UDC 54,02;55

ISOTOPIC GEOCHEMISTRY OF MUD VOLCANO FLUIDS

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This work is focused on the study of isotope geochemical characteristics of mud volcano fluids on the basis of 39 objects of research within the territory of Shamakhy-Gobustan and Low Kura oil and gas bearing regions of Azerbaijan. Chemical and isotopic composition of gases and waters of mud volcanoes are considered in the paper. As the results of fluid studies show, methane (86-95%) is the predominant gas, the isotopic composition of methane carbon changes in the range from - 61‰ to -25‰, carbon dioxide - from -39.4‰ to +30.6‰, with the total concentration in the samples not exceeding 5%. The isotopic composition of nitrogen was considered for the first time and its average value doesn't exceed -3‰.Water of mud volcanoes is represented mainly by hydrocarbonate-sodium type, and their formation depths are estimated at 2-5 km.

Keywords: *mud volcanoes, fluids, geochemistry, isotope composition*

Introduction

Geological and geochemical studies of the products of mud volcanic activity include several important aspects, and the solution of mud volcanic genesis problems, confirmation of a theory of their formation, are directly related to the results of studying the sources of mud volcanic matter, as well as physicochemical conditions of its formation and migration. The analysis of geochemical parameters of products of mud volcanic activity makes it possible to understand the connection between mud volcanism and regional geological peculiarities and endogenous processes, as well as to estimate the contribution of mud volcanic activity to the total budget of greenhouse gases in the Earth's atmosphere.

The problem of chemical and isotopic composition of mud volcanoes' fluids is addressed in the works of such scientists as K.V. Kharichkov, S.A. Kovalevsky, V.V. Weber, L.A. Potolovsky, V.A. Buinitsky, Y.G. Mamedaliyev, D.N. Ibadova, D.V. Zhabrev, V.S. Melik-Pashayev, F.G. Dadashev, S.G. Salayev, I.S. Guliyev, A.A. Feizullaev, F.I. Aliev, R.A. Huseynov, A.Y. Kabulova, A.M. Dadashev, B.M. Valyaev and many others.

Research area

According to data for 2015 [1], the planetary distribution of mud volcanism is limited to 42 countries, mainly within the Alpine-Himalayan, Pacific and Central Asian mobile belts. Of the world's 2505 mud volcanoes, 583 are located in Azerbaijan. However, within the republic it is not widespread on land, for example, mainly within the following oil and gas bearing regions: Near-caspian-Guba, Shamakha-Gobustan, Low Kura, Absheron archipelago. The territory of the study was limited by two regions - Shamakhy-Gobustan and Low Kura. A total of 39 mud volcanoes were considered, where samples of fluids for isotopic and geochemical studies under laboratory conditions were taken during the field studies.

The Shamakhy-Gobustan region is confined to the southeastern immersion of the Greater Caucasus, within which the Northern, Central, Southern and Shamakhi segments can be distinguished geomorphologically. There are also differences in the geological structure, as the stratigraphic section of the northern segment is characterized by the presence of upper chalk terrigenous-carbonate rocks [2.4]. The Central segment is characterized by the presence of Paleogene of Lower Miocene clays with interlayers of sand and marls (4), while the Southern segment is dominated by sand-clay sediments of the Pliocene period.

The Low Kura region is located between the folded structures of the Greater and Lesser Caucasus and has the shape of a triangle with the dimensions of 100x50x80 km and is characterized by a thick sedimentary cover of about 16 - 20 km, and most of it belongs to the Pliocene - quaternary

stage of development. It should be noted that the Pliocene-Quaternary structural deflection has a rather complicated structure. The Low Kura depression is divided into two tectonic zones: Shirvan and Mugan [2].

Research results

The chemical composition of the gas phase of the Shamakhy-Gobustan and Low Kura regions mud volcanoes activity is quite conservative - the methane content varies from 86.74 to 96.7% (extreme values belong to the mud volcanoes Akhtarma-Pashaly and Bahar (northern group), respectively), carbon dioxide from 0.6 to 5.9%, nitrogen from 0.4 to 2.83% (Fig.2.).

The content of inert components is insignificant. Small amounts of gases contain hydrogen (H_2), helium (Ne), argon (Ar).

Isotopic composition. Within the framework of this work, the isotopic composition of carbon, oxygen, deuterium and nitrogen in the mud volcanoes of Shamakha-Gobustan and Low Kura regions is considered. Current data on the geochemistry of mud volcanoes in Azerbaijan are presented in Planke et al., 2003; Guliev et al., 2004; Mazzini et al., 2009; Aliyev et al., 2009; Feizullaev, 2018; and others. Figure 1 shows the histogram of the isotopic composition of the studied mud volcanoes' fluids.

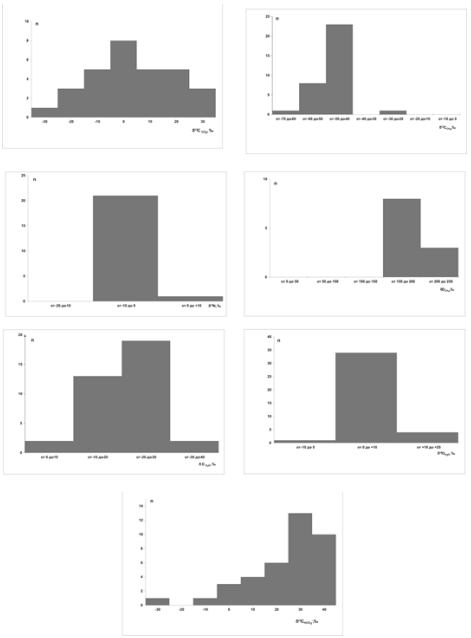

Fig.1. The histogram of isotopic composition of mud volcano fluids of Shamakhy-Gobustan and Low Kura regions

The isotopic composition of carbon (ICC) of mud volcano gases was considered in the works of Dadashev et al., 1982, Yakubova et al, 1971, Aliyev, Guliyev, Feizullaev, Huseynov, Poletayev, noted the genetic relationship of mud volcanic gases with sedimentary rocks, i.e. the roots of each volcano are confined to a limited interval of depths, despite the fact that at different times the sources of gases may be different oil and gas bearing horizons, from here and the fluctuations in the isotope composition.

As is known, both the isotopic composition of carbon in carbon dioxide and methane depends on the conditions of formation. Thus, the smallest values of δ13CCH4 = -70‰ are characteristic of biogenic methane, while the higher values correspond to the thermo catalytic methane [Galimov, 1973]. According to Prasolov, 1977; Prasolov, 1990; Prasolov, the values of δ13CH4 increase with the temperature from ~ -55‰ - T~ 100 °C to -35‰ - T ~ 300 °C.

The isotopic composition of carbon (ICC) of methane varies from -61‰ to -25‰. However, in most cases the methane ICC in mud volcano gases varies from -50‰ to -40‰. In general, the isotopic composition of methane in the spatial distribution of mud volcanoes is clearly zoned - isotopically heavy, that is, catagenetically mature gases are typical for the volcanoes of the Shamakhy-Gobustan zone (average δ13C -45‰). In the direction of the Low Kura depression, the isotopic composition of methane carbon is significantly facilitated (on average δ13C-50‰), which corresponds to the degree of maturity of the early and middle stage of catagenesis. Such zoning, as noted above, is connected with different geological conditions of HC gases formation and preservation in the sedimentary strata.

The range of mud volcanoes' ICC of carbon dioxide values is quite wide: from -39.4‰ to +30.6‰ (about 70‰), which indicates the presence of carbon dioxide of different genesis. As is known, for carbon dioxide of metamorphogenic origin the values range from +8‰ to -4‰, for thermocatalytic gas the range of values already varies from -16‰ to +2‰, for biochemical gas - 16‰ and less, and for hydrothermal gas the limits

of values correspond to the interval from -7‰ to 0‰. (Fig.2). If we consider the dependence of the change in the concentration of carbon dioxide on its isotopic composition, we can observe a correlation, i.e. positively correlate. On the other hand, according to A.A. Feizullaev, if in addition to the mud volcanoes' carbon dioxide ICC the isotopic composition of gases from oil fields is still considered, the positive values of the carbon dioxide ICC are characteristic of the structures located at shallow depths, where the temperatures do not exceed 70°C and the oil in this case are oxidized and biodegradated. Thus, the presence of isotopically heavy carbon dioxide in the mud volcanoes' gases can be considered as a sign of possible oil-bearing area of its location.

Isotopic composition of nitrogen - 28 samples were used for the first time to determine the isotopic composition of nitrogen (δ15N). It should be noted that the range of change in the values of the isotopic composition of nitrogen is not large on average -3‰, which does not provide sufficient information to identify its source in the gases of mud volcanoes.

The mud volcano water, as was mentioned by A.A. Yakubov, is represented by all four types of water, but despite this, the predominant type of water according to the classification of V.A. Sulin's (1948) is sodium bicarbonate or sodium soda water. At the same time, on a number of mud volcanoes water corresponds to the calcium chloride and magnesium chloride types. As can be seen from Figure 2, the magnesium chloride type of water is observed on the mud volcanoes of Davaboynu, Khydyrly, Neftchala south, Khydyrly, and Dashgil, and on the mud volcanoes of Yandar, Akhtarma-Pashala, and Bandovan the calcium chloride type is noted (Fig. 3.)It is worth noting that on the territory of one mud volcano, as a result of gryphone-salsa activity, water of different classes of the same genetic type and several others can be brought to the surface. Proceeding from this fact, we can conclude that within one mud volcano, griffins and salts have their own unrelated sources, channels, located, most likely, at different depths.

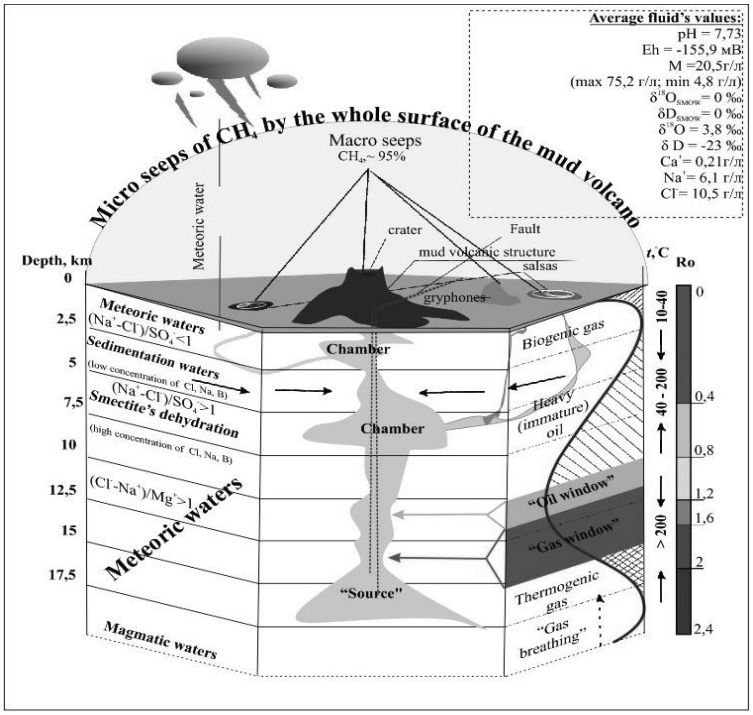

Fig. 2. The model of fluids formation in Azerbaijan mud volcanoes

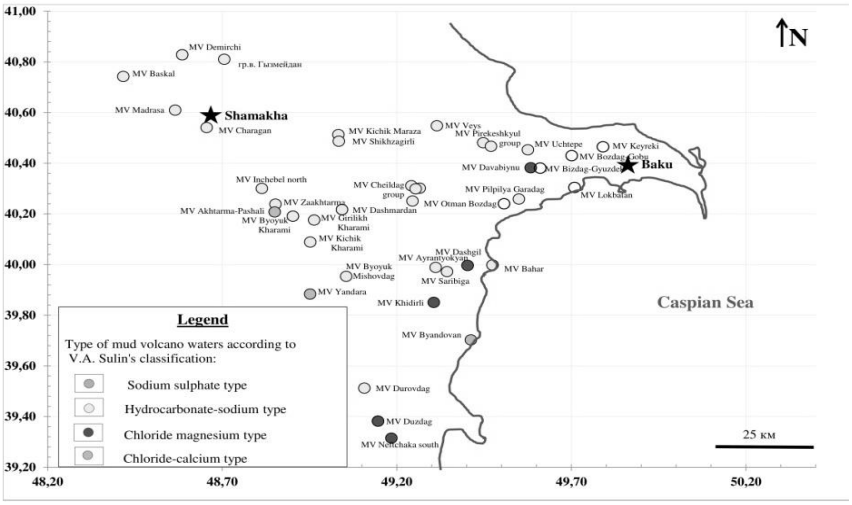

Fig. 3. Spatial distribution of mud volcanoes water phase according to V.A. Sulin's classification

This conclusion is consistent with the data of Aliyev, Buniyat-Zade, who in 1959 suggested the mixed nature of mud volcanic waters, the sources of supply of which are located in different stratigraphic horizons.

Mineralization - in most of the samples studied, the values of mineralization change in a fairly wide range from 8.2 g/l (mud volcano Demirchi (brown pulp) of Shamakhy-Gobustan region) to 75.2 (mud volcano of Neftchala Yuzhnaya – Low Kura region). However, it should be noted that the maximum value of minimum mineralization was noted on the mud volcano Baskal, also located in Shamakhy-Gobustan region. The total mineralization of mud volcano waters in Azerbaijan varies from 28 mg/eqv to 1380 mg/eqv per 100 g [3].

The content of cations (sodium, calcium, magnesium and potassium) has a positive correlation with the values of water salinity. Of these cations, sodium prevails; its content varies from 1.67 g/l Shamakhy-Gobustan mud volcano Baskal to 24.29 g/l Low Kura mud volcano Neftechala Yuzhnaya, averaging 6.67 g/l. It should be noted that in the geochemical processes sodium and chlorine ions are closely related to each other and it is between them that the direct dependence is most often observed. The content of anions - of the four most common anions (chlorine, hydrocarbonate, sulfate and bromine) only chlorine and bromine ions have a positive correlation with the value of water salinity.

The temperature of the water in the study objects varies in a wide range from 9℃ to 23.8℃, the average value of which is about 16˚C. It should be noted that the maximum values of measured temperatures correspond to salts and griffins without any activity. Most likely, this is due to the warming of the surface of the sun, as sampling was most often carried out in the summer of the day, the air temperature was about 35 - 38˚C.

Alkalinity (pH) - values of alkalinity of mud volcano waters and redox potential (ES, mV) max and min of which varies in the range from 6.51 to 8.65 and from -256 to -20 MV, respectively.

As in the case of temperature values, the maximum values of EV are also typical for mud volcanic manifestations with less or complete absence of activity (gas emission). For mud volcanoes in the Low Kura region, the alkalinity of water is 6.6 mV, which is lower than the average.

However, the data do not give an idea of the depths of mud volcano water generation and do not give any information about the water temperature at the depth. Determination of thermo baric conditions necessary for HC generation is a very important factor from the point of view of HC prediction and assessment of the investigated areas' potential. In this regard, the geothermal gradient (or geothermal stage) for the territory of Azerbaijan, the average value of which corresponds to 33 ℃/km, is more representative. Figure 3 presents data on the water phase formation temperatures of mud volcanoes based on Mg/Li geothermometer and their calculated depths taking into account the average value of geothermal gradient.

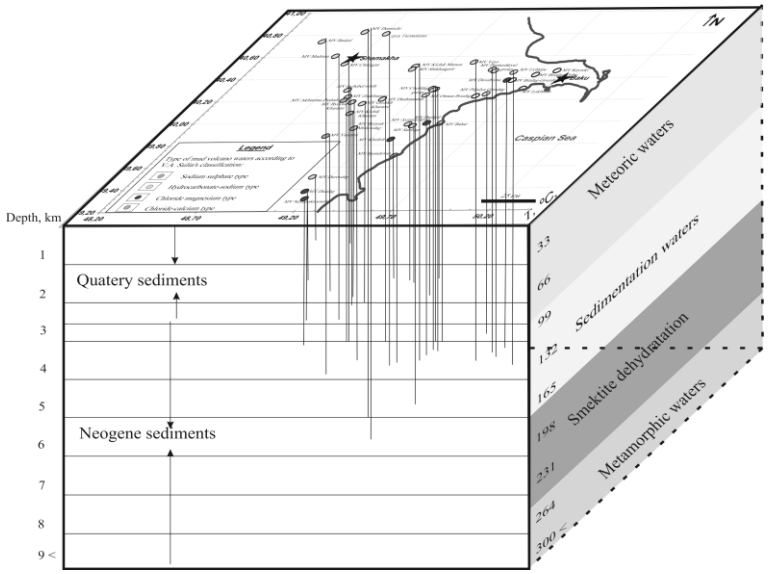

Fig.4. The scheme of mud volcano water formation by the data of geothermometers

According to Figure 4, it can be seen that the water formation depths calculated from the geothermometer do not exceed 6 km and are mainly related to either meteor or sedimentation, and the formation temperatures are not higher than 170 ℃.

Conclusion

The following conclusions can be made from the analysis of the obtained data:

- The data on the chemical composition of carbon dioxide together with the isotopic composition indicate the presence of liquid hydrocarbons within the structures complicated by mud volcanism;

- the results of the isotopic study of methane carbon show that its generation occurs at great depths;

- Formation of the water phase takes place at the depth interval from 2 to 5 km.

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PALÇIQ VULKANLARININ FLÜİDLƏRİNİN İZOTOP GEOKİMYASI

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Hazırkı iş Azərbaycanın neft-qaz bölgələri olan Şamaxı-Qobustan və Aşağı Kür çökəkliyindəki 39 tədqiqat obyektinin nümunəsində palçıq vulkanlarının flüid tərkibinin izotop-geokimyəvi xüsusiyyətlərinin öyrənilməsinə yönəldilmişdir. Bu işdə palçıq vulkanlarının su və qazlarının kimyəvi və izotop tərkibləri nəzərdən keçirilir. Flüidlərin tədqiqatı zamanı nəticələr göstərir ki, metan qazı (86-95%) üstünlük təşkil edir, metan karbonunun izotop tərkibi – 61‰-dən -25‰-ə kimi, karbon dioksid -39,4‰-dən +30,6‰-a kimi aralıq diapozonda dəyişir, ümumi qatılıq sınaqlarında isə 5%-dən çox olmur. Azotun izotop tərkibinin -3‰-dən çox olmayan ortalama izotop tərkibi ilk dəfə nəzərdən keçirilmişdir.

Palçıq vulkanlarının suları, əsasən, hidrokarbonat-natrium tiplidir, onların formalaşma dərinliyi isə 2-5 km kimi qiymətləndirilir.

Açar sözlər: *palçıq vulkanlar, flüidlər, geokimya, izotop tərkibi*

ИЗОТОПНАЯ ГЕОХИМИЯ ФЛЮИДОВ ГРЯЗЕВЫХ ВУЛКАНОВ

А.Б.Гусейнова

Данная работа сосредоточена на изучении изотопно геохимических характеристик флюидов грязевых вулканов на примере 39 объектов исследований в пределах Шамаха-Гобустанского и Нижнекуринского нефтегазоносных районов Азербайджана. В работе рассматриваются химический и изотопный состав газов и вод грязевых вулканов. Как показывают результаты исследований флюидов преобладающим газом является метан (86-95%), изотопный состав углерода метана изменяется в диапазоне от - 61‰ до - 25‰, углекислоты - от -39,4‰ до +30,6‰, при общей концентрации в пробах не более 5 %. Впервые был рассмотрен изотопный состав азота, среднее значение которого не превышает -3‰.

Воды грязевых вулканов представлены, в основном, гидрокарбонатно-натриевым типом, а глубины формирования их оцениваются в 2-5 км.

Ключевые слова: *грязевые вулканы, флюиды, геохимия, изотопный состав*