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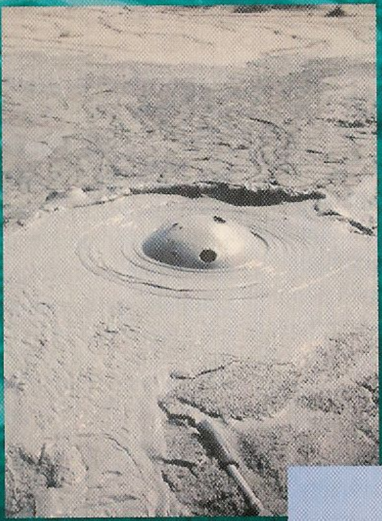

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Mud volcanic natural phenomena in the South Caspian Basin: geology, fluid dynamics and environmental impact

Dadash A. Huseynov · Ibrahim S. Guliyev

Abstract The South Caspian sedimentary basin is a unique area with thick Mesozoic-Cenozoic sediments (up to 30–32 km) characterized by an extremely high fluid generation potential. The large amount of active mud volcanoes and the volumes of their gas emissions prove the vast scale of fluid generation. Onshore and offshore mud volcanoes annually erupt more than 10^9 cubic meters of gases consisting of CH_4 (79–98%), and a small admixture of C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, CO_2, N, H_2S, Ar, He. Mud volcanism is closely connected to the processes occurring in the South Caspian depression, its seismicity, fluctuations of the Caspian Sea level, solar activity and hydrocarbon generation. The large accumulations of gas hydrates are confined to the bottom sediments of the Caspian Sea, mud volcanoes crater fields (interval 0–0.4 m, sea depth 480 m) and to the volcanoes body at the depth of 480–800 from the sea bottom. Resources of HC gases in hydrates saturated sediments up to a depth of 100 m and are estimated at 0.2×10^{15}–8×10^{15} m^3. The amount of HC gases concentrated in them is 10^{11}–10^{12} m^3. The Caspian Sea, being an inland closed basin is very sensitive to climatic and tectonic events expressed in sea level fluctuations. During regressive stages as a result of sea level fall and the reducing of hydrostatic pressure the decomposition of gas hydrates and the releasing of a great volume of HC gases consisting mainly of methane are observed. From the data of deep drilling, seismoacoustics, and deep seismic mud volcanic activity in the South Caspian Basin started in the Lower Miocene. Activity reached its highest intensity at the boundary between the Miocene and Pliocene and was associated with dramatic Caspian Sea level fall in the Lower Pliocene of up to 600 m, which led to the isolation of the PaleoCaspian from the Eastern ParaTethys. Catastrophic reduction of PaleoCaspian size combined with the increasing scale of mud volcanic activity caused the oversaturation and intoxication of water by methane and led to the mass extinction of mollusks, fishes and other groups of sea inhabitants. In the Upper Pliocene and Quaternary mud volcanism occurred under the conditions of a semi-closed sea periodically connected with the Pontian and Mediterranean Basins. Those stages of Caspian Sea history are characterized by the revival of the Caspian organic world. Monitoring of mud volcanoes onshore of the South Caspian demonstrated that any eruption is predicted by seismic activation in the region (South-Eastern Caucasus) and intensive fluid dynamics on the volcanoes.

Keywords Mud volcano · Fluid dynamics · Environment · Gas and oil emission · Oil slick

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Introduction

The South Caspian Basin (SCB) is a unique region on the Earth. The giant oil and oil-gas-condensate fields and hydrocarbon manifestations in the form of mud volcanoes are widely distributed here. In fact, mud volcanoes accompany all oil-gas fields in the SCB. From about 900 onshore mud volcanoes known on the Earth about one-fourth are within the western and eastern flanks of the SCB and more than 160 mud volcanoes are on the South Caspian sea bottom (Fig. 1a). The sources of the mud volcanoes are located at significant depths and are the natural channels of the matter re-distribution in the sedimentary basin (Fig. 1b). The study of mud volcanoes as geological objects bearing rich information concerning the deep structure of the Earth, and the presence of HC accumulations at depth, has a long history. A wide range of geological, aero-satellite, geochemical, geophysical, geodetic and other methods are being applied in their study.

The South Caspian Basin is situated in the central part of the Mediterranean-Himalayan folded zone. Its present

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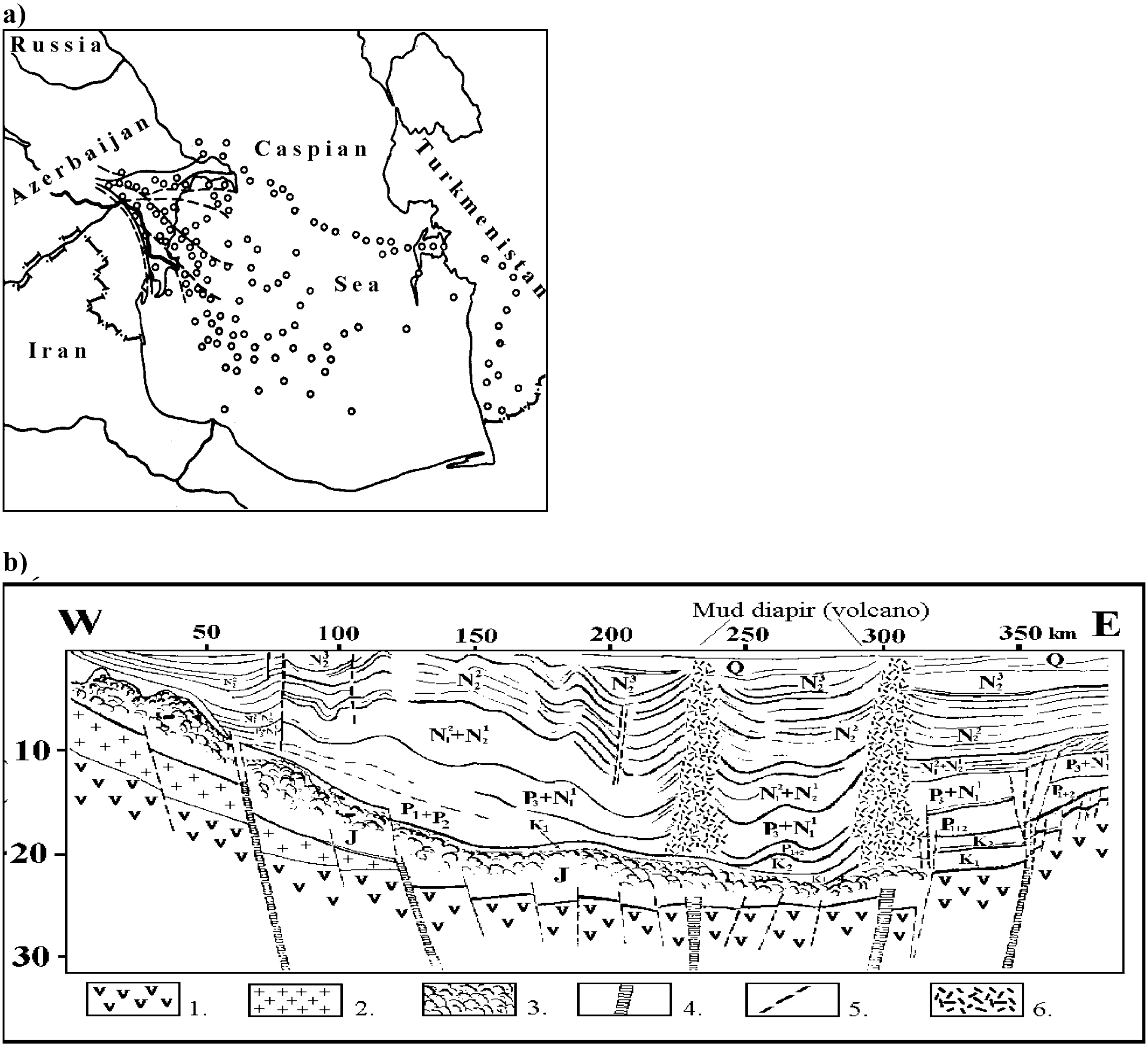

Fig. 1a, b
Location map of the mud volcanoes (**a**) and regional 12th sec seismic profile cross South Caspian Basin (**b**) (after Mamedov 1991). 1-basaltic layer; 2-granitic layer; 3-Mesozoic igneous rock; 4-crustal faults; 5-faults; 6-zone of no seismic information presumably mud diapir

shape and petroleum system were formed as a result of the interaction of Eurasian, Indian and Arabian plates and numerous microplates starting from the Triassic. The available geologic-geophysical data shows the presence of a marginal-marine basin with a typical crystalline crust of oceanic type, a morphostructure of flanks and sedimentary complex in the South Caspian region. The present deep-sea basin of the South Caspian is a relict of the Mesozoic-Paleogene uncompensated depression. To the orogenic stage it had experienced three main cycles (stages) of geodynamic development, (Zonenshine and others 1990; Guliyev and others 2003) namely: (1) riftogenic, with origination of the deep trough of the Great Caucasian marginal sea; (2) mature, with stages of marginal sea widening and isolation; (3) and island arc, with stages of volcanic arc development, compression and subduction processes. Starting with the Oligocene and especially in the Neogene-Pleistocene the marine basin went through a fourth stage. This stage is characterized by its transformation into a unique intracontinental basin, which has the following typical features:

- Non-unidirectional folding zones formed at different tectonic stages;
- High density of non-unidirectional fractured zones and abyssal faults;
- High velocity of vertical and horizontal movements; paleomagnetic and GPS data point to continued displacement of the Arabian plate and its north periphery northeastward with a velocity of 10–12 mm/year

(Guliyev and others 2002). Vertical movements on the anticlinal structures are +1.2±4.5 mm/year, in some areas they reach +90 mm/year. At the same time, in adjacent areas sinking can be observed with a velocity of −25 to −50 mm/year. Thus, the relative velocity of the vertical movements can reach 140 mm/year;
– Very high velocities of subsidence and sedimentation (up to 3.5 km/My) for a very short period of geological time (Pliocene-Quaternary);
– Formation of a sedimentary cover of a huge thickness (according to the latest data it is up to 30 km) (Knapp and others 2000);
– Mainly clayey composition of rocks in the Cenozoic section;
– Several source-rocks of different stratigraphic age;
– Abnormally low temperature gradients (1.5–1.8° C/100 m) and thermal flows (25–50 mW/m^2).

All of this set conditions for very high fluid generation in sedimentary complexes and abnormally high porous (close to geostatic) and formation pressures, which appeared as mud volcanism and diapir folding.

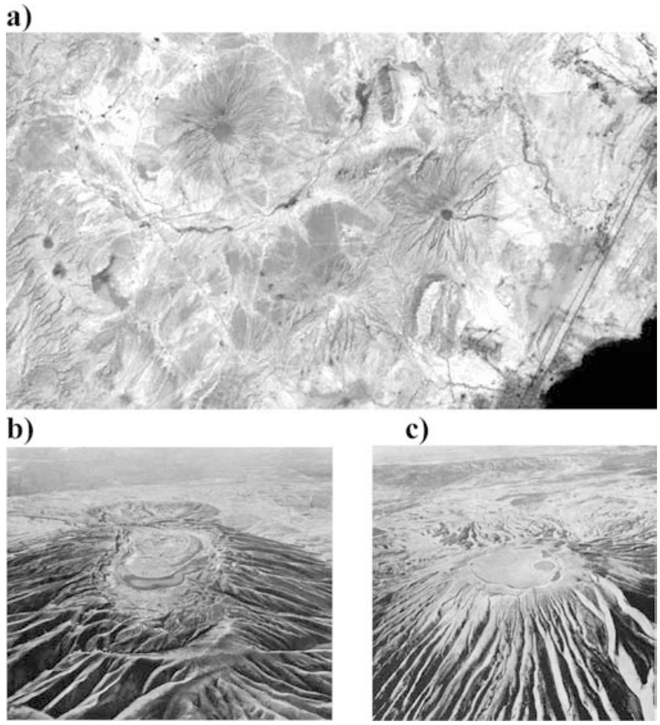

Fig. 2a–c
(**a**) Landsat 7 satellite image of the group biggest in the World South Caspian mud volcanoes Touragay (*left*) and Boyuk Kyanizadag (*right*). Smaller mud volcanoes located in the south-west part of observed area. Processed band 7. **b,c** Air photo of the Galmaz (**b**) and Touragay (**c**) mud volcanoes

Forms, scales and dynamics of development of the mud volcanic processes in the SCB

Mud volcanism presents one of the most interesting and unusual phenomena with periodical eruptions of large amounts of gases (hydrocarbons mainly) and breccia with inclusions of rock fragments with sizes from small grains up to blocks of some meters. Eruption products accumulate near the mouth and crater volcano cone. The size of the volcano cone depends on the eruption frequency and the character of hard material as well. The frequent eruptions and big cones of the mud volcanoes are observed in places where plastic rocks have a large thickness in the section. Together with this the relative height, slope forms and other morphological features of the volcano are determined by the consistency of the erupted breccia.
Morphological peculiarities of the mud volcanoes are clearly observed on the aero and satellite images (Fig. 2). The value of the latter one is especially useful for observing the dynamics of mud volcano development.
Marine volcanoes take a special place among the mud volcanoes of the SCB. They form mud volcanic islands, underwater banks and uplifts on the sea bottom. Activity of the underwater (submarine) volcanoes is observed on the sea surface as strong gas seething and slicks, which are well identified on satellite images. During eruptions the underwater banks turn into temporary mud volcanic islands, which are quickly (after some days) washed out after the volcano activity. The formation of gas hydrate accumulations is related to underwater mud volcanic structures.
Volumes of solid and gaseous products as well as the sizes of the mud volcanic bodies show the huge scale of the mud volcanic process. The calculations have shown that the total volume of the mud volcanic breccia which flowed from the 220 volcanoes of the SCB western flank is about 100–110 million km^3. As a result of repeated eruptions the fresh flow of breccia overlaps previous flows and the total thickness grows. The thickness of breccia flows varies from 40 to 100 m. The length of breccia flows, having fan- or finger-shaped forms, reaches 2–3 km, and the width is 200–500 m. Hard products form the mud volcanic body. Bigger volcanoes have a body with a height of 300–400 m and base diameter of 3–3.5 km (Touragay, Boyuk Kyanizadag, Kursanga, Galmaz etc.) (Fig. 2a,b,c)).
The mud volcanic eruption is usually accompanied by a great column of flame reaching 200–300 m in height and 50 m at the base. The burning flame is usually observed at a distance of 100–150 km. The amount of gases ejected into the atmosphere during the eruption is 2×10^7–5×10^8 m^3. During the quiet period their emanation is 2–3 times lower.
The formation of the mud volcanic constructions takes place not only in the periods of their intensive activity. An intensive flow of mud breccia out of the crater is observed even during long quiet periods.
The dynamics of development and grandiosity of the mud volcanic process in the scale of geologic time can be recognized by determination of the total number of eruptions of separate mud volcanoes. It can be easily calculated for each mud volcano from the ratio of total volume of the mud breccia to volume of the mud breccia ejected during

one eruption. So, during the eruption of the Touragay volcano in 1947 there were ejected 50,000 m^3 of mud breccia whereas its total volume on the volcano is 343×10^6 m^3. This means that this mud volcano erupted more than 6,000 times. Similar calculations can be made for other mud volcanoes. For example, the volume of breccia on the Boyuk Kyanizadag mud volcano is 735×10^6 m^3 and during its last eruption 10^5 m^3 of breccia was ejected. Thus, the total number of Boyuk Kyanizadag eruptions is about 7,000.

The formation of smaller volcanoes (Dashmardan, Keireki, Dashgil) was accompanied by 360–1,200 multiple eruptions (Table 1).

The mentioned data allow calculations of the gaseous potential of deposits of the mud volcanoes source zone. For Boyuk Kyanizadag and Touragay it is $7\times10^3\times2\times10^8=1.4\times10^{12}$ m^3; $6\times10^3\times5\times10^8=3.0\times10^{12}$ m^3 respectively.

Upon studying the dynamics of mud volcano development in the Recent stage, it becomes possible to reconstruct the paleodynamics of the mud volcanic process.

Mud volcanism, cycles of sun activity, tidal forces of the moon and seismicity

The statistical processing of 150-year eruptions of the mud volcanoes and the astronomic periodicity of mutual location of the Earth, Sun and the Moon allowed establishing the closest relation between these phenomena and the important regularity. It showed that about 60% of all (over 200) eruptions take place during a new moon or full moon. On this basis the prediction of volcanic activity for the coming years was made. This prediction was 75% confirmed (Gorin and Buniatzadeh 1971).

Results of the study of the activity of 300 mud volcanoes from various parts of the World in connection with an 11-year cycle of the sun's activity revealed a good correlation of the mud volcanic periodicity and sun activation (Fig. 3a) (Mekhtiev and Khalilov 1988).

The sun's activity for years 2000–2001 provoked an activation of the record number—15 mud volcanoes on the western flank of the SCB. One volcano was considered as extinct because it had not acted for about 150 years.

Mud volcanoes of the SCB are closely related with the tectonic processes taking place in the South Caspian sedimentary basin and mountain-folded systems of the Greater and Lesser Caucasus framing it. The periodical "brightening" of the faults from the northern flank of the SCB towards the southern one determines the analogous intensity of the mud volcanism. Two-century observations show that waves of volcanic activity flash roll with a definite sequence from the southern slopes of the Greater Caucasus to the northern slopes of the Lesser Caucasus. The intervals are as follows: 60–65 years for the near-flank zone and 25–30 years for the depression (submerged) part of the basin (Gorin and Buniatzadeh 1971). At the same time the tectonic movement along the faults provokes the spasmodic or uneven fluctuations of the Caspian Sea bottom (Gorin and Buniatzadeh 1971; Lilienberg 1999). Ten earthquakes of various amplitude are recorded in the South Caspian region every year. For example, for 2002

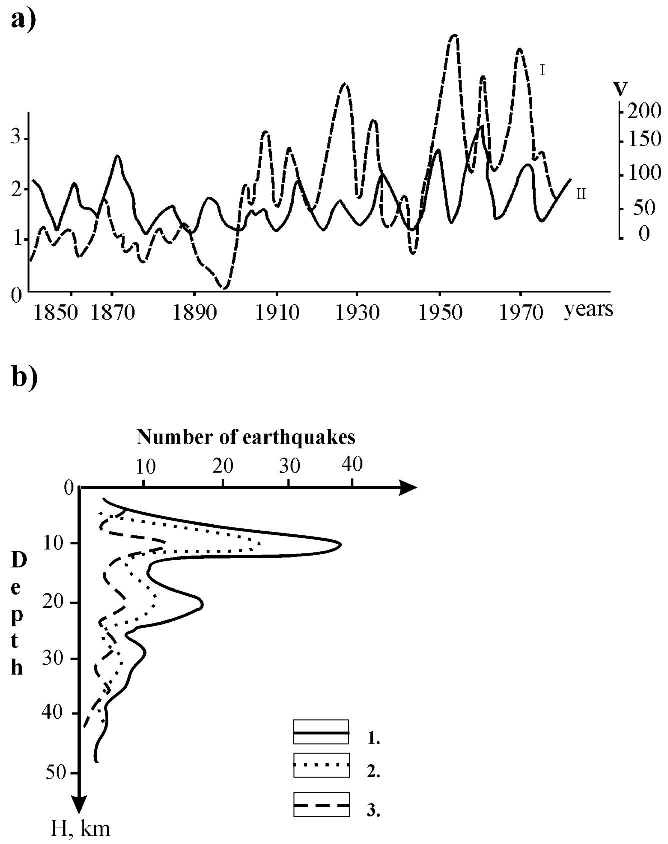

Fig. 3a, b
Correlation plots of the solar and mud volcanic activity (**a**) (I—mud volcanic activity plot; II—solar activity plot (Vulf numbers) and frequency distribution of the earthquake on the South Caspian west flank (**b**) (1—on the whole SCB west flank; 2—Ismailly block; 3—Shamaha block)

Table 1
Volume of ejected mud breccia and number of mud volcanic eruptions

Mud volcano	Volume ejected breccia during eruption (m^3)	Total volume of breccia (m^3)	Number of eruptions
Boyuk Kyanizadag	100,000	735×10^6	7,350
Touragay (1947)	50000	343×10^6	6,860
Dashmardan (1954)	2000000	2500×10^6	1,250
Keireki (1952)	375,000	136×10^6	360
Dashgil	470,900	259×10^6	550

there had been registered 26 earthquakes in the Caspian region with magnitudes of 3.5–5.2.

It is necessary to mention that the beginning of great mud volcanic eruptions in connection with the most intensive seismic-tectonic processes in the South Caspian region was observed repeatedly.

It is important to emphasize that the bulk of the earthquakes in the region are shallow-focus, the hypocenters of which do not exceed 10–12 km (Fig. 3b). It corresponds to depths of occurrence of highly plastic sandy-clayey masses of the Paleogene-Miocene complex saturated with hydrocarbonaceous fluids (Fig. 1b). The joint manifestation of the mud volcanic and shallow-focus earthquakes shows the intensive conversion and re-distribution of the sedimentary matter and fluids causing their phase and mechanical instability as well as the formation of zones of regional and local decompaction of the sedimentary rocks.

Geochemistry of mud volcanic environments

Increased concentrations of Ni to 2×10^{-2}%, Cr to 4.7×10^{-1}%, V to 2×10^{-1}%, Cu to 3×10^{-1}%, Ba to 2×10^{-1}%, Sr to 1×10^{-1}%, Rb, Cs, Co to 4×10^{-2}%, Mo to 1×10^{-2}% in hard ejects of mud volcanoes are determined. Mud volcanic breccias of tens and hundreds of times is strongly enriched of B to 4×10^{-1}%, Hg to 1.5×10^{-3}% and As to 5×10^{-2}%.

A great contamination with oil of territories adjacent to volcanoes is the reason for high radioactivity, 25 to 30 mR/h with values of radioactive background 5–6 mR/h (Aliyev and others 2001) due to heightened concentrations in the oils radioactive elements, U: 2.2×10^{-6}% and Ra: 1.9×10^{-13}%. Average metal content in oil is: Cr: 1.1×10^{-4}%, Cu: 2.2×10^{-4}%, Pb: 6.7×10^{-6}%, Zn: 9.3×10^{-5}%, Mo: 5.1×10^{-6}%.

Submarine discharge of waters from mud volcanoes and ejection of various components are crucial in the saline balance of marine and bottom sediment water. So, the annual ejection of salts into the sea is 200,000 t (Na^+: 9×10^4, Ca^{2+}: 9×10^2, Mg^{2+}: 16×10^2, Cl^-:1×10^5, $SO^{2-}{}_4$: 3×10^3, ($HCO_3{}^-$+$CO_3{}^{2-}$): 2×10^4, NH_4: 3, Si: 35, I: 140, Br: 550, B: 700, F: 25 t), with the average salinity of marine volcano waters 24 g/l, it makes about 5% of salt run-off of Kura, the main river of the South Caspian. Vast anomalies of salinity and concentrations of the above-mentioned components in marine water and mud solutions of bottom sediments are formed on the background of South Caspian's water with a salinity of 10–12 g/l. Concentration of some microelements greatly exceeding the background are observed in bottom sediments (in brackets the background is given): Ba to 0.5% (0.06–0.08%), Sr to 0.3% (0.06–0.08%), Cr to >$n\times10^{-2}$% (6×10^{-3}%), Hg to 87×10^{-5}% (2×10^{-5}%), Mo to >$n\times10^{-3}$% (2.5×10^{-4}%), Pb to >4×10^{-3}% (1.2×10^{-3}%).

The vast multi-component abnormal zone had been revealed in the central deepwater part of the South-Caspian depression (Zafar-Mashal-Alov). The degree of bitumization of organic matter in sediments of this zone sharply grows, the share of the oil fraction in bitumen increases up to 45%. The abnormally high values of other direct indicators of oil-gas content have also been determined. For example, the ratio of ammonium to iodine in oozy solutions exceeds 4 times the background values in the upper layer of the sediments (0–50 cm), and 7 times—in interval 0.5–1.5 meters. The content of hydrocarbon gases in this zone also grows.

Geochemistry and deep sources of fluids

Gases of the mud volcanoes have a hydrocarbon composition and consist mainly of methane (CH_4) (79–98%), a small admixture of ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}) and other non-hydrocarbon gases, such as CO_2 (0.54–10.3%), N, H_2S, Ar and He. Isotopic composition of the carbon of methane $\delta^{13}CCH_4$ varies from −61‰ up to −36‰. About 75% of the volcanoes have $\delta^{13}CCH_4$ from −50‰ up to −40‰, and correspond to the average stage of the methane maturity. Methane with heavy $\delta^{13}CCH_4$ (from −40‰ up to −36‰) characterizing methane of the mature late stage is typical for 15% of the volcanoes. Generally, the methane isotopic composition reflects a clear zonality in spatial distribution of the mud volcanoes.

The study of isotopic composition of the carbon of CO_2 of the mud volcano gases revealed its variation in very wide ranges: from −49‰ up to +25‰; which points to CO_2 presence of various genesis (Guliyev and others 2001): as metamorphogenic (from +8‰ up to −4‰), thermokatalitic (from −16‰ up to 2‰), biochemical (<−16‰), hydrothermal (from −7‰ up to 0‰) (Fig. 4a). The main maximum covers an interval from +16‰ up to 10‰ corresponding to ultra heavy $\delta^{13}CCO_2$, and side ones—from +2‰ up to −2‰ and from −6‰ up to 10‰.

The oils of mud volcanoes are strongly oxidized and biodegraded. Isotopic composition of carbon in oils varies from −28.5‰ to −25.4‰ (in the saturated fraction). These isotopic marks allowed the determination of the contribution of various stratigraphic complexes into the formation of mud volcanic oil manifestations. Here oils with the typical Paleogene-Lower Miocene isotopic mark of carbon are distinguished as well as oils with a mixture of oils produced by Paleogene-Lower Miocene and Diatomic (Middle and Upper Miocene) complexes of deposits (Huseynov and others 2000; Huseynov 2000; Guliyev and others 2001a, 2001b).

Water related with mud volcanoes of the SCB are mineralized, mainly hydrocarbonate-sodium. A clear tendency of mineralization and water type increases towards the central parts of the SCB from weakly mineralized (5–7 g/l) hydrocarbonate-sodium to very mineralized (85–100 g/l) chlorine-calcium. More mineralized waters of brine type are typical for the Lower

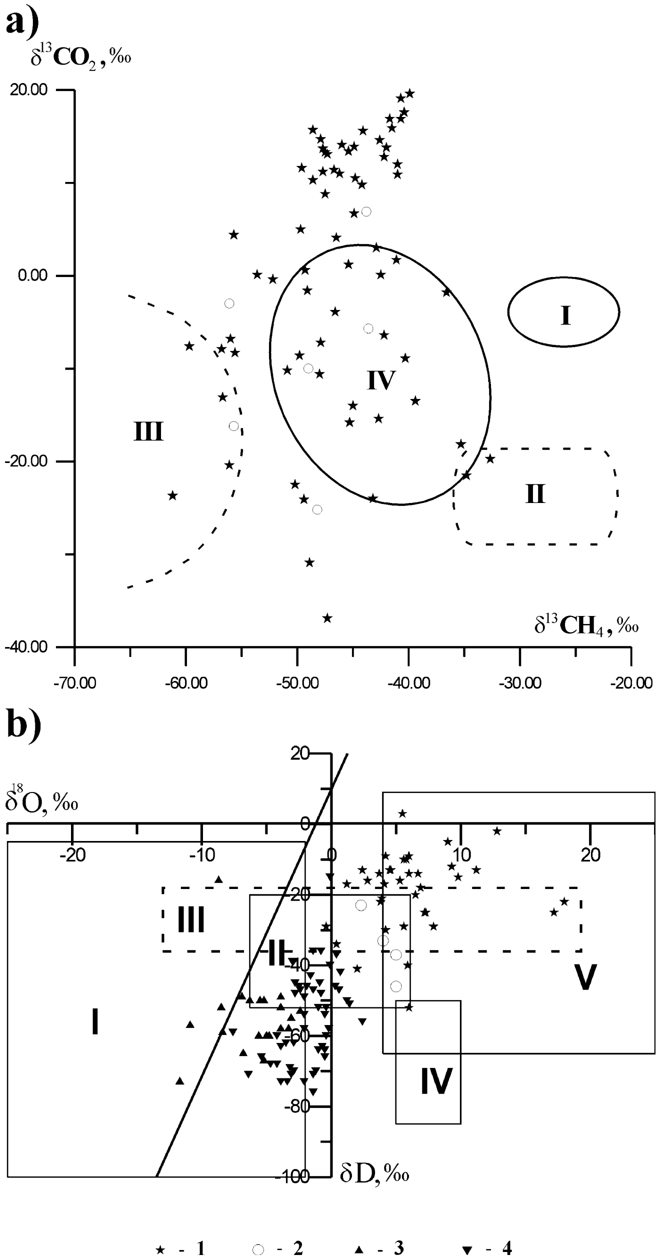

Fig. 4a, b

a Relationship plot of isotope composition of carbon of CO_2 and CH_4 in the South Caspian mud volcano gases. Contour of field for natural gas group: I—hydrothermal gases; II—thermometamorphic (OM pyrolitic) gases; III—soil and marsh gases; IV—oil field's gases on the depth >1,000 m. 1—mud volcanoes of the western flank of SCB; 2—mud volcanoes of eastern flank of SCB. **b** Plot of δD and δ^{18}O relationship in the SCB mud volcanoes and oil fields water. Fields of water types: I—meteoric; II—oceanic; III—water of condensate fields; IV—magmatogene; V—dehydration and metamorphogene. 1—mud volcanoes water of western flank; 2—mud volcanoes water of eastern flank; 3—formation water of oil field from western flank; 4—formation water of oil field from eastern flank

Kura oil-gas bearing region (western flank) and Cheleken (western flank). According to the isotopic composition of hydrogen and oxygen the waters of absolutely all mud volcanoes differ essentially from formation waters of oil-gas fields and are characterized by enrichment with deuterium (δ D) (+3‰to−52‰) and δ ^{18}O (−0.4‰to−17.2‰) (Fig. 4b).

According to the isotopic composition the waters of mud volcanoes refer to a dehydration and metamorphogene type (Guliyev and others 2001; Huseynov and others 2003). In comparison with formation waters of oil-gas fields, they contain very high concentrations of metal (e.g., Sr: up to 153 mg/l, Ba: up to 117 mg/l, Mo: 0.185 mg/l, Fe: up to 84 mg/l, Mn: 1.5 mg/l, Cu: up to 25.5 mg/l, Pb: up to 8.8 mg/l, U: 0.0045 mg/l, Ra: up to 4.9×10^{-7} mg/l). Also waters contain very high concentrations of B, I, Br, Zn, Ta, Hg, As. An intensive deposition of sulfide ores takes place on the eastern flank (Cheleken peninsula) of the SCB in craters of mud volcanoes from discharging waters.

Gas hydrates: The chemical composition of gas hydrates is methane (58.7–87.8%), ethane (10.4–19.4%), propane (1.6–15.8%), butane (0.4–2.68%), and pentane (0.00–0.68%). Isotopic composition of methane carbon varies from −44.8‰ to −55.3‰, and ethane from −28.4‰ to −25.7‰.

Deep sources: Mud breccia emanated to the surface by the mud volcano consists of rock fragments composting the stratigraphic series on which this volcano locates. Petrographic and paleontologic studies of rock-ejects show that the "roots" of the majority of the mud volcanoes of the western flank of the SCB are related to the Cretaceous and Paleogene-Miocene deposits. In some volcanoes the age of the breccia is Pliocene-Quaternary.

Generally, there is observed a clearly expressed rejuvenation of eruption products and a reduction of part of the Cretaceous and Paleogene microfauna up to their full absence in composition from the flank zones towards the basin center (from the northwest to the southeast). So, the "roots" of the mud volcanoes in this direction move from the Cretaceous deposits into the upper-lying stratigraphic horizons.

The quantitative calculations based on experimentally revealed dependence between the ICC of ethane and the level of its maturity (Ro) δ $^{13}CC_2H_6$ (‰)=22.6 lg R_o (%)−32.2 (Faber 1987) and the relationship of "Ro-T°C-Depth" also shows the correspondence of centers of mud volcano gas generation to the different hypsometric and stratigraphic depths according to their location in the SCB. The ethane maturity in these volcano gases is 1.3–1.79% (Ro). Proceeding from the measures of Ro in the SCB up to a depth of 6,100 m and extrapolation of its values up to deeply seated horizons, the hypsometric depth of ethane correspondence of the studied mud volcanoes in the region is within 6–8 km (Huseynov and others 2000, 2003; Guliyev and others 2001a, 2001b). In the northern and northwestern flank parts of the basin these depths are corresponded to the Mesozoic complex of the deposits. In more submerged parts of the western flank of the basin the center of ethane formation is at the depths corresponding to the Paleogene-Miocene complex (Fig. 1b).

The evaluation of oils' maturity of mud volcanic seeps equivalent of the vitrinite reflectance (Ro), calculated on degree of sterane aromatization (C_{28} triaromatic/C_{28} triaromatic + C_{29} monoaromatic) shows a low level of their maturity (Ro=0.46–0.64%).

Thus, different levels of maturity of hydrocarbonaceous gases and oils of the mud volcanoes show that sources of oil- and gas formation are displaced relative to each other and confined to different hypsometric and stratigraphic levels.

The above mentioned testifies of the existence of some stratigraphically isolated sources of hydrocarbon formation in the Mesozoic, Paleogene-Lower Miocene and Middle-Upper Miocene (Diatom suite) deposits. It means that in conditions of the SCB with a thickness of sedimentary filling reaching 25–30 km and a lower geothermic gradient one can expect a very extended interval of oil-gas formation. Results of the modeling of zones of HC generation in the most subsided central part of the South-Caspian oil-gas bearing basin (Zafar-Mashal- Alov area) allow the prediction of the presence of a large source of oil and gas generation reaching to 8–10 km with an upper border at a depth of 10 km and lower one at 18–20 km (Guliyev and others 2001). The presence of such a thick zone of "oil" and "gas" window in the central part of the SCB allows the prediction of the involvement of the whole complex of deposits of different stratigraphic age (from the Mesozoic up to Lower Pliocene) into the zone of hydrocarbon formation. It allowed the authors to suppose the existence of a strong fluid flow in this zone.

Results of complex geochemical and hydrochemical studies of the bottom sediments, oozy solutions and waters of the Caspian Sea confirmed this supposition. At the same time in the bottom sediments and mud volcanic breccia of the mentioned abnormal zone there had been revealed significant accumulations of gas hydrates. The estimated maturity of ethane calculated on dependence of $\delta^{13}C$ C_2H_6–Ro is 1.47–1.94%. It corresponds to the depth of over 10 km and the stratigraphical correspondence of gas generation centers to the Miocene-Paleogene deposits (Javadova and others 2001).

The presence of volcano groups confined to the large mud volcanic caldera structure Alov can be examined as a channel of the fluid flows migration to the surface and a factor of the formation of the multicomponent geochemical anomaly on sea bottom sediments.

Timing of mud volcanic fluid dynamics activity in the South Caspian and its environmental impact

According to the data of deep seismic and drilling mud volcanic activity in the South Caspian Basin, it started in the Lower Miocene. The highest intensity was reached at the boundary of the Miocene and Pliocene and was associated with dramatic Caspian Sea level fall in the Lower Pliocene of between 600 and 1,500 m (Reynolds and others 1998), which led to the isolation of the PaleoCaspian from the Eastern Paratethys. Catastrophic reduction of PaleoCaspian size (Fig. 5) was accompanied by an increasing scale of mud volcanic activity. The last point is proved by seismic data analysis where buried paleovolcanic cones and other types of mud volcanic structural-morphology elements in the Lower Pliocene (Productive Series) sedimentary complex are very well shown (Fig. 6 a,b). As a result the over saturation and intoxication of water by methane led to a mass extinction of mollusks, fishes and other groups of sea inhabitants. In the Upper Pliocene and Quaternary mud volcanism occurred under the conditions of a semi-closed sea periodically connected with Pontian and Mediterranean Basins (Fig. 5). Those stages of Caspian Sea history are characterized by the revival of the Caspian organic world.

Volumes of fluxes—emanated hard, liquid and gaseous products as well as sizes of mud volcanic bodies show the scales of influence of mud volcanic oil-gas manifestations upon the environment and the processes occurring in the South Caspian depths in geological time and present days. The conducted calculations had shown that the general volume of mud volcanic breccias emanated from 220 onshore volcanoes over an area of about 5,900 km^2 is 100–110 million km^3. The area covered by mud volcanic breccias is absolutely unsuitable for agricultural use. Water emanating from volcanoes forms salt lakes, strongly salinize and contaminate the soil and ground waters over a vast territory with heavy metals.

Oils emanating from onshore mud volcanoes form oil lakes and vast covers of oil-saturated rocks. At the same time large-scale contamination with oil of territories adjacent to volcanoes is a reason for high radioactivity. Even being in the state of a relatively "quiet" mud volcano represents an actively functioning gas-emanating system, causing a great negative influence upon the environmental state. Regime observations in the onshore of Azerbaijan show that daily medium mud volcanoes emanate into the atmosphere 2,200–4,000 m^3 of gas. About 250 mln m^3 of gas is emanated per year by all onshore mud volcanoes during calm activity. Upon eruption a volcano emanates from 20 million to 500 million m^3 of gases. Every year an average of two volcanoes erupt onshore Azerbaijan, therefore, the total volume of the ejected gases can prevail at 1 billion m^3 (Yagubov and others 1971; Aliyev and others 2002).

The influence of submarine mud volcanoes upon sea ecology, and the geochemistry of seawater and bottom sediments is great. During periods of calm activity they supply the marine basin with least 60–120 million m^3 of gases per year. Considerably larger volumes of gas are emanated by eruptions. The consequences are: (1) disturbance of the carbonate-calcium balance, origination of a reduction environment and abundant carbonate formation, (2) emphasized vertical replacement of sea waters, (3) enrichment of bottom sediments HC gases near volcanoes, and (4) development of colonies of methane oxidizing bacteria.

Here high heat flows, saturation of bottom sediments and mud solutions with liquid and gaseous hydrocarbons, carbon dioxide, nitrogen, silicate, sulfates are observed; the degree of bituminisation of organic matter increases sharply reaching 12–13% with a general syngenetic

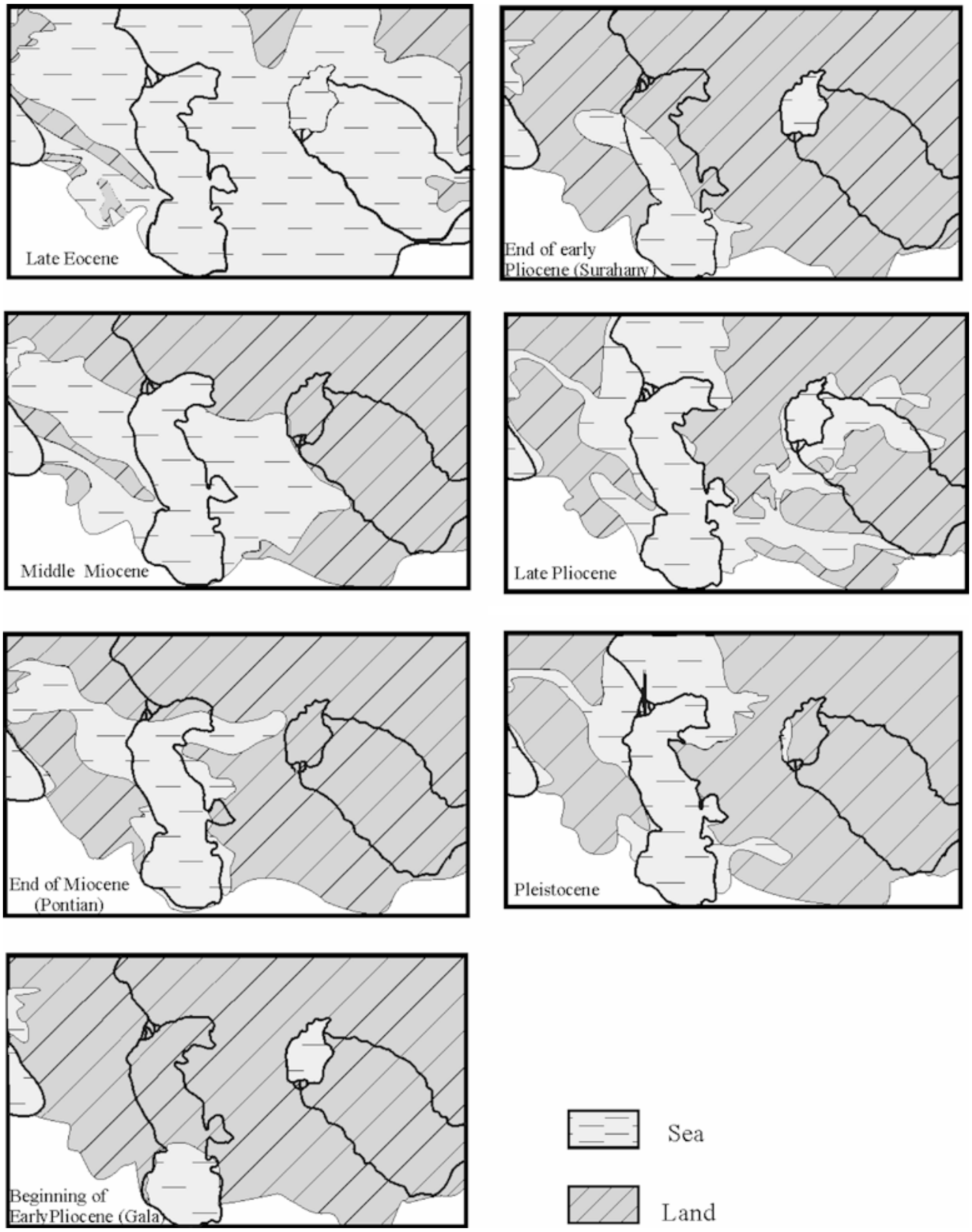

Fig. 5
Paleogeography of the Eastern Paratethys in the Cenozoic (Vinogradov and others 1968)

background of 3%, i.e. a supplied environment and favorable state for activity of microorganisms, bottom fauna and flora arises. Studies conducted in different seasons in a region of groups of the underwater volcanoes (Shah-Gum) and sea areas where volcanoes are practically absent (Lenkaran-Astara) show the degree of influence of mud volcanic activity upon the state of bottom organisms. Results are given in Table 2; it is noticeable that biomass and density of benthos is higher in regions of mud volcanism development than where the last is absent. However when submarine volcanic eruption occurs the influence of mud volcanoes on the Caspian sea ecology is very bad. This may be illustrated by events of 2000–2001. This period is characterized by the maximum seismic, mud volcanic activity for the last 15 years and an intensive hydrocarbon fluid dynamic in the Caspian Sea as a result of underwater eruptions. It is very important to note that during the spring of 2001 in the Caspian Sea the death of a huge mass of anchovy and macro-eyed sprats, which live at a depth 50–100 m and more in an open deep part of the sea, was observed (Katunin and others 2002). This large-scale phenomenon during the period of the migration of sprats had no analogues in the last life of the Caspian Sea and has caused significant damage to industrial fishing. The death of sprats was observed in the area of the Middle Caspian Sea and near the western coast of the South Caspian Sea. The extinction of sprats had not been marked along the east coast of the South Caspian Sea where amounts of submarine mud volcanoes are much less. Special places of the environment of the Caspian Sea and the surrounding area have gas hydrates associated with submarine volcanism. There are large accumulations of gas hydrates confined to bottom sediments of the Caspian Sea mud volcanoes crater fields (interval 0–0.4 m, sea

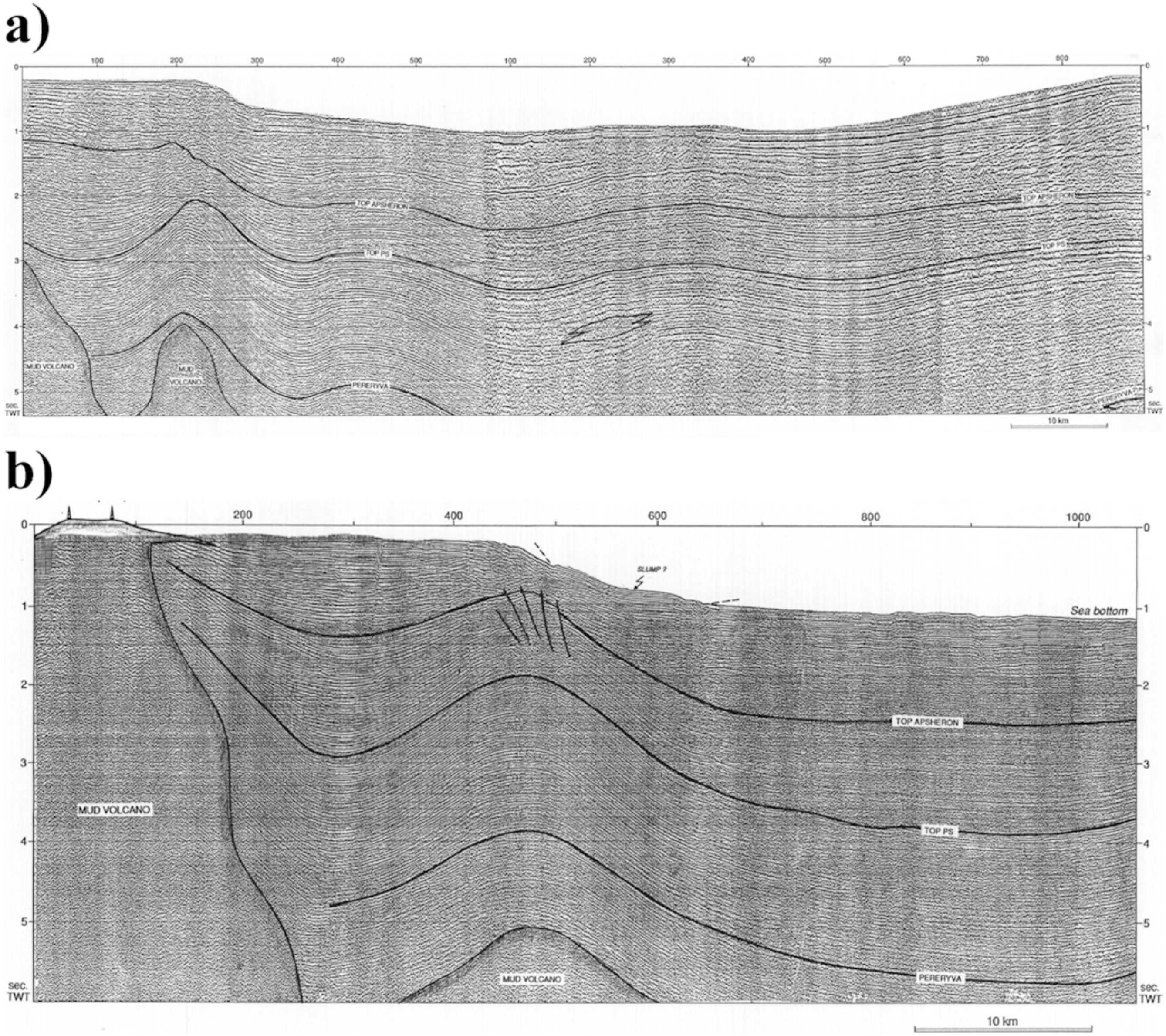

Fig. 6a, b
Seismic profiles across buried and active mud volcanoes in different parts of South Caspian: (**a**) Absheron archipelago; (**b**) deep-water part

depth 480 m) and to volcano bodies at the depth of 480–800 m from the sea bottom. Resources of HC gases in hydrate-saturated sediments up to a depth of 100 m are estimated as 0.2×10^{15}–8×10^{15} m^3 (Muradov 2002). According to the average rate of sedimentation in these parts of the Caspian Sea (2 mm/year) the age of submarine gas hydrates is not older than 200 years. The amount of HC gases concentrated in them is 10^{11}–10^{12} m^3.

The Caspian Sea, being an inland closed basin is very sensitive to climatic and tectonic events expressed in sea level fluctuations. In regressive stages as a result of sea level fall and reduction of hydrostatic pressure the decomposition of gas hydrates and the releasing of great volumes of HC gases consisting mainly of methane are observed. According to paleogeographical and paleotectonic reconstruction, paleoseismic and geochemical data very good conditions for large gas hydrate formation and accumulations existed in the South Caspian Basin in the Late Miocene (Pontian). Consequently, the dramatic sea level fall in the Lower Pliocene could provoke destabilization of gas hydrates and massive release of hydrocarbon gases to the water column that brought strong intoxication to marine water also.

Monitoring of mud volcano fluid dynamics and natural disasters prediction

Monitoring of mud volcanoes onshore of the South Caspian demonstrated that any eruption is predicted by seismic activation in the region (south-eastern Caucasus) and intensive fluid dynamics on the volcanoes and around the last ones. The latter is expressed by the

Table 2
Biomass (g/m^2) and density ($spec./m^2$) of benthos in the South Caspian

Organism	Lenkaran-Astara				Shah-Gum			
	Winter		Summer		Winter		Summer	
	Biomass	Density	Biomass	Density	Biomass	Density	Biomass	Density
Nereis diversicolor	2.3	142	3.44	504	4.23	222	18.89	2,119
Rhithropanopeus harrisii	5.44	40	3.47	82	2.81	20	3.62	371
Balanus improvisus	35.07	1,361	6.56	386	26.05	980	10.73	177
Mytilaster lineatus	50.07	191	6.74	204	119.9	570	42.55	6,942
Cerasstoderma lamarskii	19.47	32	38.23	80	54.33	1,112	134.7	937
Abra ovata	3.14	44	23.73	1,269	14.35	2,398	49.24	34.27
Total	**115.5**		**82.17**		**221.6**		**259.7**	

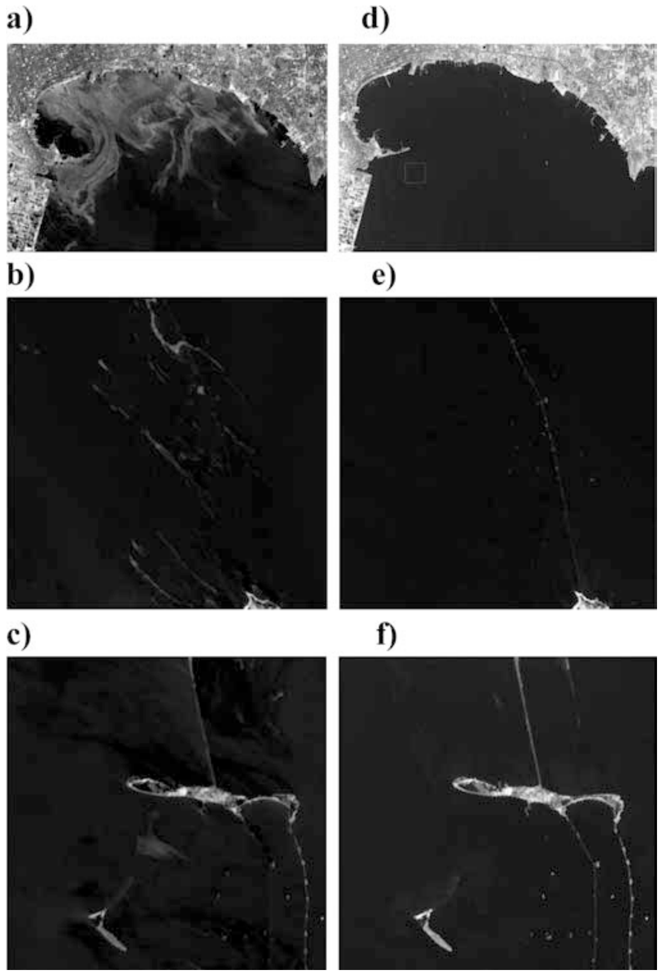

Fig. 7a–f
a,b,c ASTER image of oil slicks in three different areas of Caspian Sea acquired on 23 July 2000. Four months before the November 25th earthquake. Magnitude of the earthquake estimated to 6.8. **a** Baku Bay. Strong oil slick is a result of fluid emission from Bibieybat's volcano submarine channel; **b** north-western from Pirallahi Island (north-east of Absheron peninsula); **c** between Gum and Vulf Islands (south-east from Baku); **d,e,f** ASTER image same areas acquired on 20 August, 2001. Eight months after the November 25th earthquake. Sea surface is absolutely clear of oil. Processed band 3, 2 and 1

arising of mineral springs, renewing of mud, gas and oil discharge out of crater fissures and sleeping gryphons. The regime observations of the mud volcanoes of the Black-Caspian Sea region allowed the revealing of a range of geochemical indices, and their relation with the seismicity. The gas component change is considered as such indices on the volcanoes of the Kerch peninsula: CO_2 in gases of the mud volcanoes and mercury (Hg) in the atmosphere of their location region. On the mud volcanoes of onshore Azerbaijan the increase of gas debits was established, and the significant increase in the share of carbon dioxide (CO_2), nitrogen (N_2) and helium (He) in its composition. The increase of these components in gas composition precedes the earthquake.

The energy accumulation in the earthquake sources reflects on the change of definite dynamic and geochemical fields of the mud volcanoes. The elevations of covers of early eruptions cause the formation of some concentric and radial fractures from some centimeters to 1.0–1.5 m which often precede the great mud volcanic eruptions. These fractures are additional ways for fluid flow emphasizing gaso-geochemical and thermal anomalies of the mud volcano on the size and intensity as well. The increasing dynamic tension of the depths, passing on the mud volcano center and its outlet channels during the seismoactive periods and before the mud volcanic eruption reflect on the rate and volume of the mud and breccia emanated from the mouth. It is necessary to point out that the eruptive channel of the mud volcano is a channel on which the more intensive passing of depth heat to the day surface takes place. The latter influences upon the unusual character of the depth heat distribution in the sedimentary cover within the territory adjoining the mud volcano. The agents transporting the depth heat to the surface are known fluids, the gases and water in the present case. This means that the quantity of the transporting heat (or heat flow) is determined by the fluid dynamics of the mud volcanic system, which, as was mentioned above, reacts closely to seismic activity of the territory.

More than 80% of epicenters of earthquakes which occur in the region (south-east Caucasus) is situated in the Caspian Sea. Hence, activation of fluid dynamics in the

Caspian Sea floor preceding eruption of mud volcano, earthquake and seismicity on the whole should be manifested in the sea surface, by the arising of fresh oil slicks and muddy spots. This is proven by the above-mentioned seismic events of 2000–2001 in the South Caspian and intensive oil-gas pollution of the Caspian Sea as a result of underwater mud volcano eruptions and active fluid dynamics. The beginning of fluid dynamics activization on mud volcanoes in the Caspian Sea preceded a strong earthquake in Baku and the surrounding area in 2000, November 25th with a magnitude of 6.8 at least four months before. This very active fluid dynamic appearing on the sea surface as strong oil slicks is clearly fixed on the ASTER image of July 23, 2000 around Absheron peninsula in different parts of the Caspian Sea (Fig. 7 a,b,c). Observation of the same areas eight months after the November 25th earthquake when the seismic activity in the South Caspian region had significantly weakened, it was revealed that the sea surface was absolutely free of oil (Fig. 7d,e,f).

Conclusions

The South Caspian sedimentary basin is a unique area with thick Mesozoic-Cenozoic sediments (up to 30–32 km) characterized by an extremely high fluid generation potential. A great amount of active mud volcanoes and the volume of their gas emissions prove the vast scale of fluid generation. From onshore and offshore mud volcano estimations there annually erupt more than 10^9 m^3 of gases consisting of CH_4 (79–98%), and a small admixture of C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, CO_2, N, H_2S, Ar, He.

The large accumulations of gas hydrates take place in bottom sediments deposited in mud volcano fields (interval 0–0.4 m, sea depth 480 m) and in volcano bodies at the depth of 480–800 m from the sea bottom.

Isotope-geochemical studies show that fluids had been generated by Mesozoic, Paleogene and Miocene complexes and the fluid generation zone is very extended reaching 8–10 km and extending to basement—20 km.

Mud volcanic fluid dynamics in the South Caspian Basin are closely related to seismic and solar activity.

Mud volcano fluid dynamics have an enormous influence on land and Caspian Sea ecology.

It is impossible to prevent the depths' degassing, but the prediction, true estimation and control for areas of distribution of gas and oil contamination of mud volcanic areas during the eruptions of mud volcanoes and their "quietness" is a really solvable and important task. In this connection it is crucial to determinate the dependence between the activities of processes of the mud volcanic areas degassing—the significant suppliers of the hydrocarbonaceous gases into the ocean, atmosphere and climate global changes (Etiope and Klusman 2002; Judd and others 2002; Milkov and others 2003). The present problem comes from the frames of a separate country and the geologic science as well; therefore it requires the consolidation of the efforts of researchers worldwide and scientific methods.

The important environmental aspect of mud volcanism is the development of qualitative and quantitative criteria of prediction of catastrophic mud volcanic eruptions and the earthquakes provoking them on the basis of study of the dynamics of variation of the geochemical and physical fields on the mud volcanoes together with data of the regional seismic activity.

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References

Aliyev ChS, Feyzullayev AA, Zolotovitskaya TA (2001) Peculiarities of radioactive fields of mud volcanoes of Azerbaijan. Geophysics News in Azerbaijan 3:25–32

Aliyev AA, Guliyev IS, Belov IS (2002) Catalogue of recorded eruptions of mud volcanoes in Azerbaijan (for period of years 1810–2001). Nafta Press, Baku, 87 pp

Etiope G, Klusman RW (2002) Geologic emissions of methane to the atmosphere. Chemosphere 49:777–789

Faber EZ (1987) Isotopengeochemie gasformiger Kohlenwasserstoffe. Erdole Erdgas Kohle 103:210–218 (in German)

Feyzullayev AA, Huseynov DA (2002) Peculiarities of oil-gas formation within Baku archipelago. Azerbaijan Oil Industry, Baku, N4, pp 1–5

Gorin VA, Buniatzadeh ZA (1971) Deep faults, gas-oil volcanism and oil-gas pools of the western flank of South Caspian depression. Azerbaijan State Publishing House, Baku, 190 pp

Guliyev IS, Aliyeva EH, Huseynov DA (2001) Deep sources of hydrocarbon formation in the South Caspian basin. Proceedings of Geology Institute, Baku, No 29, pp 79–99

Guliyev IS, Feyzullayev AA, Huseynov DA (2001a) Isotope geochemistry of oils from fields and mud volcanoes in the South Caspian Basin, Azerbaijan. Petroleum Geoscience 7(2):201–209

Guliyev IS, Feyzullayev AA, Huseynov DA (2001b) Isotopic composition of carbon of the hydrocarbon fluids in the South Caspian megadepression. Geochemistry, Moscow 3:271–278 (in Russian)

Guliyev IS, Huseynov DA, Aliyeva EG (2001) Mud volcanoes in the South Caspian basin-deep sources and dynamics of development. In: Natural Hydrocarbon Seeps, Global Tectonics and Green House Gas Emission. Delft, The Netherlands, pp 23–27

Guliyev IS, Kadirov FA, Reilinger RE, Gasanov RI, Mamedov AR (2002) Active tectonics in Azerbaijan based on geodetic, gravimetric and seismic data. Transactions (Doklady) of the Russian Academy of Sciences/Earth Science Section 383(2):174–177

Guliyev IS, Mamedov PZ, Feyzullayev AA, Huseynov DA, Kadirov FA, Aliyeva EH, Tagiyev MF (2003) Hydrocarbon systems of the South Caspian basin. Nafta-Press, Baku, 206 pp

Huseynov DA (2000) Origin of oils in the western part of the Kura-South Caspian oil-gas bearing basin. In: Extended

Abstracts Book, 62th EAGE Conference and Technical Exhibition, Glasgow, UK, pp A-55
Huseynov DA, Guliyev IS, Feyzullayev AA (2000) Isotope-geochemical prognosis of the stratigraphic origin of the oil seepage sources in the South Caspian. In: Abstract book of AAPG's Inaugural Regional International Conference "Oil and Gas Business of the Greater Caspian Area-Present and Future Exploration and Production Operations", July 9–12, Istanbul, Turkey, pp 28–30
Huseynov DA, Guliyev IS, Feyzullayev AA (2003) Geochemical features and sources of fluids of mud volcanoes of the South Caspian basin according of carbon, hydrogen and oxygen new isotopic data. Accepted to publication in J. Geochemistry in No 6 of 2004, Moscow
Javadova R, Muradov Ch, Feyzullayev A (2001) About Nature and stratum occurrences of gas-hydrates hydrocarbon gases in the Caspian Sea. In: Abstract book of EAGE 63th Conference and Exhibition, Amsterdam, The Netherlands,11–15 June, 561 pp
Judd AG, Hovland M, Dimitrov LI, Garcia G, Jukes V (2002) The geological methane budget at continental margins and its influence on climate changes. Geofluids 2:109–126
Katunin D, Golubov B, Kashin D (2002) Hydrovolcanism and degassing of earth bowel as the possible reason of scale death of sprats on the Middle Caspian Sea during 2001 spring. In: Abstract book of 7th International Conference "Gas in Marine Sediments", October 7–12. Nafta-Press, Baku, 93 pp
Knapp JH, Diaconescu CC, Conner JA (2000) Deep seismic exploration of the South Caspian Basin: Lithosphere-scale imaging of the World's deepest basin. In: Abstract book of AAPG's Inaugural Regional International Conference "Oil and Gas Business of the Greater Caspian Area-Present and Future Exploration and Production Operations", July 9–12, Istanbul, Turkey, pp 35–37
Lilienberg DA (1999) Morphostructure and tectonic-climatic mechanism of the Caspian Sea level fluctuation. In: Recent tectonic and its impact on formation and location of oil-gas pools. Nafta Press, Baku, pp 112–124
Mamedov PZ (1991) Seismostratigraphic studies of the geologic structure of the South Caspian megabasin in connection with the prospects of petroleum presence. Doctoral dissertation, Geology Institute, Baku, 491 pp
Mekhtiev ShF, Khalilov EN (1988) How the Earth develops. Znanie, Baku, 23 pp
Milkov AV, Sassen R, Apanasovich T, Dadashev FG (2003) Global gas flux from mud volcanoes: A significant source of fossil methane in the atmosphere and the ocean. Geoph Res Lett 30(2):9.1–9.4
Muradov ChS (2002) Estimation of resources of gas in gas hydrate accumulations of Southern Caspian Sea. In: Abstract book of 7th International Conference "Gas in Marine Sediments", October 7–12. Nafta-Press, Baku, pp 149–150
Reynolds AD, Simmons MD, Bowman MB, Henton J, Brayshaw AC, Ali-Zade AA, Guliev IS, Suleymanova SF, Ataeva EZ, Mamedova DN, Koshkarly RO (1998) Implications of outcrop geology for reservoirs in the Neogene Productive Series: Absheron Peninsula. AAPG Bulletin 82:25–49
Vinogradov AP, Keller BM, Predtechenskiy NN, Nalivkin VD, Pozner VM (1968) Atlas of lithology-paleogeographical maps of the south of USSR, Vol. 4. GUGK, Moscow
Zonenshine LP, Kuzmin MI, Natanov LM (1990) Tectonics of the lithosphere plates of the USSR territory, Book 2. Nedra, Moscow, 400 pp
Yagubov AA, Alizade AA, Zeynalov MM (1971) Atlas of mud volcanoes of Azerbaijan. Baku, Publishing house of the Academy of the Sciences, 258 pp