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In memory of Tamara Alekseevna Kiryukhina

The Oil and Gas Potential of the Kuma Rocks of the Bakhchisarai Region of Crimea

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Abstract—The oil and gas potential of the Kuma Formation of the Bakhchisarai region (southwestern Crimea) was substantiated on the basis of a lithological and micropaleontological study of the rocks of the section of the formation and geochemical (luminescent-bituminous, gas-liquid chromatographic, pyrolytic, and isotope) studies of the organic matter of the rocks. New regions for study that are favorable for the origination of the oil system in this formation were identified.

Keywords: Kuma Formation, source rock, organic matter, organic carbon isotopy

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INTRODUCTION

The Kuma Formation, or the layers with *Lyrolepis caucasica* Romer, were distinguished for the first time by Vassoevich in 1934 in the Khadyzhensk region of the northwestern Caucasus (Vassoevich, 1934; Vassoevich and Grossgeim, 1951). The Middle Eocene rocks of the formation of up to 60–80 m thick are abundant in the Crimea–Caucasus region and mostly include dark bituminous marbles and clays. In the western part of the Kuban–Black Sea area, the interlayer of sandstones of the Kuma Formation contain economic amounts of oil, which attracts definite interest. Thus, its characteristics and the interpretation of the accumulation conditions of the bituminous matter of the formation are still urgent. The Kuma rocks have been studied by Vassoevich and Grossgeim (1951), Beketov (1981), Neruchev et al. (1986), Gavrilov et al. (1997), Fadeeva (1979), Fadeeva et al. (2003), and Distanova (2007).

We studied the rocks of the formation in the southwest of the Crimean Peninsula, whose most complete section is located in the suburb of Bakhchisarai (Fig. 1). This section has already been described in the literature and the most detailed characteristic of its composition and biostratigraphic microfossil division are provided by Beniamovsky et al. (2003). The aim of our work was evaluation of the oil and gas potential of the rocks of the Kuma Formation in the territory of southwestern Crimea, Bakhchisarai region.

MATERIALS AND METHODS

The material was collected by the authors during the study of the section of the Kuma Formation in the Bakhchisarai region in 2012. Geochemical studies included the quantitative and qualitative analyses of the organic matter (OM) and identification of its genetic type, degree of maturity, and generation potential, as well as lithological and microfaunistic analyses.

Twenty-three thin sections were made and carbonate and terrigenous material contents, as well as the foraminifera complex, were determined in 17 samples. The samples of the foraminifera shells were washed following the standard methods for the micropaleontological study of carbonate rocks (Kopaevich, 1986; Alekseev et al., 2007).

The geochemical studies included the following analytical methods. *Luminescent–bituminous analysis* (LBA) determines the qualitative composition and approximate quantitative content of bitumens in the rock (Florovskaya, 1957). Bitumoides, whose content is a very informative geochemical parameter for esti-

Fig. 1. The general appearance of the studied gully with the outcrop of the Kuma and Belaya Glina formations.

mation of the oil and gas properties of rocks, were extracted by chloroform from the rock.

Pyrolytic studies via the Rock-Eval method allow simultaneous determination of the type and the degree of maturity of OM. The method is based on extraction of free hydrocarbons (HCs), which are desorbed from the surface of a solid body, and decomposition of OM as a result of cracking at different temperatures. The content of the released HCs is measured by the chromatographic method and registered in the forms of peaks. The first peak (a temperature of 300°C for 3 min) shows the content of free HCs in the rock (mg HC/g rock). Further heating of the charge (25–30°C/min) to 550°C results in the formation of the S2 peak, which indicates the level of HC of the oil series and asphaltene–resin constituent of OM or so-called remnant oil potential (mg HC/g rock). The maximum temperature T_{max} (°C), which is used for estimation of the degree of OM maturity, is measured in the apex of this peak. The peak (O-bearing components of kerogene) is recorded in the temperature range from 300 to 390°C and the peak (relict carbon) is registered at temperature up to 880°C.

The total content of organic carbon (C_{org}) (TOC) is the sum of the S4 peak and carbon from the S1 and S2 peaks taking the fact into account that 83% of their elemental composition consists of carbon. The direct determinations are the basis for calculation of the following indicators: the productivity index PI (PI = S1/(S1 + S2)), which reflects the degree of reworking of kerogene and the relative degree of catagenesis and oxygen OI (OI = S3/TOC × 100, mg CO_2/g TOC) and hydrogen HI (HI = S2/TOC × 100, mg HC/g TOC) indices, which characterize the type of kerogene on the basis of the modified Van-Krevelen diagram. The HI reflects the oil and/or gas source potential of kerogene (Tisso et al., 1981; Espitalie et al., 1985).

G*as–liquid chromatography* analyzes the individual composition and relative content of normal and isoprene acyclic alkanes (n- and i-alkanes, respectively). According to the values of these parameters, we can judge the maturity and genesis of OM and determine the redox conditions of diagenesis of sediments (Robert et al., 2004).

Isotope analysis is a reliable geochemical method for identification of the source of OM (Tisso et al., 1981) by the values of $\delta^{13}C$ (‰) of the aromatic and saturated bitumen fractions.

Geological Description of the Section

The studied section of the rocks of the Kuma Formation is located on the slope of Mt. Kazantash near the Bakhchisarai quarry. The section includes (from bottom to top) the Keresta (in the bottom of the quarry), Kuma (both in the upper part of the quarry and in the gully on the slope), and Belaya Glina (in the upper part of the gully, which covers the upper part of the mount) formations. The age of the Kuma Formation is Bartonian (Middle Eocene) (Beniamovsky et al., 2003). Forms of plankton and benthic foraminifers that were almost identical to those from (Beniamovsky et al., 2003), were found in our samples. The Kuma Formation lies concordantly on the Keresta Formation; however, several meters of rocks in the lower part of the Kuma Formation are covered by dense plants, thus their description was almost impossible.

The visible thickness of the 10-member section is 73 m (Fig. 2). In the lower part of the gully (members 1–3), the section is composed of the alternating strongly weathered and oxidized light yellow and light red clays with fine parallel and vague layering. The middle part (members 4–7) consists of clay rhythmites made up of alternating lighter brownish white and darker brownish gray fine-layered clays and local concordant bituminous interlayers with inclusions of scale and bone tissue of fishes. In the upper part (members 8–10), the rocks are characterized by a green tint and the presence of interlayers of bituminous clays and bioturbation traces.

The rocks are concordantly overlapped with grayish green thinly laminated, locally silty, clayey carbonate rocks, which belong to the Belaya Glina Formation

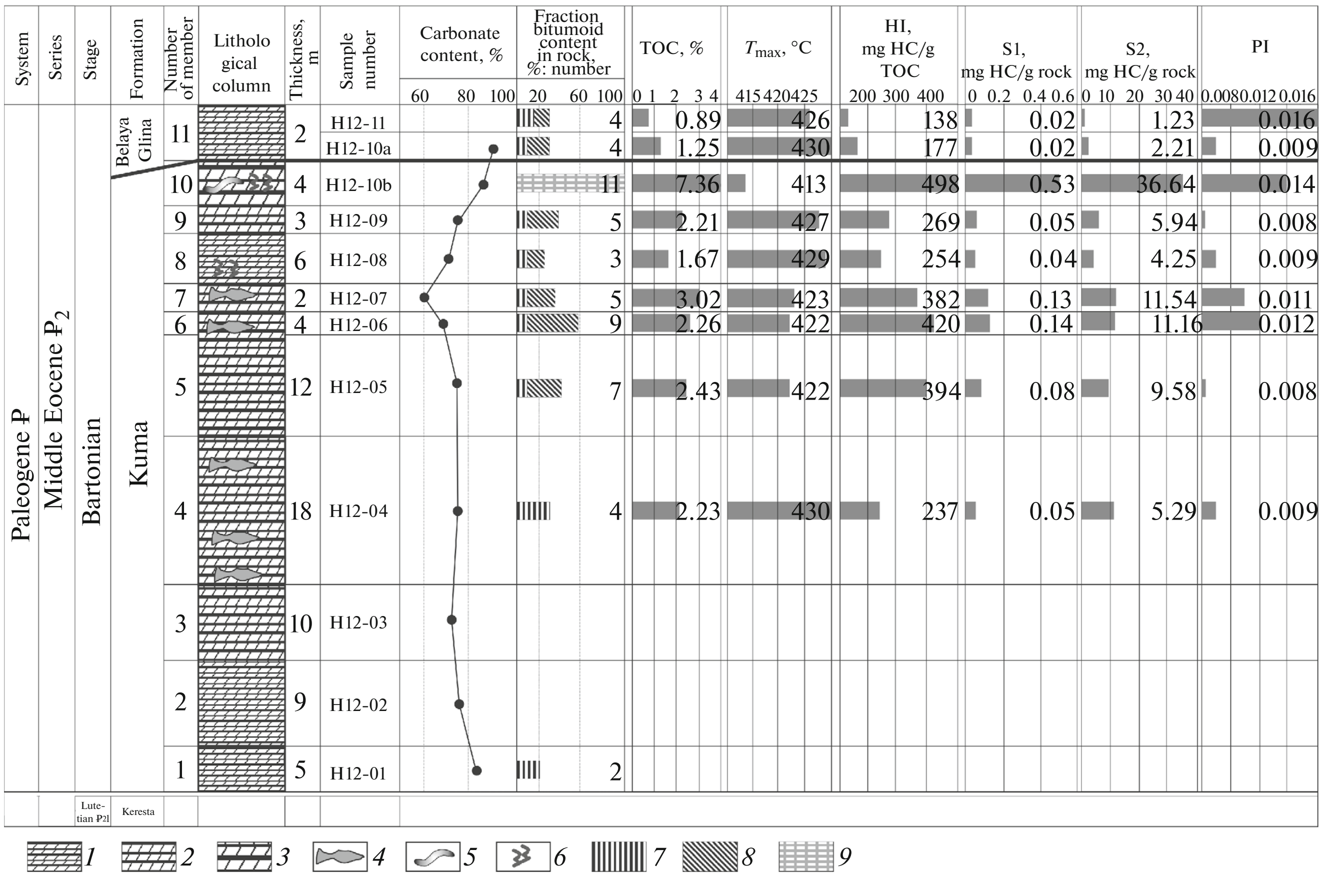

Fig. 2. The lithological–geochemical column of the studied section. (*1*) Fine-scaly clay; (*2*) moderate layered clay; (*3*) thick-layered clay; (*4*) relict bone tissue and scale of fishes; (*5*) oxidation traces; (*6*) traces of bioturbation; (*7*) oils; (*8*) resins; (*9*) asphaltenes.

(member 11). A more detailed description of the section of the Kuma Formation is provided below.

Layer 1. Light yellow, loose, calcareous, strongly weathered and oxidized, thinly and parallel laminated clayey limestones. The thickness of the weathered part is 0.5 m of more.

Layer 2. Light red, thinly laminated, banded, strongly fractured and weathered clayey limestones 9 m thick, which are exposed along the thalweg of the gully. The fragments of the fresher dark-gray rocks without bioturbation traces are found in the talus slope. In thin section, the rock is a light-gray, reddish layered micrite (Fig. 3.1) composed of terrigenous–calcareous cement (85%), pyrite (8%), organic relics (3%), calcite (less than 2%), OM (less than 1%), and potassium feldspar (≤1%).

Layer 3. Rhythmic alternation of clayey, brownish white (light layers) and brownish gray (dark layers) bituminous fine- and parallel-layered limestones without bioturbation 10 m thick.

Layer 4. Rhythmic alternation of underlying clayey limestones 18 m thick, which contain relict fish scale and bones in bituminous interlayers. In thin section, the rock is a brown pelitic micrite with fine parallel layering, a clear horizontal orientation of grains, a high level of OM and pyrite, and well-preserved foraminifera shells (Fig. 3.2). The rock consists of a terrigenous–carbonate matrix (73.5%), pyrite (11%), organic relics (10%), dispersed OM (≤2.5%), calcite (≤2%), and potassium feldspar (≤1%).

Layer 5. Rhythmic alternation of clayey limestones 12 m thick. The thickness of the dark brownish gray bituminous interlayers varies from 0.3 to 1–1.5 m.

Layer 6. The lowest four meters of the layer are grass covered. The structure of the sequence is almost the same with the addition of relict bone tissue and fish scales. The visible thickness is 4 m.

Layer 7. The alternation of light and dark clayey limestones and black fine-layered bituminous clayey limestones up to 1 m with relict fish scale along the layer surface. The thickness of the layer is 2 m.

Layer 8. Rhythmic alternation of the dark and light interlayers of clayey limestones, locally, with bioturbation traces. The thickness of the layer is 6 m.

Layer 9. Greenish dark-gray, fine-layered, massive clayey limestones 3 m thick.

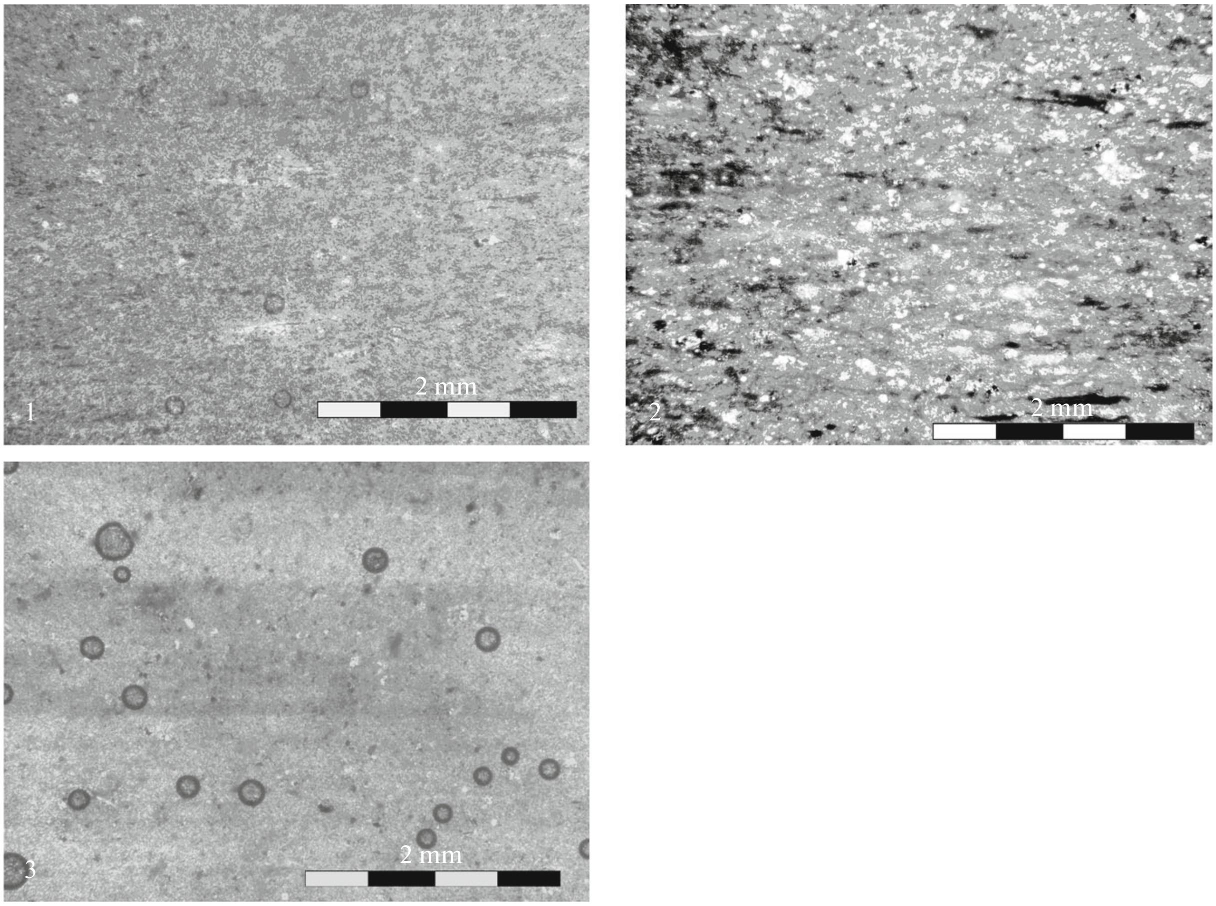

Fig. 3. The thin-section images of clayey limestone: (1) sample H12-02, member 2; (2) sample H-04, member 4; (3) sample H-10b, member 10.

Layer 10. Reddish dark-gray oxidized clayey limestones 4 m thick with strong bioturbation. In thin section, the rock consists of brownish red clay with fine parallel layering, visible orientation of grains, a significant carbonate cement, and a low level of pyrite (Fig. 3.3). The rock is composed of a terrigenous–carbonate matrix (90%), pyrite (5%), organic relics (4%), dispersed OM (≤1%), calcite (≤1%), and potassium feldspar (≤1%).

Layer 11. The lowest two meters of the layer are grass covered. The layer is composed of grayish green fine-layered silty clayey limestones of 4 m thickness or greater. The composition and the color of the rocks indicate that they belong to the Belaya Glina Formation.

Geochemical Studies

The oil and gas (OG) potential of the sedimentary sequence is caused by its OM properties and the thickness. The value of the OG potential of OM depends, first of all, on the composition and the amount of bioproducents and burial conditions. The OG potential of OM is based on live matter; it begins to be formed in the water column during sedimentogensis and is almost completely terminated during diagenesis (Tisso et al., 1981).

According to the results of the previous regional studies, the Kuma rocks, which are widespread from the Cis-Caucasus to Crimea, are characterized by increased and high OG potential of OM, the formation of which is caused by the high lipid initial material of algae and an insignificant amount of humus matter. The potential of the Kuma Formation is caused by favorable geochemical conditions in early diagenesis (Vassoevich et al., 1951; Fadeeva, 1979; Distanova, 2007).

On the basis of the lithological characteristics of the section of the Kuma Formation in the Bakhchisarai region, it may be suggested that the samples of three lower members are of little geochemical interest due to their light color and strong weathering. On the basis of LBA, sample H12-01 was characterized by the minimum extraction number (2 of 12 by the Florovskaya scale (1957), Fig. 2, Table 1), which corresponds to 0.00013% of bitumoid content and, in our opinion, this sample is of no interest for further geochemical studies. Let us note the striking dark-gray

Table 1. The indicators of the relative fraction distribution of the soluble OM and number by extraction via LBA of samples

Sample	Relative fraction extraction, %			Number by extraction (from 1 to 12)	Bitumoid content in rock, %
	oils	resins	asphaltenes		
H12-11	16	16	0	4	0.00125
H12-10a	11	21	0	4	0.00125
H12-10b	0	0	100	11	0.16
H12-09	11	16	0	3	0.000625
H12-08	11	16	0	3	0.000625
H12-07	11	26	0	5	0.0025
H12-06	11	47	0	9	0.04
H12-05	11	32	0	7	0.01
H12-04	32	0	0	4	0.00125
H12-01	21	0	0	2	0.000313

color of the rocks of member 10 (sample H12-10b), which, according to the LBA, is distinguished by a high number according to the extraction (11) results, which corresponds to an 0.15% level of the soluble OM content. Only the asphaltene fraction was released; the oil and resin fractions are absent. At the same time, almost all of the other samples contain an oil fraction, which is evidence of a favorable forecast for the oil source properties of the rocks.

For further geochemical studies, we chose the samples that are characterized by at least a number of 3 according to LBA extraction in accordance with the suggestion that these samples can contain a sufficient OM level for reliable geochemical information. Thus, we collected nine samples, whose bitumoids include, as a rule, oils and resins, except for sample H12-10b, which only has asphaltenes.

According to the pyrolytic studies, the TOC content of the studied limestones (carbonate content = 60–90%) of the Kuma Formation varies from 1.67 to 7.36% (median value of 2.26%). The genetic potential values (S1 + S2) are 4.25–36.65 mg HC/g rock. The HI values range from 237 to 498 mg HC/g TOC. The degree of catagenetic transformation determined for T_{max} = 413–430°C is low and corresponds to protocatagenesis (Fig. 2).

Thus, we can draw the following conclusions on the basis of these results: the rocks of the Kuma Formation are the Domanik oil source sequence with weakly concentrated OM (Bazhenova et al., 2012) and a sufficient generation potential. Their PI (Fig. 2) is extremely low (≤0.1), which, first of all, indicates weak transformation of the OM that stopped short of the main zone of oil formation. This is also confirmed by the low T_{max} values.

The low catagenic transformation of these rocks is evidence of their low OM potential due to the shallow submergence of the rocks, i.e., the sequence can be considered only as a potential oil source. The conclusion of the immature state of the Kuma rocks of Crimea is supported by previous results (Distanova, 2007). The HI value indicates the medium OM quality, which is more or less favorable for the formation of liquid HCs. The OI value points to the relatively oxidized state of OM. The comparison of HI and OI val-

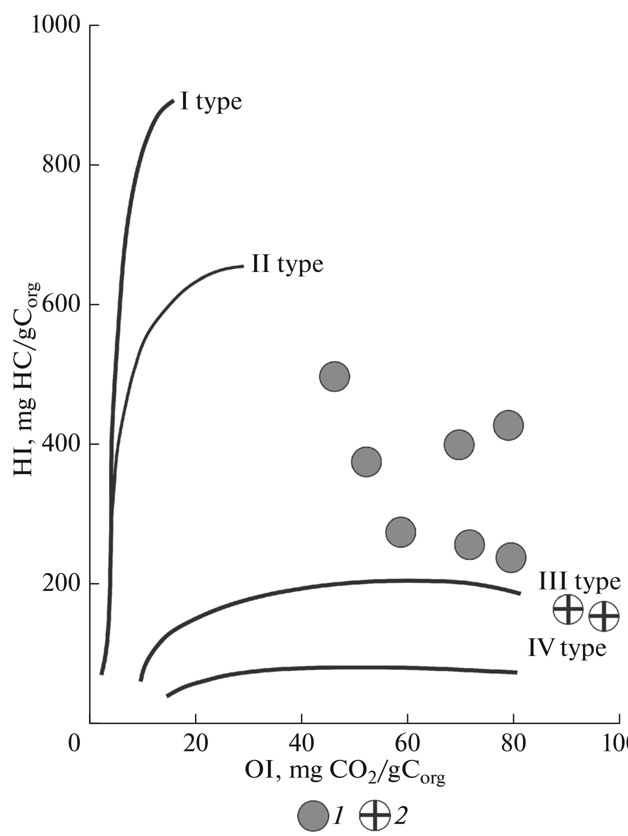

Fig. 4. The modified Van Krevelen diagram of the pyrolytic data of the studied samples. (*1*) Kuma Formation; (*2*) Keresta Formation.

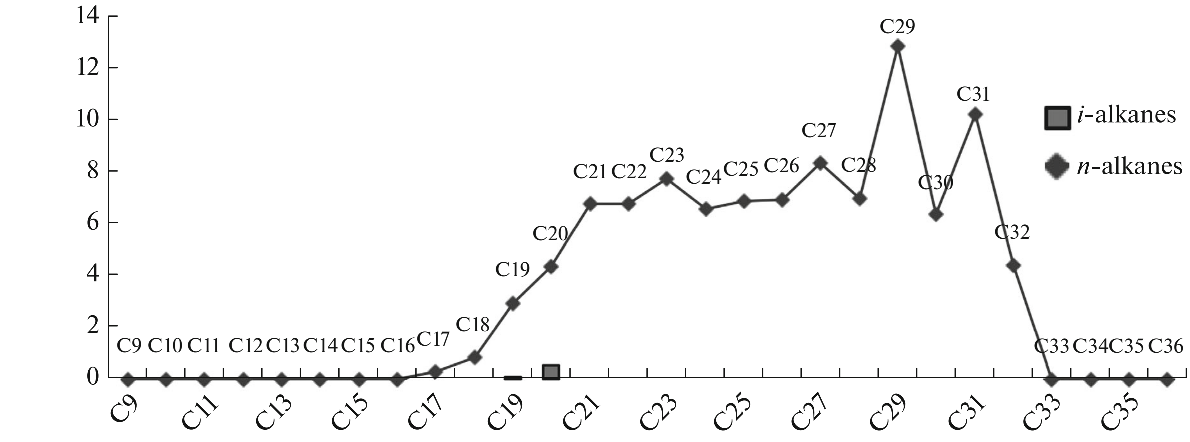

Fig. 5. The distribution of *n*- and *i*-alkanes according to the results of gas–liquid chromatography of sample H12-10b.

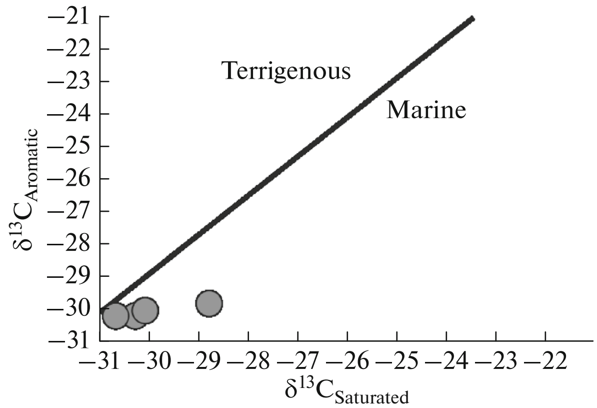

Fig. 6. The distribution of the $\delta^{13}C$ ratio of the aromatic and saturated HC fractions.

ues in the modified Van Krevelen diagram (Fig. 4) shows that OM is of a mixed humus–sapropel origin (type II of kerogene) and may generate both gas and oil. The data of (Distanova, 2007) exhibit lower values of HI (167–250 mg HC/g TOC), which indicates the lower OM quality and the distinct burial of OM in different regions of the occurrence of the Kuma Formation in Crimea.

Table 2. The carbon-isotope composition of the HC fractions

Sample	$\delta^{13}C$ (‰VPDB) of saturated HCs	$\delta^{13}C$ (‰VPDB) of aromatic HCs
H12-10b	−28.7	−29.8
H12-09	−30.3	−30.2
H12-07	−30.3	−30.1
H12-06	−30.7	−30.1

Samples with a bitumoid content of more than 0.0025% (number 5 by extraction) were taken for extraction. The bitumoids from samples H12-06, H12-10b, H12-09, and H12-07 were studied using gas–liquid chromatography. Only sample H12-10b has a classic chromatogram that can geochemically interpreted (Fig. 5); however, the content of alkanes and isoprenoids was low. Other chromatograms defy interpretation because of the low content of the oil fraction of the HCs.

In the chromatogram of sample H12-10b, n-alkanes have a unimodal distribution with dominant odd high-molecular weight *n*-alkanes and peaks of C_{27}, C_{29}, and C_{31} and a maximum of $C_{29.}$ No light fractions are present. The similar distribution indicates the predominance of land plants in the primary OM of the studied sample, which confirms the mixed OM origin, whereas the dominant odd n-alkanes are evidence of immature primary OM, which is consistent with the pyrolytic data. The pristane/phytane ratio (Pr/Ph = 0.15) indicates the reducing conditions of the diagenesis of the sediments. These results confirm the data of (Distanova, 2007).

According to the carbon-isotope composition of aromatic and saturated fractions of samples H12-06, H12-10b, H12-09, and H12-07, the initial OM was of marine origin (Fig. 6, Table 2).

CONCLUSIONS

The rocks of the Kuma Formation (Bakhchisarai region of the southwestern Crimea) contain OM of type II kerogene and a high oil source potential, which is favorable for the generation of liquid and gaseous HCs. The oil-source potential of these rocks is weakly expressed, probably because of insufficient tectonic submergence of rocks in the marginal part of the petroleum basin and weak catagenetic transformation of the OM in the studied area. These facts prohibit consideration of this oil-source rock as an element of the active oil system within the studied region and, consequently, give no grounds for searching for hydrocarbons within this system. The OM composition is locally heterogeneous, with a high level of continental OM. The absence of vitrinite in thin sections may indicate the contribution of humus material, mostly in soluble form. In general, we established the marine genesis of the OM of the Kuma Formation, which was precipitated under marine/coastal–marine or even estuary sedimentation conditions.

The section of the Kuma Formation from bottom to top varies from lighter to darker rocks, which reflects the change in the level of the burial OM. The low dynamic sedimentation results in the parallel bedding of the fine-layered members. The upper member is strongly bioturbated, which is evidence of the shoaling of the basin to the end of the formation of the sequence.

Further studies are necessary to reveal the regions of occurrence of more mature oil-source rocks of the Kuma Formation, which correspond to the submerged areas of the basin. Such regions probably occur at the Black Sea and Azov shelf with a high potential of the Kuma rocks.

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