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SHORT COMMUNICATIONS

Fluids of Mud Volcanoes in the Southern Caspian Sedimentary Basin: Geochemistry and Sources in Light of New Data on the Carbon, Hydrogen, and Oxygen Isotopic Compositions

I. S. Guliev, D. A. Huseynov, and A. A. Feizullaev

Institute of Geology, National Academy of Sciences of Azerbaijan, pr. G. Dzhavida 29-A, Baku, 370143 Azerbaijan
e-mail: d_huseynov@yahoo.com

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The Southern Caspian Basin (SCB) is a unique region of the Earth where giant oil and oil–gas-condensate fields occur in association with oil–gas mud volcanoes. Practically all exploited hydrocarbon fields of this region are accompanied by manifestations of oil–gas mud activity, which confirms their close relations. Mud volcanoes have deep roots, penetrating to zones of oil and gas generation, and, hence, they serve as fluid pathways to upper structural levels.

Mud volcanism is a very interesting phenomenon. It is characterized by the recurrent eruptions of huge volumes of different gases (predominantly, gaseous hydrocarbons) and solids (clayey masses with rock fragments measuring from small grains to blocks up to several meters across) separated by periods of gryphon–cone activity (mud, water, gas, and oil outflows). Note that mud volcanoes differ in gas and oil discharges and in gas–oil ratio.

According to petrographic and paleontological data, rock fragments and breccias of the mud volcanoes have ages from the Cretaceous to Pliocene. Hence the stratigraphic level and depths of the gaseous hydrocarbon generation is a complicated problem.

Its solution can be based on the isotopic geochemistry of mud-volcanic fluids, with regard for isotopic geochemical relations established earlier at oil–gas fields of SCB.

Mud volcanism is related to tectonic activity in the Southern Caspian Sedimentary Basin and adjacent Great and Lesser Caucasus oregenic belts. These megastructures have a Prealpine fault-block basement step-dipping toward the depression center. Inherited faults in upper structural floors control the distribution of mud volcanoes and fault-related folds (Fig. 1). Tectonic activity in deep fault zones causes eruptions of gaseous hydrocarbons and related mud volcanism. Tectonic motions are responsible for the abrupt changes in the seafloor level of the Caspian Sea and simultaneous mud volcanic activity. Mud volcanoes are most abundant in the Shemakha–Gobustan zone of SCB, where seismic activity is the highest (Fig. 1). Tens of earthquakes of different magnitudes occur in this area annually. Note that all of the earthquakes are shallow-focus, with hypocenters located at depths of less than 20 km. Many great mud volcanic eruptions in this area were triggered by strong earthquakes.

FACTUAL MATERIALS

The gases, oils, and waters of mud volcanoes were sampled in the Absheron, Shemakha–Gobustan, and Nizhnyaya Kura oil–gas-bearing regions; the Baku Archipelago; and in western Turkmenistan.

Stable isotopes of carbon were analyzed in oils (samples from 25 volcanoes) and gaseous hydrocarbons and carbon dioxide (samples from 80 volcanoes); stable isotopes of hydrogen and oxygen were determined in water (samples from 45 volcanoes). The analytical data were compared with the carbon isotopic composition of oil and gas samples from 38 fields of these areas. The isotopic ratios were studied and interpreted using diagrams and histograms.

In addition to the original analytical data, we used materials compiled from [1–8].

RESULTS

The *gases* of mud volcanoes consist of methane (CH_4, 79–98%) with subordinate ethane (C_2H_6) and nonhydrocarbon gases, including CO_2 (0.54–10.3%), N_2, H_2S, Ar, and He. The carbon isotopic composition (CIC) of the methane belongs to the interval from –61 to –36‰. About 75% of the volcanoes have methane with CIC from –50 to –40‰, which shows its moderate maturity. Methane from 15% of the volcanoes has a heavy CIC (from –40 to –36‰), typical of the gas related to a late stage of organic matter maturation (Fig. 2a). Distribution of the methane CIC values in the mud volcanism area is distinctly zoned (Fig. 3). Highly mature gases are typical of mud volcanoes of the She-

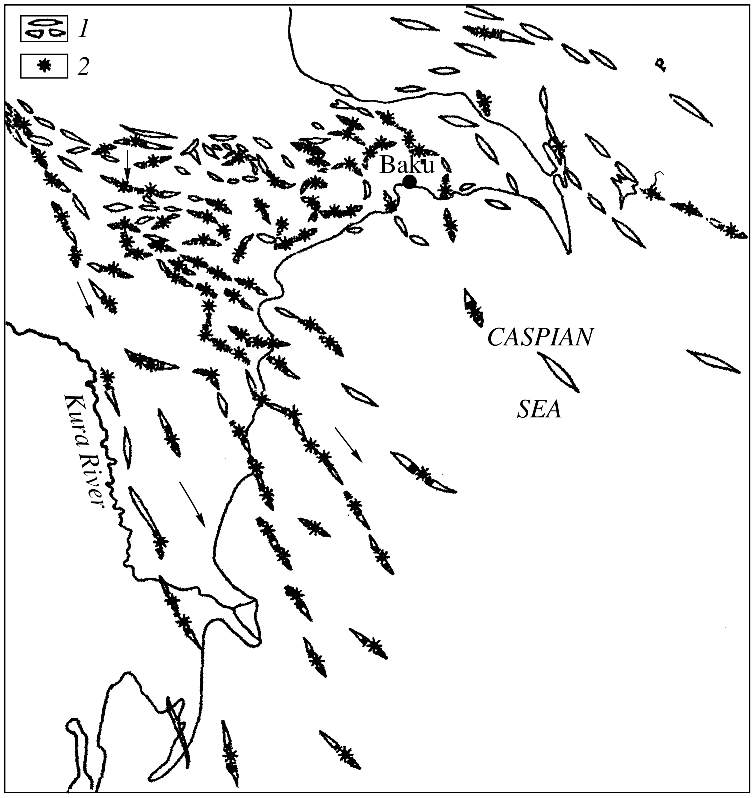

Fig. 1. Distribution of mud volcanoes and oil–gas-bearing folded structures in the western SCB zone. (*1*) Folded structures; (*2*) mud volcanoes.

makha–Gobustan zone: the average $\delta^{13}C = -40‰$, with a concentration of fat gases of 0.1%. Toward the Nizhnyaya Kura zone, the methane CIC becomes lighter (the average $\delta^{13}C = -47‰$, with the concentration of fat gases equal to 2.1%), which indicates early and moderate catagenesis stages of the organic matter. This zoning is explained by geologically different formation and accumulation conditions of gaseous hydrocarbons in the sedimentary deposits. For example, Mesozoic–Paleogene organic-bearing source deposits are shallow-sitting, extensively exposed, and strongly faulted in the Shemakha–Gobustan zone. When seismically activated, they readily emit immature gases. Consequently, this zone is noted for several hydrocarbon occurrences but has no large hydrocarbon pools.

The Mesozoic and Paleogene–Miocene sedimentary rocks of the Nizhnyaya Kura Depression are overlain by a thick (up to 6 km) Pliocene–Quaternary sequence. Compared with the Shemakha–Gobustan zone, this depression is much less abundant in mud volcanoes, and their eruptions are less frequent. As is evident from the scarcity of oil–gas occurrences in the depression and from presence of large hydrocarbon pools in the Pliocene–Quaternary reservoir rocks, the hydrocarbons are well preserved, and the degassing of the fields is low.

Gaseous CO_2 of the mud volcanoes has a CIC varying from –49 to +25‰, which suggests the presence of metamorphic (from +8 to –4‰), thermocatalytic (from –16 to +2‰), biochemical (<–16‰), and hydrothermal (from –7 to 0‰) fractions (Fig. 4). The greatest peak belongs to the interval of +16 to +10‰ (ultraheavy CO_2), while two other peaks occur in intervals from +2 to –2‰ and from –6 to –10‰ (Fig. 2c). About half of the volcanoes emit CO_2 with ultraheavy CIC ($\delta^{13}C >$ +8‰), whose origin remains unexplained. Gases of oil–gas fields in the western SCB wall contain CO_2 with ultraheavy CIC, which is typical of oil pools at shallow depths, where temperature is lower than 70°C and the oils are considerably oxidized and biodegraded. The $\delta^{13}C$ of this CO_2 directly correlates with its bulk concentration. It is known that much gaseous CO_2 is generated during the oxidation of liquid hydrocarbons, and isotopic studies of similar CO_2 revealed its ultraheavy CIC [9].

Note that a similar correlation between the $\delta^{13}C$ of gaseous CO_2 and its bulk concentration was revealed in the gasses of mud volcanoes. Thus the presence of CO_2 with ultraheavy CIC in the gasses of mud volcanoes indicates that these geologic structures contain pools of liquid hydrocarbons affected by strong bacterial oxidation. The revealed isotopic-geochemical relations are

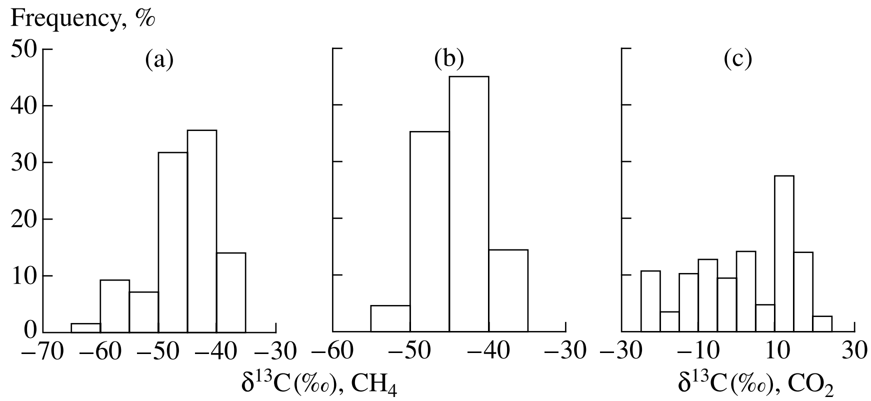

Fig. 2. Distributions of (a) $\delta^{13}C$ of methane of mud volcanoes, (b) $\delta^{13}C$ of methane of oil–gas deposits, and (c) $\delta^{13}C$ of gaseous carbon dioxide in SCB.

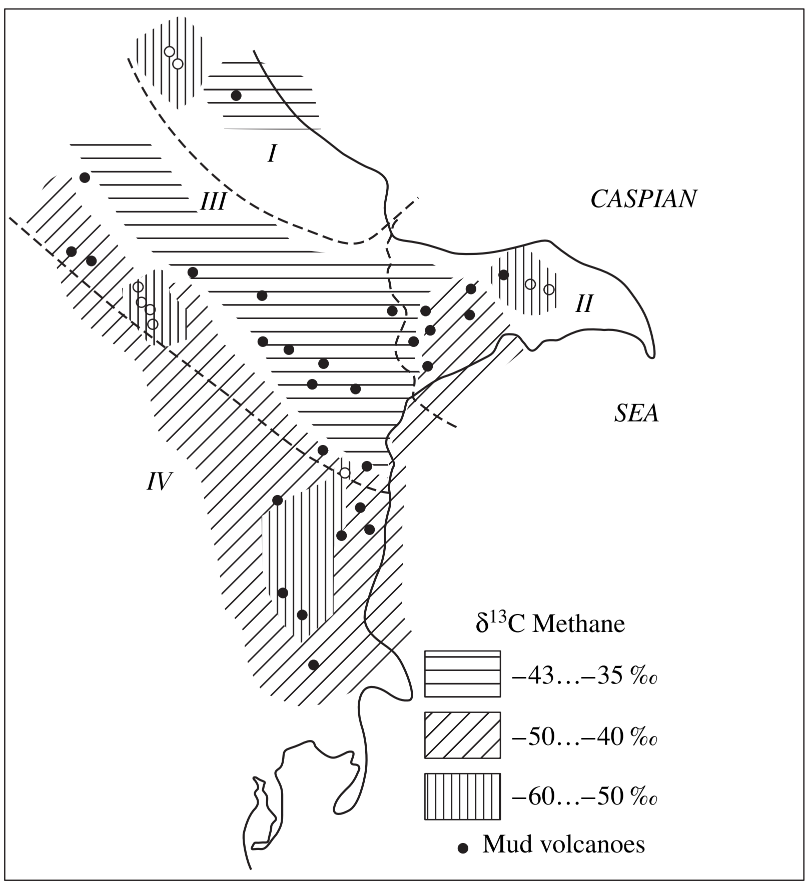

Fig. 3. Distribution zoning of carbon isotope composition of methane in mud volcanoes of the western SCB wall [5]. Oil–gas-bearing fields (depressions): *I*—Caspian–Gubinskii; *II*—Absheron; *III*—Shemakha–Gobustan; *IV*—Nizhnyaya Kura.

important not only for identifying mud volcanoes but can also be used as a reliable geochemical indicator of concealed pools of liquid hydrocarbons.

The *oils* of the mud volcanoes are strongly oxidized and biodegraded. The CIC of their saturated fraction varies from –28.5 to –25.4‰. The isotopic characteristics of SCB reservoirs were used as a basis for studying the genetic relations of the oils with stratigraphic complexes [10, 11]. The oils generated by Paleogene–Lower Miocene complex (Eocene, Maikop, and Chokrak) have a light CIC ($\delta^{13}C$ from –28.5 to –27‰), while the Middle to Upper Miocene oils (diatomic) have a heavy CIC ($\delta^{13}C > -24.5$‰) (Fig. 5).

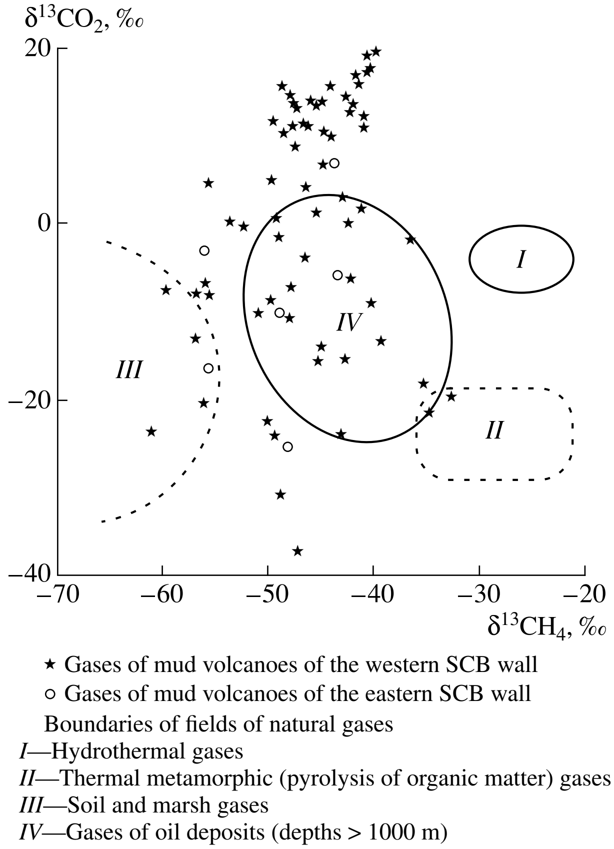

Fig. 4. Correlation between the carbon isotopic compositions of methane and gaseous carbon dioxide in the gases of mud volcanoes of SCB.

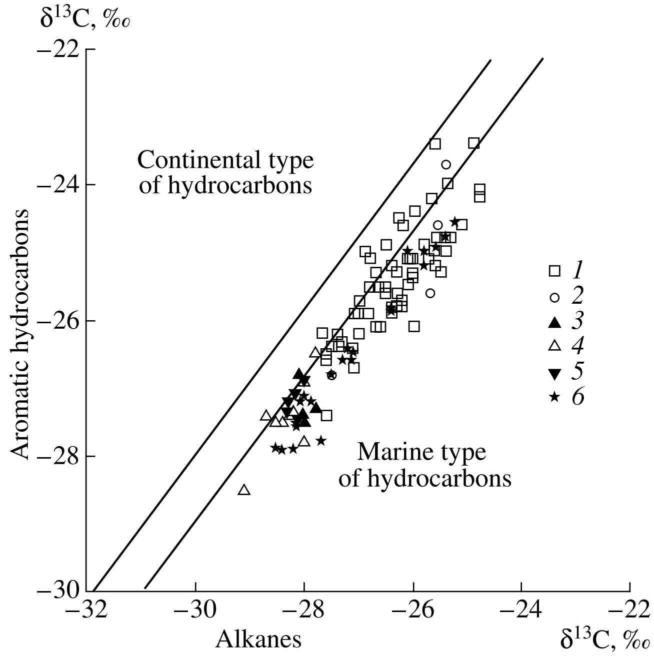

Fig. 5. Correlation between the isotopic characteristics of oils from reservoirs and mud volcanoes of different ages in the SCB. (*1–5*) Oils from (*1*) Pliocene, (*2*) diatomic, (*3*) Maikop and Chokrak, (*4*) Eocene, and (*5*) Upper Cretaceous complexes; (*6*) oils of mud volcanoes.

The CIC of mud volcano-related oils suggests that some of them were generated by the Paleogene–Lower Miocene complex, while other oils are hydrocarbon mixtures genetically related to the Paleogene–Lower Miocene and diatomic sedimentary complexes. Note that, according to this marker, there are no oils with the isotopic signatures of the diatomic complex.

About 50% of the mud volcanoes emit exclusively Paleogene–Lower Miocene oil; 17% of them have oil with a predominant diatomic component; and the remaining 33% possess mixtures with approximately equal percentages of oils from the Paleogene–Lower Miocene and diatomic complexes (Fig. 6).

Oil occurrences with the predominance of the diatomic component are confined to the northwestern part of SCB (Fig. 7), where Paleogene–Lower Miocene pools of the Nizhnyaya Kura zone are thrust northeastward onto the Middle–Upper Miocene and Pliocene sedimentary deposits of the Nizhnyaya Kura zone along the Adzhichai–Alyatskii deep fault. Oils in the upper and lower slabs of the thrust fault have similar CIC, which suggests that they originate mainly from the diatomic complex of the Nizhnyaya Kura Depression. This conclusion is confirmed by the fact that these oils and the oils in the northern part of the Nizhnyaya Kura Depression (Kalamadyn and Malyi Kharami) are the least mature.

The *water* of all mud volcanoes is low saline, sodium–hydrocarbonate. It notably differs in hydrogen and oxygen isotopic compositions from the formation water of oil–gas pools. The water of mud volcanoes is enriched in deuterium (δD up to +3‰) and ^{18}O ($\delta^{18}O$ up to +11.2‰) (Fig. 8). Most of the $\delta^{18}O$ and δD values belong to intervals from 4 to 10‰ and from –30 to 0‰, respectively.

In terms of isotopic composition, the water of the mud volcanoes is comparable with the water genetically related to metamorphic dehydration and condensation [6, 12, 13]. The elevated δD and $\delta^{18}O$ values of this water can also be explained by underground evaporation related to multiple (thousands of times over the geologic history) mud volcano eruptions and emission of the hydrocarbon–vapor mixture, with isotopically heavy water accumulated in the source.

DISCUSSION

The ages of emitted rock fragments and volcanic breccias vary within a wide interval (from Cretaceous to Pliocene), and, hence, it is difficult to determine stratigraphic levels and depths of the hydrocarbon generation. Nevertheless, their values can be calculated from the experimentally revealed correlation between the CIC of the emitted gasses and their catagenetic maturity (Ro) [14]. Based on this correlation and the values of vitrinite reflectance (Ro), we can estimate a hypsometric depth at which gaseous hydrocarbons of a given mud volcano are generated. Then, based on a model for the deep geologic structure of this volcanic area, we can estimate the stratigraphic level of hydrocarbon generation.

In estimating hypsometric and stratigraphic levels of hydrocarbon generation, we used the correlation between the CIC and Ro of ethane approximated as $\delta^{13}C_{C_2H_6}(‰) = 22.6\ \log Ro\ (\%) - 32.2$ [14].

According to our calculations based on this dependence, the mud volcanoes located at the western SCB wall emit ethane with maturity of 1.3–1.79% (Ro). The Ro values, measured in SCB deposits to a depth of 6100 m and extrapolated to deeper levels, show that this ethane is generated at depths of 6–8 km, which corresponds to the Jurassic–Cretaceous complex at the northern and northwestern walls of this basin. In the more depressed central zone of this basin (southeastern Gobustan), ethane is generated at depths corresponding to the Paleogene–Miocene complex. In this context, it is worth noting the studies of gas hydrates accumulated in bottom deposits and mud volcanic breccias of the deep zone of the Caspian Sea [8]. According to visual evaluations, the concentration of gas hydrates in the rocks varies from 2–3 to 25–30 vol %. The gas hydrates consist of methane (58.7–87.8%), ethane (10.4–19.4%), propane (1.6–15.8%), butane (0.4–2.68%), and pentane (0–0.68%).

The CIC of methane varies from –44.8 to –55.3‰, and the ethane has CIC from –28.4 to –25.7‰. The ethane maturity calculated from the $\delta^{13}C\ C_2H_6$ –Ro dependence equals 1.47–1.94%, which corresponds to depths of more than 10 km and indicates that the gas was generated in the Miocene–Paleogene deposits [15].

Let us also consider He/Ar_r in the gases of the mud volcanoes. The highest values of this ratio (2.5) are typical of gases related to mud volcanic oil occurrences in northern and northwestern SCB zones, where these gases are generated by the Cretaceous sedimentary deposits of the Mesozoic structural floor. Mud volcanoes with CIC-light oils generated by Paleogene–Lower Miocene deposits emit gases with He/Ar = 0.5. Gases from mud volcanoes with CIC-heavy diatomic oils have He/Ar_r = 0.13–0.17.

Vitrinite reflectance (Ro) calculated from the degree of sterane aromatization (C_{28} triaromatic/C_{28} triaromatic + C_{29} monoaromatic) indicates a low maturity grade of the oils (Ro = 0.46–0.64%) [16].

Thus the gaseous hydrocarbons differ in maturity grade from the oils, which indicates that their generating centers occur at different hypsometric and stratigraphic levels.

The depth of rock dehydration is a more difficult problem. Comprehensive studies of Cenozoic pools in SCB revealed montmorillonite and other clay minerals

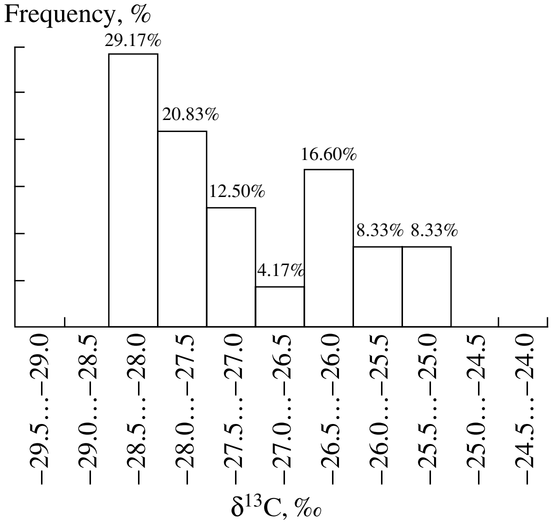

Fig. 6. Frequencies of $\delta^{13}C$ distribution in oils of SCB mud volcanoes.

at young Lower Pliocene sedimentary deposits of the Nizhnyaya Kura Depression and Baku Archipelago at depths exceeding 6000 m [17]. Hence, these deep-seated rocks are practically unaltered by catagenesis, and their alteration grade corresponds to protogenesis and, occasionally, mesocatagenesis MC_1 and MC_2. These data show that the dehydration potential of this clayey sequence remains unrealized. As is known, the intense dehydration of clays is related to the release of their interlayer water during montmorillonite transformation to hydromica. Provided that the geothermal gradient is normal (3°C/100 m), the temperature of this process (120–150°C) should correspond to depths of 4–5 km [18–21]. However, the geothermal gradient in the Nizhnyaya Kura Depression and Baku Archipelago is very low (1.3–1.7°C/100 m), which explains the very low rate of clay dehydration. In these zones of SCB, the temperature at a depth of 6000 m does not exceed 100–110°C. Hence, based on the average geothermal gradient of 1.5°C/100 m, the temperature conditions necessary for montmorillonite transformation to hydromica and the formation of isotopically heavy water occur at depths of 9–10 km and greater. Note that geophysical evidence (correlation method of retracted waves, and deep seismic sounding) points to regional decompaction zones in the clayey rocks at depths of 8–12 km [22]. We suppose that these zones represent areas of montmorillonite transformation to hydromica with the development of abnormally high formation and pore pressures and related paleo-quicksands and hydrous injections.

According to the geothermal gradient, metamorphic waters are formed in the SCB pools at depths of 20–25 km, where the temperature should be as high as 250°C.

A higher geothermal gradient (2–2.2°C/100 m) is typical of the northwestern and northern walls of the

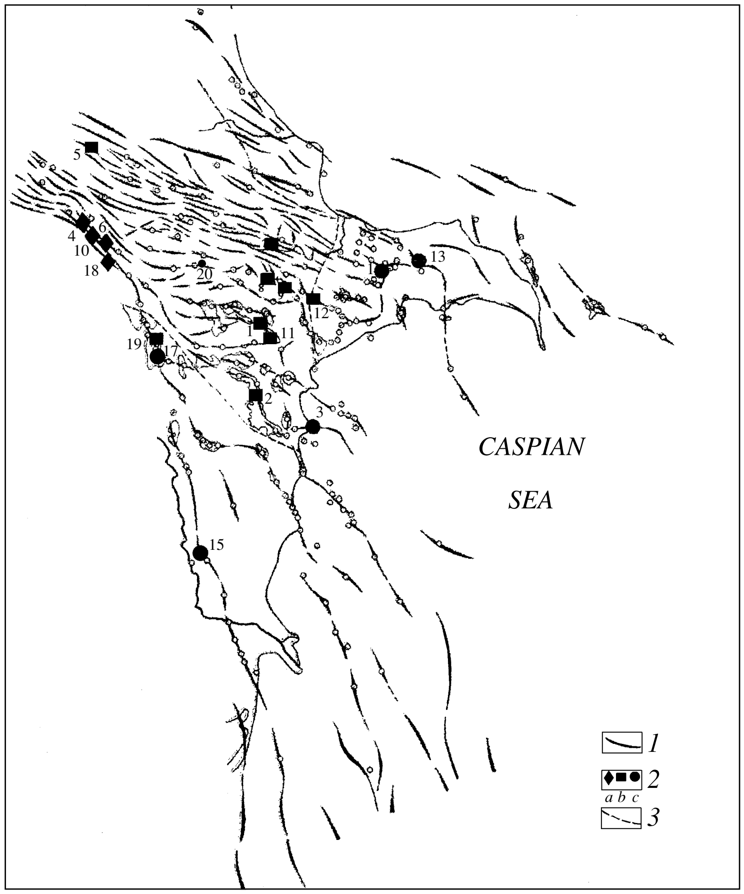

Fig. 7. Distribution of mud volcanoes and carbon isotope composition of their oils. (*1*) Anticlines; (*2*) mud volcanoes emitting oils with a carbon isotopic composition corresponding to that of (*a*) diatomic oils, (*b*) Paleogene oils, and (*c*) mixture of diatomic and Paleogene oils; (*3*) boundaries of oil–gas-bearing fields.

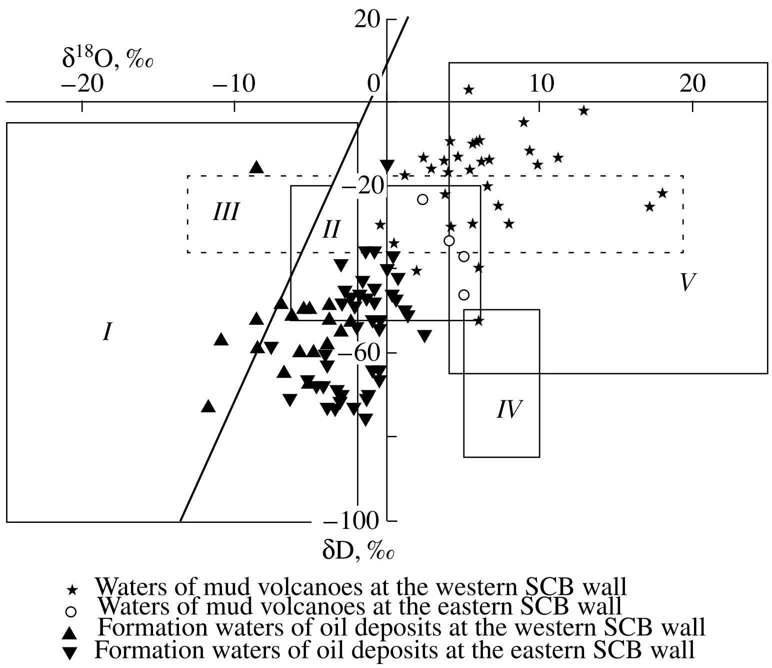

Fig. 8. Correlation between the hydrogen and oxygen isotopic compositions of mud volcanic waters and oil–gas deposits of SCB. Fields of water types: *I*—meteoric; *II*—oceanic; *III*—condensate deposits; *IV*—magmatic; *V*—dehydration and metamorphic.

basin (Shemakha–Gobustan and Absheron zones), where dehydration-related and metamorphic fluids are generated at shallower hypsometric levels.

Thus there are several isolated centers of fluid generation in SCB, and they belong to several stratigraphic (Mesozoic, Paleogene–Lower Miocene, and diatomic deposits) and hypsometric levels. Fluid generation in this thick (25–30 km) sedimentary sequence with a low geothermal gradient must occur within a very wide depth range. According to the model of the most lowered SCB part (the Zafar-Mashal–Alov zone), the oil and gas generation centers are restricted to depth interval from 10 to 18–20 km [23, 24]. Hence a very thick zone of hydrocarbon formation, including sedimentary deposits from the Mesozoic to Lower Pliocene, occurs in the central SCB part.

CONCLUSIONS

Fluids in SCB are generated in a wide stratigraphic interval, including Mesozoic and Lower Pliocene sedimentary deposits.

Isotopic data show that the roots of the SCB mud volcanoes occur at depths of 10–12 km and coincide with zones of intense fluid generation.

The generation zones of oil and gas are shifted relative to each other. In the deepest part of SCB, the oil window occupies a depth interval from 6 to 12 km, while the lower boundary of the gas window occurs at a depth of 18 km. The gas window at SCB walls occupies a depth range of 6 to 8 km.

Hydrocarbon gasses are generated at the same hypsometric and stratigraphic levels as the aqueous fluids. Nevertheless, the lower boundary of the aqueous fluid generation occurs at a greater depth and includes the generation zone of thermo-metamorphic carbon dioxide.

The spatial coincidence of the zones where the gas and aqueous fluid are generated (dehydration of clayey minerals) and the high depression and sedimentary deposition rates caused the oversaturation of the clayey sequences with the gas– aqueous fluids, the development of abnormally high pore and layer pressures, and the development of “loosened” bodies.

REFERENCES

1. B. M. Valyaev, Yu. I. Grinchenko, V. E. Erokhin, *et al.*, “Isotopic Signatures of gases at Mud Volcanoes.” Litol. Polezn. Iskop., No. 1, 72–87 (1985).
2. B. M. Valyaev, V. S. Prokhorov, and Yu. I. Grinchenko, “New Data on the Carbon Isotopic Composition of Mud Volcanoes of South USSR,” in *Proceedings of VII All-Union Symposium on Stable Isotope Geochemistry, Moscow, 1978*, pp. 67–69.
3. B. M. Valyaev, Yu. I. Grinchenko, V. S. Prokhorov, and G. A. Titkov, “Zoning in the Carbon Isotopin Composition of Mud Volcano Gasses and Its Dependence on Tectonics,” Dokl. Akad. Nauk SSSR **267** (5), 1222–1225 (1982).
4. A. A. Dadashev, L. M. Zor’kin, and G. G. Blokhina, “New Data on the Carbon Isotopic Composition of Mud Volcano Methane of Azerbaijan,” Dokl. Akad. Nauk SSSR **262** (2), 399–401 (1982).
5. A. A. Dadashev, A. A. Feizulaev, and I. S. Guliev, “Vertical Zoning of Oil–Gas Formation: Constraints from the Carbon Isotopic Composition of Methane from Mud Volcanoes of Azerbaijan,” Neftegaz. Geol. Geofiz., No. 6, 24–26 (1986).
6. Yu. B. Seletskii, “Dehydration of Clays as a Probable Formation Factor of the Isotopic Composition of Deep-Seated Waters,” Vodnye Resursy, No. 3, 48–153 (1978).
7. I. S. Guliev and Ya. A. Aslanov, “The Genesis of Groundwaters in the Southern Caspian Depression: Constraints from the Oxygen and Hydrogen Isotopic Compositions,” Azerbaidzh. Neft. Khoz., No. 4, 18–23 (1993).
8. G. D. Ginzburg, Ch. S. Muradov, and A. A. Dadashev, “Submarine Mud Volcanic Accumulations of Gas Hydrates,” Dokl. Akad. Nauk SSSR **300** (2), 253–258 (1988).
9. R. Dimitrakopolos and K. Muehlenbachs, “Biodegradation of Petroleum as a Source of 13C-Enriched Carbon Dioxide in the Formation of the Carbonate Cement,” Chem. Geol., Isotope Geosci. Sec. **65**, 283–291 (1987).
10. I. S. Guliev, A. A. Feizulaev, and D. A. Huseynov, “Carbon Isotopic Composition of Oils in the Southern Caspian Depression,” Azerbaidzh. Neft. Khoz., No. 5 (1999).
11. I. S. Guliev, A. A. Feizulaev, and D. A. Huseynov, “Carbon Isotopic Composition of Hydrocarbon Fluids in the Southern Caspian Depression,” Geokhimiya, No. 3, 271–278 (2001) [Geochem. Int. **99**, 237–244 (2001)].
12. M. G. Tarasov, “Genesis of Deep-Seated Desalinated Waters of Artesian Basins,” Vodnye Resursy, No. 6, 157–162 (1982).
13. H. P. Taylor, Jr., “The Application of Oxygen and Hydrogen Isotope Studies to Problems of Hydrothermal Alteration and Ore Deposition,” Econ. Geol. **69**, 843–883 (1974).
14. E. Z. Faber, “Isotopengeochemie Gasformiger Kohlenwasserstoffe,” Erdole, Erdgas und Kohle **103**, 210–218 (1987).
15. A. A. Feizulaev, Ch. S. Muradov, and A. A. Dadashev, “Depth of Gas Generation of Submarine Mud Volcanic Gaseous Hydrates,” in *Proceedings of the Third International Conference “New Ideas in the Geology and Geochemistry of Oil and Gas”* (Mosk. Gos. Univ., Moscow, 1999), pp. 276–277.
16. I. S. Guliyev, A. A. Feyzullaev, and D. A. Huseynov, “Isotope Geochemistry of Oils from Fields and Mud Volcanoes in the South Caspian Basin, Azerbaijan,” Petrol. Geosci. **7**, 201–209, (2001).
17. M. B. Kheirov, “Catagenesis of Clayey Deposits and Forecasting ApoVD and APVD before Drilling,” Azerbaidzh. Neft. Khoz., No. 4, 5–10 (1987).

18. J. F. Burst, "Diagenesis of Gulf Coast Clays Sediments and Its Possible Relation to Petroleum Migration," Bull. Amer. Assoc. Petrol. Geol. **53** (1), 73–93 (1969).
19. M. C. Powers, "Adjustment of Clay Minerals to Chemical Change and the Concept of Equivalence Level," in *Proceedings of National Conference on Clays and Clay Minerals, 1959*, pp. 309–326.
20. V. N. Kholodov, "Formation of Gas–Water Fluids in Sandy–Clayey Deposits of Elision Basins," in *Sedimentary Basins and Their Oil–Gas Potential* (Nauka, Moscow, 1983), pp. 28–44 [in Russian].
21. A. M. Blokh, "About the Universality of a Dehydration Model for Powers and Berst Sedimentary Sequences," Izv. Akad. Nauk SSSR, Ser. Geol., No. 6, 119–124 (1977).
22. I. S. Guliev, N. I. Pavlenkova, and M. M. Radzhabov, "A Decompaction Zone in the Sedimentary Cover of Southern Caspian Depression," Litol. Polezn. Iskop., No. 5, 130–136 (1988).
23. I. Lerche, Ak. Ali-Zade, I. Guliev, *et al.*, *Southern Caspian Basin: Stratigraphy, Geochemistry, and Risk Analysis* (Nafta, Baku, 1997), p. 430.
24. I. S. Guliev, E. G. Alieva, and D. A. Huseynov, "Deep Centers of Hydrocarbon Formation in the Southern Caspian Oil–Gas Basin," Tr. Inst. Geol. Nat. Akad. Nauk Azerb., No. 29, 79–99 (2001).