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Geological Conditions and Peculiarities of the Mud Volcanoes Formation

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Examination of the geographical distribution, geological and tectonic environment in which mud volcanoes (MV) occur shows that, although they are found throughout the world, they are mainly associated with sedimentary oil-gas bearing basins within the Alpine-Himalayan and Pacific Ocean mobile belts, i.e. zones in which earthquakes and intense modern earth's crust movements have been observed. Such oil-gas bearing basins are characterized by high sedimentation rate in Cenozoic time (more than 1 km/M.y.), significant thicknesses of sedimentary cover (>10 km), low thermal regime (<200C/km temperature gradient) and abnormal high pore pressures. Depending upon the values of these parameters the development of mud volcanism is characterized by the space inequality within the limits of abovementioned tectonic belts. So, MV have been noted only in 26 of more than 170 hydrocarbon-bearing and prospective basins within mobile belts. Besides, while the number of mud volcanoes is over 300 in Azerbaijan (South Caspian Basin), only one volcano is known in Mexico and two in Ecuador and China.

MV mainly formed along faults where the critical stress of breakthrough is less than that of abnormally high pore pressure in the volcanic kitchen. Formation of volcanoes happen as a result of system equilibrium violation evoked by seismic and tide waves. For example, tens of earthquakes with different magnitude are annualy recorded within the South Caspian Basin (SCB). It is necessary to mention that all earthquakes have shallow focus. Most earthquake hypocenters do not exceed 10-15km.

The overpressures must be an important clue as to the origin of mud volcanoes too. In rapidly subsiding basins the clay sequences are buried so quickly that they do not have time to get rid of all excess water in them, so they become overpressure.

During age-old history of MV study in Azerbaijan main peculiarities of their distribution, morphology, geological composition, activity and content of their products (breccia, rock fragments, gas, oil, water), and also character of their manifestation in geophysical fields were discovered. It was established that MV distribution in SCB is also unequal. They are mostly developed onshore (about 200 MV); in the southern part of the Caspian Sea their amount is about 160. At the same time, onshore MV are mainly concentrated in SE subsidence of Greater Caucasus and about 80% of offshore MV is located within sea depths which do not exceed 100m (table 1). Some offshore MV (in shallow water area) form permanent or temporary islands and numerous submarine banks.

Table 1 Distribution of offshore MV in SCB

Depth of seabed, m	0-100	100-200	200-300	300-400	400-500
Number of MV, %	78.5	8.2	4.1	4.6	4.6

Azerbaijan has no equal around the world not only in MV development density but also in their sizes (up to 400m high), variety of forms and eruption frequency. MV are clearly recognizable on satellite images. They are confined to structural lineaments and associated fractures. Changes in the morphology of some MV upon eruption can be detected from a series of images of pre-dating and post-dating eruptions.

MV have comparatively higher values of heat field on the background of low-heat field of whole basin.

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During last three-year period (2000-2002) about 17 MV eruptions were observed here. About 200 eruptions of MV in the SCB during 1900-2002 years were described. The world's most active Lokbatan MV erupted 21 times during historical period. MV have released during eruptions huge volumes of gases and mud. Up to several hundreds of tons of mud and several millions of cubic meters of gas can be thrown out to the surface during one eruption. So, in 1931, the Waimata Valley MV in New Zealand erupted, emitting 150,000 metric tons of mud; in 1954, the Tashmardan MV in Azerbaijan emitted 4 mil cubic meters of mud; in 1964, the Chatham MV ejected 255,000 cubic meters of mud and rock and formed island on the southern coast of Trinidad, reaching a height of 2 meters above sea level. In 1947, almost 500 million cubic meters of gas was thrown out to the atmosphere during eruption of Tourogay MV (Azerbaijan).

In periods between eruptions the MV also continuously emit CH_4. For example, the common volume of gas emitted by Charagan and Dashgil MV (Azerbaijan) is correspondingly about 44 000 m^3/year and 165 000 m^3/year during quiet period.

These data suggest that at global scale of MV are important natural CH_4 source into the atmosphere and they can play some role in formation of "greenhouse" effect. Up to now CO_2 had been considered as a main hydrocarbon gas stipulating the "greenhouse" effect. The impact of hydrocarbon gases wasn't taken into consideration. It was considered that their input into atmosphere is insignificant, due to that calculating the "greenhouse" effect usually neglected it. However, the affirmations on relatively small values of CH_4 input into atmosphere aren't correct because the geologic sources of its emission, first of all, mud volcanoes, widely developed (more than 800 MV in the world). Although methane's concentration in the atmosphere is only about 1,700 parts per billion by volume, it plays an important role in the heat budget of our planet. In order to assess the ability of each greenhouse gas to trap heat, the concept of global warming potential (GWP) was developed. The GWP is defined as the ratio of global warming from one unit mass of a greenhouse gas to one unit mass of carbon dioxide over a period of time. In regard to the global warming, methane, as a second contributor after carbon dioxide, has 21 times higher potential than carbon dioxide. Taking into consideration the above mentioned, it is very important to calculate the total contribution of MV methane in "greenhouse" effect.

The gases of MV consist mainly of methane (95-100%). There is a small amount of C_2H_6+, CO_2, N_2, He and Ar. $^3He/^4He$ ratio varies within the limits (0.28-9.0) 10^{-7} (an average $1.2*10^{-7}$) what proves sedimentary origin of these gases. The isotopic composition of carbon (ICC) in methane varies from-61.2‰ to-35.9‰ and in CO_2 from -49.6‰ to +23.1‰. The nature of isotopically super heavy CO_2 (> +5‰) has been controversial up to now. However, the result of studies, carried out within last years, revealed their biochemical origin and formation on the depths, which do not exceed 2000 m.

Table 2 Content of gas from different seepages of the same MV

Volcano	CH_4, %	C_2H_6+, %	N_2, %	CO_2, %	$\delta^{13}C$ CH_4, ‰	$\delta^{13}C$ CO_2, ‰
Shorbulag:						
a)	75.4	nd	23.6	1	-41.5	0.5
b)	96.6	nd	1.1	2.3	-50.6	-26.8
Melikchobanly:						
a)	84.1	0.9	2.8	12.1	-45.2	20.9
b)	72.3	nd	20.4	7.3	-44.7	-14
Cheildag:						
a)	80.3	nd	7.8	11.9	-43.3	2.4
b)	91.3	3.5	2	3.2	-37.3	23.1
Ayrantekan:						
a)	94.4	1.4	1.3	2.3	-49.8	-8.1
b)	85.2	nd	13.2	1.6	-47.9	-0.1

Variation of carbon isotope composition in CH_4 and CO_2 on the SCB area has certain regularity. One of the possible reasons for distinct methane ICC in different areas is the varying degree of gas preservation, in other words the degree of degassing of deposits. According to isotopic (an average methane δ^{13}C-47‰) and chemical (an average wet gas content 2.1%) analyses data, the mud volcano gases in the Lower Kura region are products of an early stage of organic matter (OM) maturity in comparison with gases of more dislocated and seismically active Shamakhy-Gobustan region (an average methane δ^{13}C-41‰, an average wet gas content 0.1%) mainly represented by methane of higher stage of OM maturity.

Change of the ICC in CH_4 and CO_2 within wide limits /even in gas seepages within the limits of one volcano (table 2)/ shows existence of several stratigraphic and hypsometric sources of these gases.

On the basis of known relationship between ICC in hydrocarbon gases and parameter of paleotemperature regime of the basin (vitrinite reflectance) depths and stratigraphic position of the strata, which might be a source for gases released by mud volcanoes, has been determined. It was established that strata feed these gases, which lies at 7km depths and lower. The stratigraphic location of these sources changes towards regional subsidence of strata (from southern slope of the Great Caucasus to the central deep buried SCB) from Mesozoic to Paleogene-Miocene.

The relationship between activity (frequency of eruption) of mud volcanoes and the ICC of methane has been determined. Active MV are characterized by the relatively heavier ICC of methane (Table 3), in other words, by deeper gas source. Besides, volcanoes, which erupt frequently, emit little or no fluids during periods between eruptions, what assists the energy accumulation in subsurface.

Table 3 Dependence between the ICC in methane and activity of the mud volcanoes

Number of mud volcano eruptions	0	1	2	3	5	6	7	8
$\delta^{13}CH_4$, %o	-50	-47.8	-45.2	-45.3	-44.6	-39.8	-41.5	-39.5

In 1979 submarine gas hydrates were accidentally discovered in the South Caspian Sea. The unusual peculiarity of this gas hydrate accumulation was its discovery first time in the world in the crater of submarine mud volcano. In 1986 and 1988 gas hydrides were also discovered in other marine mud volcanoes. A dredge sample from a mud volcano on the Vezirov anticline high consisted of blue-gray gas-saturated sediment, which contained a large amount of yellowish-white gas hydrate. These crystals were quite large (5-7 cm), and in the air they melted and disappeared. When ignited they burned with a blue flame. Gas released from hydrates has an essentially hydrocarbon composition and is characterized by very high contents of methane homologues (up to 24%). The isotope composition of carbon (ICC) in methane (-44.8…-57.3%o) suggests mainly catagenic origin of the gases (Ginsburg et al., 1992). Hydrogen sulfide was present from 0.03 to 0.07%, and there were clayey-calcareous nodules and saline pore water in the sediment with a mineralization of 26.2-30.1 g/L.

Some MV as well as gases, water and mud emit oil. Usually oils from MV are strongly biodegraded. Their ICC ranges from-28.2‰ to -24.76‰. A relationship between δ^{13}C in seep oils and reservoir oils has been established. The isotopically heavy seep oils are well correlated with Neogene reservoirs oils and isotopically light seep oils with Paleogene reservoirs oils. Biomarker analyses show that oils from both subsurface accumulations and natural seepages were formed from mixed Neogene and Paleogene sources. But, according to the fig.1, the ICC of oils becomes heavier towards the subsidence of the Miocene surface. It shows that the Miocene rocks contribution in the formation of oil pools in SCB gradually increases in this direction.

MV and petroleum accumulations are products of a single process of oil and gas formation being derivatives of distinct levels of their maturity. The fact, that most structures complicated by mud volcanoes contain commercial hydrocarbon accumulations is evidence of the aforesaid. The oil seeps from MV were generated at relatively low temperatures and appear to be low-maturity products. The present day maturity of the oils is rather low (0.65-0.80% in R_0 equivalent).

The age of mud volcano's rock-ejecta varies from Cretaceous to Pliocene. Maturity degree (Ro) of the Paleogene-Neogene rocks from MV varies from 0.71% to 1.49% (table 3).

Table 3 Vitrinite reflectance data of the mud volcano's rock-ejecta, SCB

Volcano	Age of rock ejecta	Ro,%
Bozdag-Gyuzdek	Paleogene	1.27
Bozdag-Gyuzdek	Miocene	0.86
Jagirli	Paleogene	1.35
Gushchi	Miocene	0.73
Gushchi	Miocene	0.71
Gushchi	Paleogene	1.03
Gushchi	Paleogene	0.85
Suleyman-Akhtarma	Neogene	0.99
Maraza	Miocene	0.72
Tourogay	Miocene	0.88
Keyreki	Paleogene	1.49

Thus, it was established, that the depth location of solid and liquid products of MV is different. According to the geochemical analyses, organic matter in mud volcano's rock-ejecta is referred chiefly to type II-III.

Despite occurrence at great depths rock-ejecta still retain good reservoir poroperm characteristic (table 4). It shows existence of favorable conditions for accumulation of hydrocarbons in the deep horizons of SCB.

Table 4 Reservoir quality parameters of the mud volcano's rock-rejecta, SCB

Mud volcano	Age of Rock-ejecta	Type of Rock	Carbonate content, %	Porosity, %	Permeability, md
Dashgil	Eocene	sandstone	0.1	10.1	21.4
Dashgil	Eocene	limestone	52.6	13.4	3.4
Dashgil	Eocene	Siltstone	3.4	14.6	10.7
Tourogay	Eocene	sandstone	17.1	27.7	50
Kichik Kharami	Eocene	sandstone	18.3	12.8	22.4
Agzybir	Eocene	Tuff-silt	8.1	15.3	56.8
Cheildag	Eocene	Siltstone	7.6	16.7	5
Dashmardan	Eocene	limestone	49.6	25.6	243.2
Ayrantekan	Eocene	sandstone	4.5	10.1	12.7

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It is known, that organic matter rich sediments in general, can be particularly radioactive due to the tendency of radionuclides to be absorbed by organic molecules. In case if organic rich Maykop (Oligocene – lower Miocene) rocks prevail in ejected mud the level of radioactivity on such MV is the highest. As a rule, radioactivity of breccia (particularly fresh-ejected breccia) is usually higher (on 3-5 mR/h), than those of surrounding rocks. Uranium (radium) play major role in formation of radioactivity field of MV.

Waters released by MV are weakly mineralized, containing mainly bicarbonates and sodium. The chemical compositions of the mud volcano waters are identical with formation waters, but differ by the isotope represented by abnormally heavy hydrogen in H_2O ($\delta^{13}O$ from +3.8 to +18‰ and δD from-10 to-25‰).

Comparison of MV of Northern Italy (Po Basin) and Azerbaijan (South Caspian Basin) showed that they have common geological history of formation because they are arranged within the limits of a unified geostructural zone - Alpine-Himalayan tectonic belt. For this reason, the results of the comparative analysis have revealed a resemblance of the geochemical and isotope composition of waters and gases of MV of Italy and Azerbaijan. At the same time some distinctive features in the quantity, sizes and activity of MV were detected.

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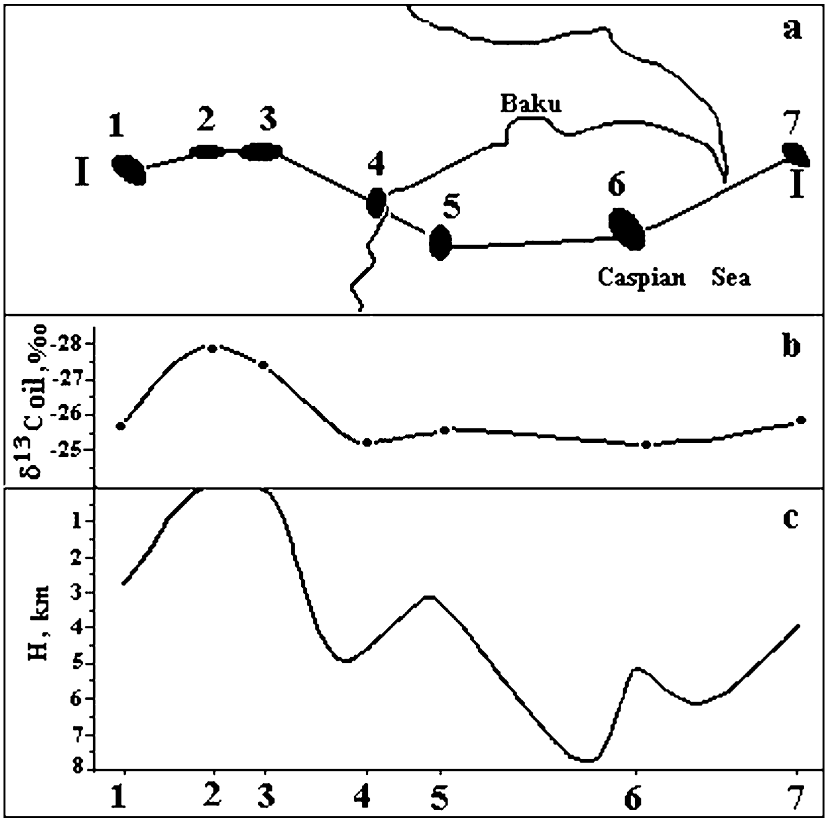

Fig. The change of the oil carbon isotope composition (b) and the depth occurrences of the surface of the Miocene deposits (c) along of the profiles I-I (a) : 1-7 – numbers of fields