 174 samples were studied to determine the TOC content. Samples with the TOC content of 0.5% or more were subjected to pyrolysis (148 analyses). Depending on the thickness and lithologic composition, the number of samples taken from a certain outcrop varied from 2 to 56.

The hydrocarbon-generating potential of the rocks was based on pyrolysis data obtained using the Oil Show Analyzer (OSA). In contrast to the Rock-Eval pyrolysis, this method lacks the block registering the S_3 curve and makes it possible to measure the peak S_0 (hydrocarbons C_1–C_7) and the ($S_1 + S_2$) sum. The TOC value is determined by a built-in microprocessor through the summation of parameters S_0, S_1, S_2, and S_4. The parameter S_4 denotes a quantity of residual (coalified) OM, which is measured by means of its oxidation to CO_2 at 600°C and subsequent volatilization in oxygen or air flux.

Indexes TAI and SCI were used as indicators of the thermal maturity of kerogen. The TAI index is a numerical measure of kerogen color change depending on the geothermal influence degree and varies from 1 to 5. This index allows one to determine three grades of OM maturity: immature (<2.2), mature (2.2–3.5), and over-

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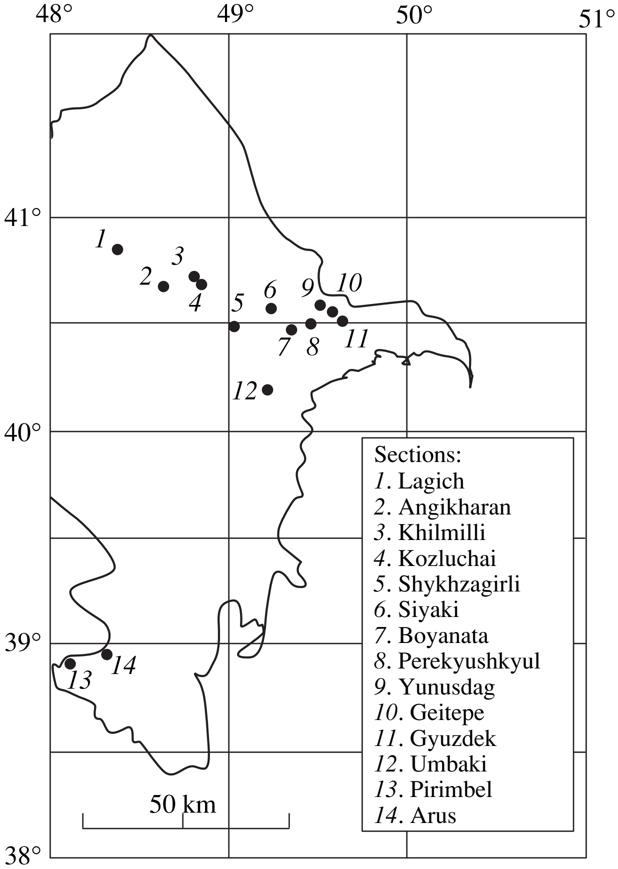

Fig. 1. Schematic map showing location of the Maikop Formation sections (natural outcrops) within eastern Azerbaijan.

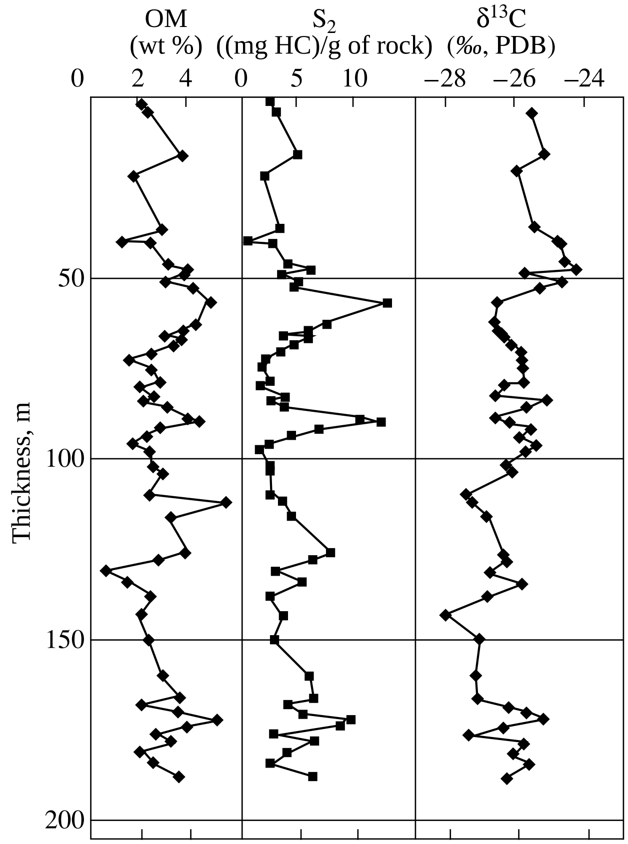

Fig. 2. Variations in the TOC, S_2 yield of pyrolysis, and carbon isotopic composition of kerogen along the upper Maikop section near the Khilmilli Settlement (location of the site is shown in Fig. 1).

mature (>3.5). The SCI index reflects spore color change provides a more detailed scale with the following grades of OM maturity: immature (<3.5), early mature (3.5–5.0), peak (5.0–7.0), late mature (7.0–9.0), and overmature (>9) (Miles, 1989).

Ratio of the isoprenoids pristane and phytane (Pr/Ph) is determined using gas chromatography data and is applied to reconstruction of sedimentation environments. High values of this index (>1) are indicative of more oxidative conditions, while low values (<1) suggest more reductive conditions.

RESULTS

In spite of significant variations in the TOC and S_2 contents along the section (Fig. 2), Maikop rocks possess the most favorable characteristics with respect to the OM quantity and quality, as compared to other stratigraphic complexes. The figure exhibits an upsection increasing trend of the $\delta^{13}C$ value in kerogen with local fluctuations. It should be noted that the Maikop Formation is characterized by substantial variations in the qualitative and quantitative parameters of the OM both in the regional scale and within individual sections, indicating long- and short-term variations in sedimentation conditions.

The wide range of Pr/Ph values (0.2–2.9) suggests wide variations in the sedimentation conditions within the Maikop basin with a predominance of reductive geochemical environment ($Pr/Ph_{aver} = 1.1$; $Pr/Ph_{med} = 0.9$).

Judging from TAI values (1–2), the Maikop rocks within the studied sites have never achieved temperature conditions of oil generation during the geological history. The SCI values (1.5–3.0) are also suggestive of a weak thermal transformation of the OM.

This conclusion is also confirmed by the vitrinite reflectance values (R_0) and pyrolysis parameters (Table 1), which can be used as reference characteristics for coeval (Maikop, in this case) rocks that occur in deep sections of the depression. Sedimentary rocks of the lower and upper subformation are characterized by certain differences. Rocks of the upper subformation are have a higher OM content, while the lower subformation contains OM varieties that are more favorable for the generation of liquid hydrocarbons (HC). It should be noted that the geochemical characteristics could be subjected to an insignificant negative influence of exogenous factors acting on exposed rocks.

Table 1. Variations and average values of the TOC content and pyrolysis parameters for different subformations of the Maikop Formation

Parameter	Number of samples	Minimum	Average	Maximum	Standard deviation
Maikop (overall)					
TOC	174	0.07	1.90	15.10	1.76
HI	148	11	142	6.13	97
S_1	148	0.08	0.86	6.51	0.86
S_2	148	0.02	3.89	74.04	8.42
T_{max}	148	400	427	562	20
R_0	52	0.21	0.42	1.11	0.18
Lower Maikop (Oligocene)					
TOC	84	0.07	1.76	15.10	2.19
HI	64	11	169	613	113
S_1	64	0.10	0.89	6.51	1.06
S_2	64	0.02	5.29	74.04	12.38
T_{max}	64	406	432	562	23
R_0	29	0.21	0.45	1.11	0.22
Upper Maikop (Lower Miocene)					
TOC	90	0.17	203	5.47	1.23
HI	84	26	121	457	77
S_1	84	0.08	0.83	3.19	0.67
S_2	84	0.12	2.82	12.90	2.59
T_{max}	84	400	424	561	18
R_0	23	0.25	0.37	0.64	0.09

Table 2. Characteristics of the OM chemically extracted from rocks of different subformations of the Maikop Formation

Subformation	Number of analyses	HC/Extract (%)	Saturated/Aromatic
Upper	23	2.19–46.28* / 11.96	0.29–13.95 / 5.17
Lower	17	6.79–48.22 / 19.41	0.36–16.80 / 4.53

*Variation limits are given in the numerator; average values, in the denominator.

To characterize OM in rocks from the different Maikop subformations, we used relationships between the pyrolysis parameters and graphic presentation by annotated diagrams. The classification of the rock-hosted OM, based on the relationship between the S_2 peak temperature (T_{max}) and hydrogen index (HI), suggests a mixed, terrigenous–marine origin (Fig. 3a). The same conclusion may be drawn based on the TOC versus S_2 diagram (Fig. 3b). Note that most of the points on both diagrams fall within the type III OM field. The relationship between T_{max} and reactive carbon index (RCI), which reflects the total HC yield of pyrolysis (in %) normalized to TOC, shows that the OM distributed in Maikop rocks is able to generate HC of various (gaseous and liquid) phase state (Fig. 4). On the whole, the HC fraction yielded by the immature OM pyrolysis ($T_{max} < 440°C$) does not exceed 40% of the initial TOC content. The bulk of the studied samples demonstrates a trend of HI increase with the TOC content (Fig. 5), although the correlation is not significant. According to the classification by Tissot and Welte (1984) based on values of the HC-generating potential, the lower and upper subformations can be assigned to the categories of source rocks with good and moderate HC-generating potentials, respectively.

With respect to the quantity of extract released from OM, rocks from the different subformations are characterized by similar values of about 70 mg/g TOC (Fig. 6). The saturated HC/aromatic HC ratio varies over a wide range, suggesting the presence of polygenous OM. At the same time, for both the subformations, average values of saturated HC exceed those of aromatic ones, which is typical of the predominantly sapropelic OM. The HC fraction in the total extract of Maikop rocks (Table 2) is higher for the lower subformation relative to the upper one. This fact suggests that the OM in Oligocene rocks is characterized by a higher oil-generating capacity and geochemical conditions favorable for its transformation existed in the Oligocene. This is also confirmed by the pyrolysis data (Table 1, HI values).

It is of methodological interest to compare the HC volume extracted from the solid matrix of certain rock specimens by pyrolysis and chemical extraction. We calculated the Spearman coefficient to estimate correlation between the obtained values. In contrast to the ordinary correlation coefficient, the Spearman coefficient does not require an obedience of the simultaneous distribution of the studied variables to the normal law. Statistical verification of the rank coefficient significance demonstrated that relationships between the pyrolysis and extraction parameters, graphically represented in Fig. 7, lack any significant correlation (significance level = 0.05; $n = 39$). The amount of HC in pyrolysis products is several times higher than the extract variety. This is explained by the fact that the pyrolysis products incorporate nonhydrocarbon compounds of carbon as well (Peters, 1986). In addition, relatively light hydrocarbons (up to C_{15}) are lost as a result of volatilization during the OM extraction.

According to results of basin modeling (Tagiyev *et al.*, 1997), Maikop rocks in the Baku Archipelago, which is situated to the southeast of their exposure areas, occur at depths corresponding to the zone of

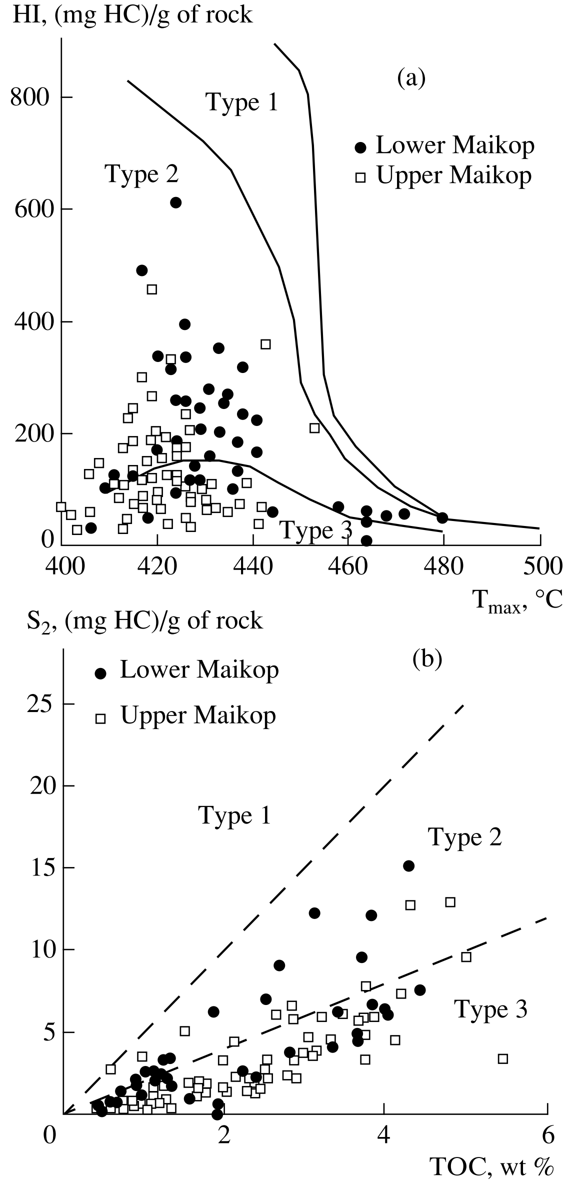

Fig. 3. Annotated diagrams showing the classification of OM in different subformations of the Maikop Formations (based on the relationship between various pyrolysis indexes): (a) T_{max} vs. HI; (b) TOC vs. S_2.

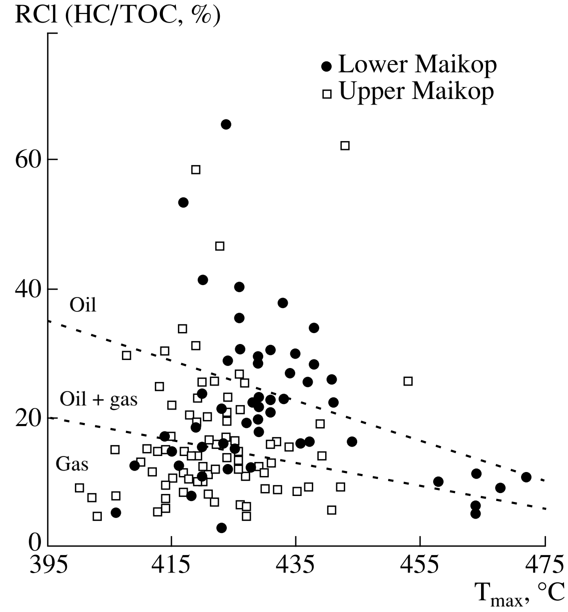

Fig. 4. T_{max} vs. RCI plot showing the phase composition of the generated HC. RCI = $(S_0 + S_1 + S_2) \times 10$/TOC expresses the total HC yield of pyrolysis (in %) relative to the TOC.

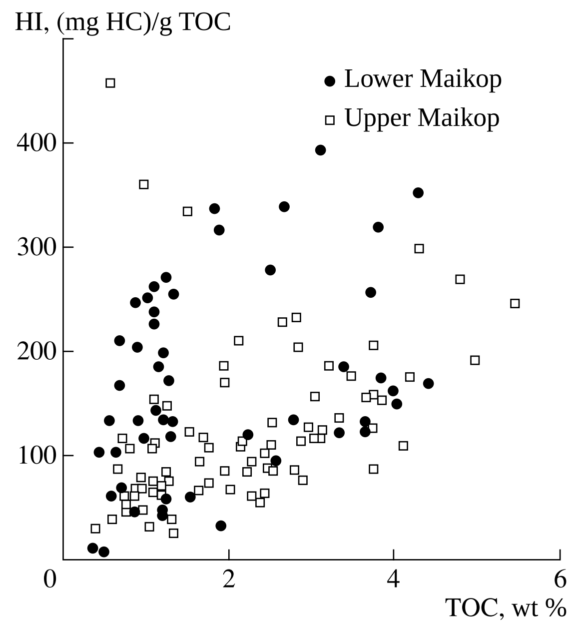

Fig. 5. TOC vs. HI in different subformations of the Maikop Formation.

intense oil and gas formation. Taking into account the predominantly clayey composition and, hence, a restricted reservoir capacity of the Maikop rocks, the bulk of HC generated within these rocks most likely migrated upward along the system of faults that are widespread in the sedimentary sequence of the basin. This supposition is confirmed by the high degree of correlation between isotopic signatures of oils in mid-Pliocene reservoirs and organic matter in Oligocene–Miocene rocks (Feyzullayev *et al.*, 2000).

The vertical distance between reservoirs in the productive sequence (Lower Pliocene), which accommodates the principal HC resources of the basin, and the interval of intense HC generation is 3–6 km. Such an HC migration distance can be explained by the predominance of vertical transportation over the lateral one. The lateral migration took place in mid-Pliocene rocks, at final stages of the oil pool formation. From this standpoint, the confinement of about 90% of oil accumulations to the 4-km-thick Lower Pliocene sequence seems to be logical. The rhythmic alternation of clayey and sandy units in the productive sequence and the

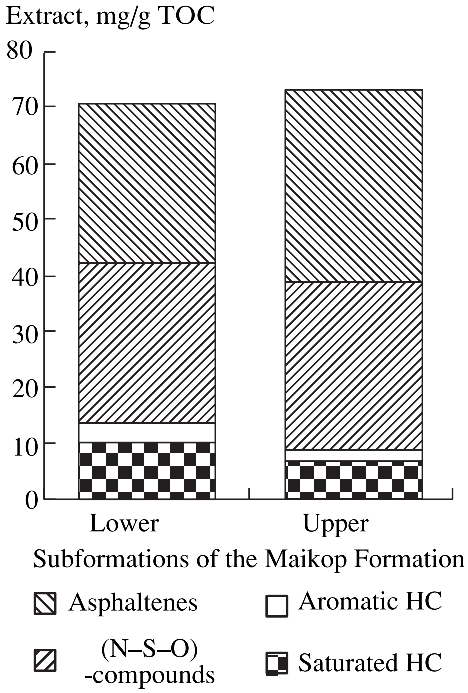

Fig. 6. Averaged distribution of saturated and aromatic HC, asphaltenes, and (N–S–O)-compounds in the extract of Maikop rocks.

presence of a regionally continuous cover in the uppermost Pliocene created favorable conditions for the HC accumulation.

Intense gas generation in the deepest sections of the basin (including Maikop rocks) is reflected in a wide distribution of mud volcanoes, which annually release (20–500) $\times$ 10^9 m^3 of gas (predominantly methane) to the atmosphere (Dadashev, 1963). Another indicator of the intense gas generation in deep horizons is elevated values of the gas factor for oil pools of the Baku Archipelago relative to those for oil- and gas-bearing districts with a thinner sedimentary cover. The Maikop rocks with high HC-generating potential are among the principal suppliers of both liquid and gaseous HC phases in the region. We believe that the great volumes of HC gases, which were formed in Maikop rocks, significantly foster the migration capacity of dissolved liquid HC.

Thus, the geochemical study of the OM from Maikop rocks of eastern Azerbaijan revealed their high HC-generating potential and their predominant role in the formation of HC pools in overlying rocks.

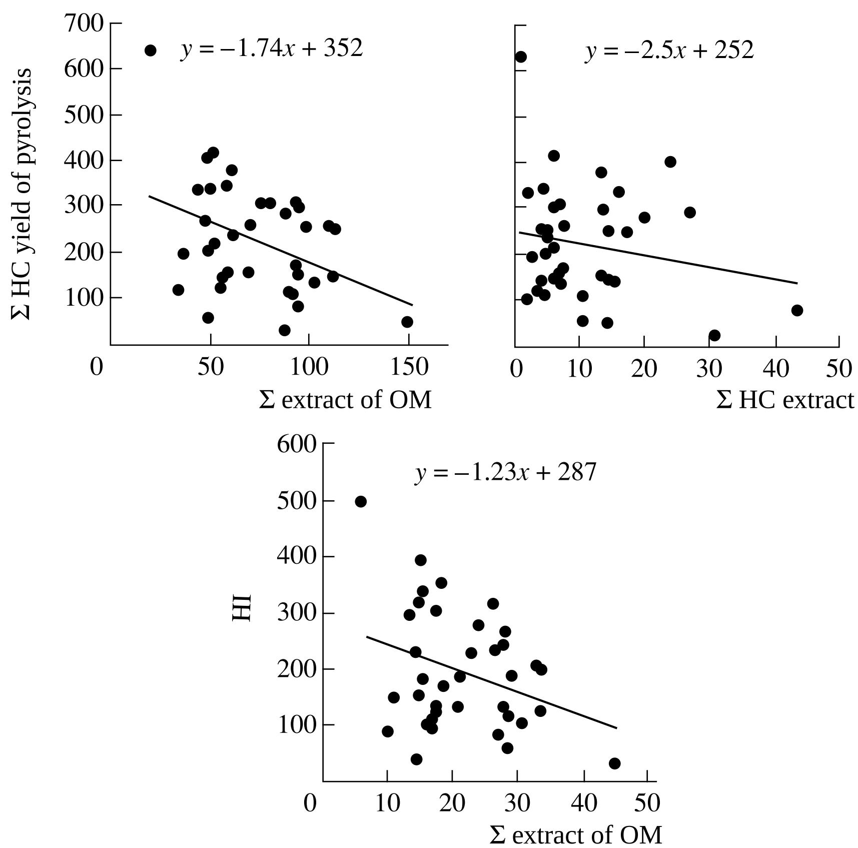

Fig. 7. Qualitative comparison between pyrolyzates and HC fractions of the OM extract from Maikop rocks. Σ HC yield of pyrolysis = S_1 + S_2; Σ HC extract = saturated + aromatic fractions of the extract; all the values are in mg/g TOC.

CONCLUSIONS

Results of the pyrolitical investigation of OM in rocks confirmed the concept of a high HC potential of Maikop rocks in eastern Azerbaijan. With respect to the HC-generating potential, lower and upper subformations of the Maikop Formation can be assigned to the categories of source rocks with good and moderate HC-generating potentials, respectively. During the Oligocene–Lower Miocene, reductive and weakly oxidative sedimentation conditions prevailed within the study region. Along with the marine sapropelic material, a significant continental fraction is present in the OM composition. The contribution of each of these components substantially varied during the accumulation of Maikop sediments. Upper and lower subformations of the Maikop Formation differ in the qualitative and quantitative OM composition. Oligocene rocks have relatively lower OM contents, but better oil-generating properties relative to lower Miocene rocks. Judging from the geochemical parameters R_0, TAI, SCI, and T_{max}, Maikop rocks in the study region were not subjected to geothermal impact that could facilitate the catagenetic transformation of OM. However, the Maikop rocks could realize the HC potential in the deepest segment (> 12 km, according to seismic data) of the South Caspian Depression. The formation of significant volumes of gas, in addition to oil, within the Maikop rocks is a favorable factor for an efficient expulsion of liquid HC from the oil-source rocks.

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