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RESEARCH ARTICLE

ORGANIC COMPOUNDS IN EJECTED ROCKS OF MUD VOLCANOES AS GEOLOGICAL AND GEOCHEMICAL INDICATORS OF SOURCE ROCK: A STUDY OF OIL SHALE IN SHAMAKHI-GOBUSTAN REGION (AZERBAIJAN)

Orhan R* and Abbasov

Department "Mud Volcanism" at the Institute of Geology and Geophysics of Azerbaijan National Academy of Sciences, Baku, Azerbaijan, AZ1143, Av. H.Javid, 119

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ABSTRACT

There are more than 350 mud volcanoes onshore and offshore in Azerbaijan, related to sediments between Paleogene and Miocene epoch. The Shamakhi-Gobustan region occupies a large area of the Greater Caucasus southeastern subsidence and is characterized by the most widespread occurrence of mud volcanoes. There are 120 mud volcanoes in the region. The region is also known as a widespread zone of surface manifestations of oil shale. Eruption of mud volcanoes finishes with emission of products at a depth of up to 6-8 km and more. These products are sole data, which contain information on geology of deep deposits of region, where have not been studied with drilling or detailed geophysical surveys. In the paper has been studied oil shale and oil-saturated rocks of the Eocene-Miocene epoch, brought from the different depths to the Earth's surface with the eruptions of mud volcanoes. The amount of organic matter in oil shale ranges between 7.56-42.55%. The results of geochemical analysis of oil shale and oil saturated rocks make possible to estimate the areas on hydrocarbon generation and accumulation in deep-seated Sediments. Also, studies in these areas provide great opportunities for exploring shale gas in Azerbaijan.

INTRODUCTION

Almost all the mud volcanic structures in the Shamakhy-Gobustan region are potentially oil-bearing. Duvanny oil and gas field is developing in Southern Gobustan (Productive series, Miocene). Commercial oil and gas content of the productive series V and VII horizons has been established (over the Garadag break-down suite) at the Dashgil mudvolcanic area; Kyanizadag gas condensate field has been discovered in the Productive series; commercial oil influx from the Miocene sediments (Chockrak horizon) has been obtained on the Dashgil structure. Eruption of mud volcanoes ends with emission of products at a depth of 6-8 km and more. These products are sole data, which contain information on geology of deep deposits of region, where have not been studied with drilling or detailed geophysical surveys [3-5]. In this regard, Shamakhy-Gobustan region is a model area to search of hydrocarbon deposits in deeper sediments. The study aimed at obtaining new information on stratigraphic intervals and depths of hydrocarbon in the study area. To clarify the potential of hydrocarbon generation in Eocene and the Maikopian deposits and its possible accumulation in relatively young rocks, the geochemical and geological indicators of mud volcanic products were analyzed. The first researches on oil shale of Azerbaijan have been carried out at the last century [9, 15, 16-19, 21, 22]. More detailed studies have been carrying out since 2000 by scientists of Institute of Geology and Geophysics of the Azerbaijan National Academy of Sciences. Employees of Department "Mud Volcanism" of the Institute have been studying geological, geochemical properties and probably reserves of oil shale [1, 2, 7, 8, 12, 13, 20].

Mud volcanoes of Shamakhi-Gobustan region

The Shamakhi-Gobustan region occupies a vast area of the Greater Caucasus southeastern subsidence and is characterized by the most widespread occurrence of mud volcanoes [23, 24, 25]. There are 120 mud volcanoes known within this region (Fig. 1).

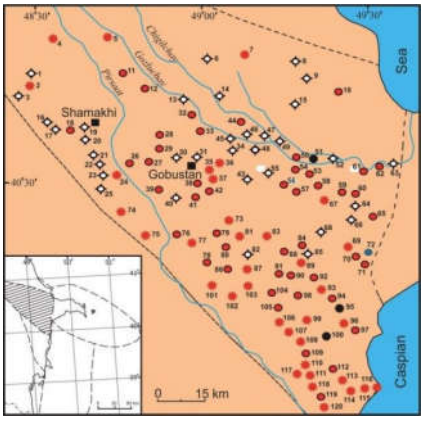

Figure 1 Location map of mud volcanoes in Shamakhi-Gobustan region

1-Sarsura; 2-Zeiva; 3-Bizlan; 4-Demirchi; 5-Gyzmeidan; 6-Yailag-Tudar; 7-Gasymkend; 8-Kekhnagyady; 9-Kemchi; 10- Kurkachidag; 11-Hajyly; 12-Khilmilli; 13-Garayaz; 14-Agdere; 15-Shikhandag; 16-Nohur; 17-Garanohur; 18-Madrasa; 19-Sarabil; 20- Kyalakhana; 21-Osmanbeili; 22-Charhan; 23-Nyuidi; 24-Melikchobanly; 25-Gyrlyg-Geoglyar; 26-Chyragly; 27-Akhar-Bakhar; 28- Jeirli; 29-Chalov; 30-Maraza; 31-Gurbanchi; 32-Nabur; 33-Chaigur-banchy; 34-Shimshadi; 35-Kichik Maraza; 36-Bozaakhtarma; 37-Shikhzarli; 38-Shorsulu; 39-Ekakhana; 40-Makhlajik; 41-Arabgadim; 42-Juan; 43-Gaiblar; 44-Yeldarasi; 45-Garajyuzlyu; 46-West Tuva; 47-East Tuva; 48-South Tuva; 49-Siyaki; 50-west Veis; 51-East Veys; 52-Neftik; 53-Jengi; 54-Syungur; 55-Iyimish; 56-Birgut; 57-Donguzdug; 58-Baygushlu; 59-Sarydash-Bayanata; 60-Gyrdag; 61-Pirekeshkul MV group; 62-Agdag; 63-Arbat; 64-Gyrgyshlag; 65- Boransyz-Jylga; 66-Agzygyr; 67-Garyja; 68-Charani; 69-Chapilmish; 70-Shakhgaya; 71-Chukhuroglybozu; 72-Gazanagyl; 73- Sheitanud MV group; 74-Gushchu; 75-Kolany; 76-Baidar; 77-Ayazakhtarma; 78-Ilkhychy; 79-Sheikh Novruz; 80-Sundi; 81- Nardaranakhtarma MV group; 82-Kyurdamich; 83-Suleymanakhtarma; 84- Cheilakhtarma; 85-Gadridere; 86-Hajiveli; 87-Agnohur; 88-West Cheildag; 89-East Cheildag; 90-Galandarakhtarma; 91-Umbaki; 92-West Davalidag; 93-East Davalidag; 94-Utalgi; 95- Agtapa; 96-Beyuk Kyanizadag; 97-Goturlug; 98-Gylynch; 99-Toragay; 100-Kichik Kyanizadag; 101-Hajivelieri; 102-Dashmardan; 103- Shekikhan; 104-Agdam MV group; 105-Arzani; 106-Durandag; 107-Gotur; 108-Agtirme; 109-Emjek-emjek; 110-Solakhay; 111-Oyoug; 112-Gyogyarchin; 113-Dilyangyaz; 114-Dashgil; 115-Bala Bahar; 116-Bahar; 117-Garakyura; 118-Airanteken; 119-Saryboga; 120- Goturdag.

The northern part of the region contains small volcanoes; relatively large ones are Demirchi, Gyzmeidan and Khadjyly. The largest and most active volcanoes are located in the south-eastern part (Fig. 2).

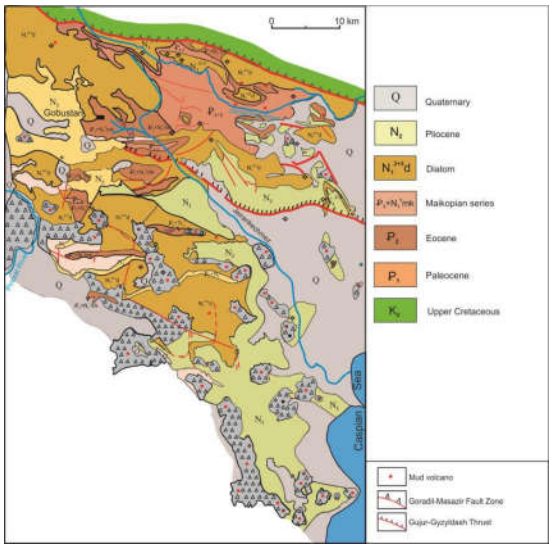

Figure 2 Geological location map of mud volcanoes in the Central and Southern Gobustan [10]

Mud volcanoes with absolute marks up to 400 m (Toragay, Boyuk Kyanizadag, Davalidag and others) are located within Jeirankechmez depression. The Alyat ridge, bordering the lower Kura region in the south is characterized by a widespread occurrence of different in the sizes and manifestation type mud volcanoes such as Dashmardan, Solakhay, Airanteken, Garakyure and etc.

Oil shale of Shamakhi-Gobustan region

The most widespread areas of oil shale in the Republic are observed in Shamakhi- Gobustan, Absheron, Pre-Caspian-Guba, Vandam-Lahij and others regions (Fig. 3). There are more than 60 surface manifestations of oil shale in these regions [1, 2, 8], and which 30 of them have found developed in the study area that distributed in a wide stratigraphic range (mainly from the Eocene to Miocene).

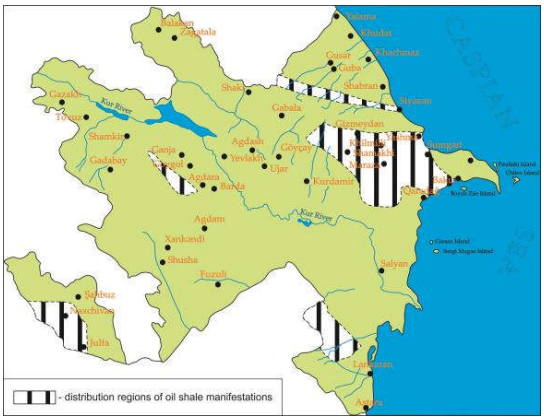

Figure 3 Schematic maps of oil shale distribution regions in Azerbaijan

The geological structure of the region consists of Mesozoic-Cenozoic sediments. In generally, related to Goradil-Masazir Fault Zone and Gujur-Gyzyldash thrust, three microblocks: north allochthonous, central para-autochthonous and southern autochthonous are separated in Gobustan (Fig. 2). Oil shale of the Northern Gobustan belonging to the Cretaceous deposits, have no commercial value [8]. Many of oil shale manifestations are observed in areas of the Central Gobustan associated with Paleogene-Miocene sediments.

The Central Gobustan covers areas, relating to para-autochthonous tectonic microblocks (Bayanata), which indicates favorable paleogeographic and paleotectonic conditions of the zone for the formation of oil shale. Paleogene-Miocene sediments are involved in the geological structure of Bayanata microblocks, have thickness of 2.5-4.5 km. In contrast to these structural and facies complexes, deposits of the same age, observed in north of Geradil-Masazir fault zone (north allochthonous) are located under the Cretaceous sediments (consisting of flyshoids). It is assumed that the sediments of Paleogene-Miocene age in Bayanata block have been compressed between the carbonate complexes (Upper Cretaceous age) of allochthonous (Toragay microblocks) and the sediments (Cenozoic age) of autochthonous, increasing up to 11 km. In such a complex tectonic environment, there were favorable facies and paleogeographic (accumulation of organic matters in silt sediments, existence of shallow, broad bays and continental lagoons) conditions for the accumulation of organic compounds, which forming oil shale. The sediments accumulated with short geochronological breaks and at subsequent stages, a result of dynamic metamorphism these exposed to the process of oil shale formation.

According to the spatio-temporal distribution, the development of oil shale in the Central Gobustan are

associated with complex tectonic structure of the region and accumulation of Organic compounds with breaks, started from the Middle Eocene, continued in the Maikopian and Konk, ended in the Meotian during the process of lithogenesis.

Geochemical characteristics of oil shale and oil saturated rocks

To study of hydrocarbon potential of these areas on the basis of geological and geochemical research of oil shale and oil saturated rock association, which found in ejected products of mud volcanoes provides interesting results [3-6]. Almost all mud volcanoes of the study area eject oil shale and oil-saturated rock during their erruptions [3, 14] (Fig. 4, 5).

Figure 4 Oil shale in the mud volcanic breccia of Dashmerdan

Figure 5 Oil- saturated sandstone in the mud volcanic breccia of Ayrantoken

Table 1 Extraction of oil shale, sampled of mud volcanoes in Shamakhi-Gobustan region

Mud volcano	Amount of dissolved organic matter,%		Amount kerogen, %
	Chloroform	Alcohol-benzol (1:1)	
Shikhzarli	0.44	0.97	6.15
Pirekeshkul	1.00	0.61	19.97
Veys	0.51	0.42	16.85
Gushchu	2.54	5.80	34.02
Chapilmish	0.34	0.22	27.31
Suleymanakhtarma	1.12	0.62	8.75
Cheildag	0.18	0.38	9.35
Galandarakhtarma	1.04	0.74	6.12
Shekikhan	0,59	0,50	10,36
Agtirme	1,16	0,48	8,47
Solakhay	0,82	1,05	9,88
Dashgil	0,72	0,56	10,02
Ayrantoken	0,93	1,02	8,96
Durandag	1,01	0,52	12,35
Gotur	1,22	0,55	10,06

The studies of oil shale, which sampled from mud volcanic products show that its organic composition ranges between 7.56-42.55%. According to data, obtained from a result of the extraction of oil shale, the largest number of soluble organic matter is observed in the composition of the mud volcano Gushchu - 8.34% (composition of kerogen - 34.02%). Relatively fewer soluble organic matters is observed in the composition of oil shale, sampled from mud volcanoes Chapilmysh and Cheildag (0.56%). Most of the organic matter in the composition of oil shale samples accumulates in their kerogen portion (Table 1). Formation and distribution of organic substances mainly depend on the processes taking place at the final stages of diagenesis and the specific properties of the initial substances. In order to explain the process of natural catagenesis held thermal laboratory analysis of oil shale. Thermolysis of samples, taken from various zones of mud volcanic areas, shows their Tmax. Samples of mud volcano Gushchu, rich with organic matter burn with several stages at tepmeratures of 300, 400 and 500°C. Samples of mud volcanoes Chapilmish and Veys, containing relatively greater amounts of organic substances lose their masses at a temperature of 400 and 200-400°C (Diagram 1, 2). Pyrolysis of oil shale samples of different mud volcanoes (Veys, Gushchu, Pirekeshkul, Galandarakhtarma and *et al*.) showed that up to 500°C temperature obtains fractions, similiar to oil, but at higher temperatures, only gases. A sharp changing is observed at a temperature of 400 °C (Table 2).

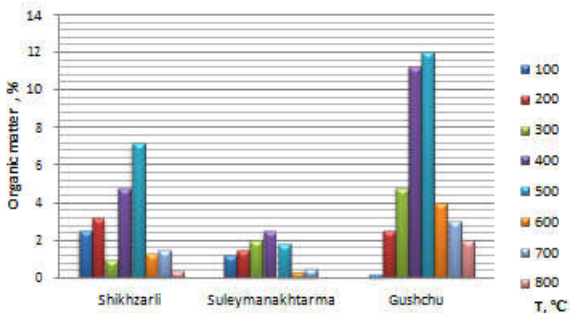

Diagram 1 Thermolysis of oil shale, sampled from mud volcanoes Shikhzarli, Suleymanakhtarma and Gushchu

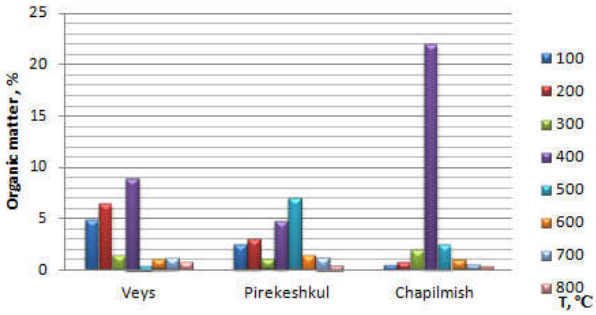

Diagram 2 Thermolysis of oil shale, sampled from mud volcanoes Veys, Pirekeshkul and Chapilmish

Table 2 Pyrolysis of oil shale, sampled from mud volcanoes in Shamakhi-Gobustan region

Mud volcano	500-550 C			800-850 C		
	Water, %	Bitumen, %	Gas, %	Water, %	Bitumen, %	Gas, %
Shikhzarli	0.24	3.21	3.13	0.84	–	2.64
Pirekeshkul	0.42	4.12	4.53	0.32	0.42	2.81
Veys	4.25	5.60	6.31	–	–	1.19
Gushchu	1.35	6.18	17.69	0.32	–	11.77
Chapilmish	0.12	1.20	24.0	1.27	–	2.81
Suleymanakhtarma	0.81	3.87	2.34	0.43	–	2.27
Galandarakhtarma	0.25	4.15	2.12	0.33	–	2.11
Dashgil	1.80	3.12	7.01	–	–	0.80
Durandag	2.78	3.38	4.17	–	–	1.30
Gotur	0.56	0.45	10.67	–	–	5.53

According to the amount of products obtained from oil shale, is making possible to define the structure of organic matter. Greater amount of bitumen indicates the structure of an aliphatic but others - like gas and light hydrocarbons an aromatic. In contrast to oil shale, oil-saturated rocks of mud volcanoes are mainly related to younger sediments (Miocene). The fraction, obtained by extraction (chloroform) mainly consists of asphaltenes (42.52-47.15%), and oil (26.86-37.96%).

Table 3 Fractional composition of bitumen of mud volcanoes in Shamakhi-Gobustan

Composition of the hydrocarbons	Mud volcanoes					
	Solakhay (SW wing)		Solakhay (NE wing)		Ayrantoken (SE wing)	
	Oil, %	Bitumen, %	Oil, %	Bitumen, %	Oil, %	Bitumen, %
Methane-naphthene	18.06	6.53	–	–	11.21	4.24
Aromatic						
Monocyclic	56.0	20.35	75.59	20.30	66.37	25.20
Bicyclic	4.52	1.65	4.03	1.08	9.0	3.42
Polycyclic	11.87	4.31	16.48	4.43	7.32	2.78
Low molecular Weight tar	9.70	3.53	3.90	1.05	6.10	2.32

Data obtained from chromatographic analysis (silica gel ASM) of oil fractions show that the majority of bitumen consists of monocyclic hydrocarbons (56, 0-75, 50%). The compounds similar to oil, but methane-naphthene relatively less than aromatic hydrocarbons. The paraffins are almost Absent in studied fractions (Table 3).

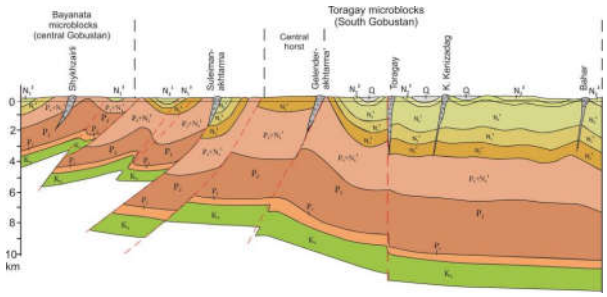

Figure 6 Geological profiles across Bayanata and Toragay microblocks [11]

CONCLUSIONS

Analysis of thermolysis process showes that the maximum interval of mass loss for oil shale depends on the structure of organic matter, initial substances, geological conditions and thermocatalytic impacts and etc. Thus, if organic substances lose mass at high temperatures correspond an aliphatic, at low temperatures an aromatic type of structures. The results of the pyrolysis show that the development of some kerogens of oil shale (found in ejected products of Chapilmish, Gotur and others mud volcanoes) has been weak in the oil generation processes, but others (Veys, Pirekeshkul, Galandarakhtarma and others) more intensive. Thus, if at low temperature the amount of obtained bitumen is much in former, but for the second group of mud volcanoes it almost absent. İf compare the amount of gases, they are much greater (24.0%) in the samples of Chapilmish mud volcano. The analytical study of such rocks show that related to re-changing of organic matter: long aliphatic C-C bonds are destroyed at the stage of ketogenesis, minerals and organic substances are separated from each other in kerogen composition and the whole process ends with formation of hydrocarbon. IQ-spectrum of kerogen indicates its similarity to oil asphaltenes and coal. In this regard, during the pyrolysis of kerogen (matured) obtains hydrocarbons. Thus, the results of laboratory tests show that some kerogens of oil shale (including of Chapylmysh mud volcano) are not yet fully matured. Geological and geochemical analysis of oil shale, related to Paleogene-Miocene sediments and traces with a thicknes of 2.5-4.5 km in the Central Gobustan (the location zone of Veys, Pirekeshkul mud volcanoes and others) provides the economic prospects in terms of the exploitation of shale gas (Fig. 6). The territory of South Gobustan is considered to be more promising in hydrocarbon generation, related to maturity of kerogen in oil shale (Eocene and Maikopian age). In addition, the comparative analysis of bitumen, whch obtained from kerogen of oil shale (Eocene and Maikopian age) and oil-bearing rocks (Miocene age) confirms their close genetic relationship. The results confirm the possibility formation of hydrocarbons in the sediments of Eocene age (probably also accumulation in its granular and fractured reservoirs) and Maikopian series in the study area and their migration to the relatively younger Miocene reservoirs.

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