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Geochemical features of Sakhalin Island mud volcanoes

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ABSTRACT

The study, based on a complex geochemical research, found that the composition of the most chemical elements in mud breccia from the Yuzhno-Sakhalinsky (YSMV) and Pugachevsky (PMV) mud volcanoes (Sakhalin Island), the unique phenomena of endogenous defluidization in the Hokkaido-Sakhalin fold system (alpine-type folding), are comparable to Clarke (C) contents of these elements ($0.8-1.2 \times C$). For Na, Li, Zn and Sn, the ratio between the elemental contents and their Clarke values ($C_{\text{sample}}/ \text{Clarke value}$) vary from 1.4 to $5.2 \times C$. But the increased contents of Na and Li are due to the ascending endogenous fluid revealed. Study of the mud breccia chemical composition changes in different explosive activity of YSMV under the seismic activity variations allowed to establish that, when the mud-volcanic gryphons are activated against the background of increase in the temperature of the water-mud mixture and the emission of spontaneous gases, the contents of a number of elements (iron, calcium, manganese, rare earth elements, etc.) are decreased. This is explained by the formation of soluble hydrocarbonate complexes. Daghinskii gasgeothermal system (DGHS) trace elements depleted ooze samples were compared with YSMV and PMV samples and exposed that the high ratios of $C_{\text{sample}}/ \text{Clarke values}$ for the majority of elements do not exceed $0.6 \times C$. Ooze samples from DGHS having higher elemental contents than Clark contents were observed only for Cd content ($2.2-3.4 \times C$) and Pb ($0.7-1.5 \times C$). Analysis of diatom flora on the DGHS site indicates the existence of an active fluid dynamic system that drains oil and gas bearing complexes. The factors determining the "weighting" of the methane carbon isotope composition in the southern part of Sakhalin Island are the increased seismic activity of deep-seated faults, as well as the presence of intrusions (diabase) and metamorphically altered rocks.

Keywords: Sakhalin Island; mud volcano; methane; hydrocarbon gas; element composition; faulting tectonics; seismic activity.

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1. Introduction

Mud volcanoes are the most interesting and rather rare manifestation of defluidization

processes on the Earth's surface. According to oil-gas geologists V.N. Weber, K.P. Kalitsky, V.D. Golubyatnikova and I.M. Gubkin, one of the main forming factors of the mud volcanic process is the hydrocarbon potential of sedimentary basins. According to the literature da-

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ta, mud volcanoes, like other sources of methane, are usually found in areas of deep subsidence, in marginal basins and in subduction zones of continental margins (Luckge et al., 2002), especially under conditions of tectonic compression (Kopf, 2002).

The occurrence of mud volcanoes is associated with the outlet to the surface under the influence of excessive pressure of hydrocarbon gases concentrated at depth. A high-pressurized fluid is formed in thick clay strata, as a rule, due to phase transformations of clay minerals in the region of high temperatures and pressures and promotes the breakthrough of mud breccias to the surface through volcanic eruptive channels (Kholodov, 2002; Shnyukov et al., 1992). One of the main factors for the formation of mud volcanoes is faulting (Melnikov and Iliev, 1989; Milkov, 2000).

The bulk of solid outputs is elastic clayish rocks, which are common in the continent-oceanic marginal areas. Also, water plays a significant role in the activity of mud volcanoes, such that, firstly, penetrating into voids and pores, it leads to swelling of the rocks, turning them into a viscous mass; and secondly, together with the gas, promotes extrusion of a clay mass with rock fragments onto the surface.

Most of the on-land mud volcanoes are located within the Alpine-Himalayan, Central Asian and Pacific mobile orogenic belts, whereas underwater mud volcanoes occur both along passive and active continental margins (Kholodov, 2002).

By analogy with magmatic volcanoes, mud volcanoes are distinguished by two stages of development: active and passive. The active stage is accompanied by a powerful outlet to the surface of gases and liquids of clay pulps (mud-volcanic or mud breccias). During the passive period (salsas-gryphon), a small amount of gases, coarse dirt and water are released from the gryphons, or the gryphon itself ceases its activity altogether (Kholodov,

2002). Both stages are subdivided by transition stage: "relaxation" after mud volcanoes activation or preparation stage before eruption.

The Sakhalin Region is a unique region of Russia, where there are thick sedimentary strata containing oil and gas deposits, with high seismotectonic activity and surficial mud volcanoes (Ershov et al., 2011; Melnikov and Iliev, 1989; Melnikov et al., 2008). There are four areas of mud volcanism. Three of them are in the south of the island: Yuzhno-Sakhalin mud volcano (YSMV), 24 km northwest of the regional center, Pugachevsky group of mud volcanoes (PMV), about 140 km north of Yuzhno-Sakhalinsk in the Makarovsky district near Pugachevo and Lenovskiy mud volcano in the Korsakovskiy district. In the north of Sakhalin, 30 km north of Nogliki village, the Darginsky gas geothermal field (DGHS) is located. Within the geothermal field, there are about fifteen water and gas sources that are used for therapeutic and prophylactic purposes (mud baths 'Dagi'). Mud-volcanic manifestations are also noted on the shore of the Gulf of Aniva. Villagers of Vostochny (Terpeniya Bay, Sakhalin Island) recounted their eyewitnesses of the extrusion of clay breccias along the shoreline during a seismo-tectonic activity in August 2006.

The study of the chemical composition of mud volcanic activity products (solid, liquid and gaseous) is one of the main directions of the mud volcanoes study (Fedorov et al., 2012; Shnyukov et al., 1992; Yakubov et al., 1980). In this paper, we present the results of a comprehensive geochemical study of mud volcanoes on Sakhalin Island, including the composition of spontaneous gases, the mineral assemblage of the mud breccia and the distribution characteristics of the wide range of its chemical elements. The main goal of the paper is to reveal the connection of the gas discharge changes, element composition, gas geochemical composition and temperature of

mud-water mixture in mud volcano gryphons with strong earthquakes in the region.

2. Initial data

Gas-geochemical monitoring of mud volcanoes on Sakhalin Island has been carried out since 2001 by employees of the Gas Geochemistry Laboratory of the V.I. Il'ichev Pacific Oceanological Institute, Far Eastern Branch of Russian Academy of Science (POI FEB RAS). Gas was sampled from the main degassing gryphons of Yuzhno-Sakhalinsky and Pugachevsky mud volcanoes and the Daginsky geothermal system. Gas samples were collected in glass bottles by displacement using a saturated solution of NaCl as a buffer. Samples of recent mud-breccias were also collected.

The Yuzhno-Sakhalinsky mud volcano (YSMV), the largest and most active, has been studied in more detail (Figures 1, 2). It is located in the field of the Bykovsky suite of Upper Cretaceous age, one of the thickest siltstone-argillaceous sequences in Sakhalin (up to 3000 m) and tectonically confined to the submeridional Central-Sakhalin deep fault (Tym-Poronaik uplift) (Geology of the USSR, 1970). Each eruption changes the relief and contours of the mud field. In August 2001, after a series of seismic shocks with an intensity of 5-7 magnitude, the southern and central groups of YSMV gryphons practically ceased to function, but the mud gryphons in the northern part became active and new gryphons were formed (Astakhov et al., 2002; Melnikov et al., 2008). From the vents of the gryphons, samples of spontaneous gases and breccias were collected during a passive period (Yu-9, Yu-10, Yu-22) as well as under an active period (Yu-9 / 17.08, Yu-10/17.08). The same group of gryphons, which were in a passive state, was tested in 2007 (samples 'Naparnik' and 'A-1') and in 2008 (samples E-21, E-22, E-23, E-24, E-25 were provided by V.V. Ershov, IMG, Yuzhno-Sakhalinsk).

Pugachevsky mud volcano (PMV), the second largest, consists of three mud volca-

noes that are close together, including the Main and two small ones termed as Small North and Small South. They are located on a rounded hollow (2 by 1.5 km), overgrown with forest (Melnikov, 2011). PMV is also confined to the Tym - Poronaik uplift and the Bykov suite is the host-terrain, likewise for YSMV (Geology of the USSR, 1970). Four samples were selected from the Main Pugachev mud volcano (Figures 1, 3), in a passive state: 1 in 2001 (P-2/2-01), 2 in 2005, (P-1-05 and P-2-05) and 1 in 2006 (P-06).

The Daghinskaya geothermal system (DGHS), also termed as the Dagin mud volcanic manifestation, (Melnikov and Iliev, 1989) is located on the coast of the Nyisky Gulf within the North-Sakhalin trough (Geology of the USSR, 1970) alongside the Dagin-sky thermal springs (Figure 1, 4). Thermo-mineral springs belong to slightly alkaline (pH = 7.4-7.5), chloride-hydrocarbonate sodium waters. The total mineralization is 2-2.5 g/l. The water temperature is 30-40°C (Yakubov et al., 1980). The hydrological regime of the Gulf is determined by the influence of river flows and the tidal currents. During the day time, there are sharp changes in temperature, salinity and water level. In the DGHS there are no explosive eruptions typical for mud volcanoes and mud breccia field, but there is a flow area of gas-and-mud mass from small craters (1.5 to 3 m in diameter), which are relatively evenly distributed along the bottom (Figure 4). DGHS is controlled by the Garomaisky fault (Lobodenko, 2010). The observed increased contents of helium (20 ppm) and hydrogen (22 ppm) may indicate the activity and significant deposition depth of the fault (Shakirov et al., 2012). At a relatively small depth, there are highly elastic clay deposits of Neogene age (Gladinkov (Editor), 1998; Zharov et al., 2013). According to the literature, DGHS is also associated with the mud volcanic process (Melnikov and Iliev, 1989). Samples from the DGHS were collected in the vicinity of the Kalmar thermal spring located in the tidal zone, including D-01 in 2001; D-05 in 2005; D-12-1, D-12-2, D-12-3 and D-12-4 in 2012.

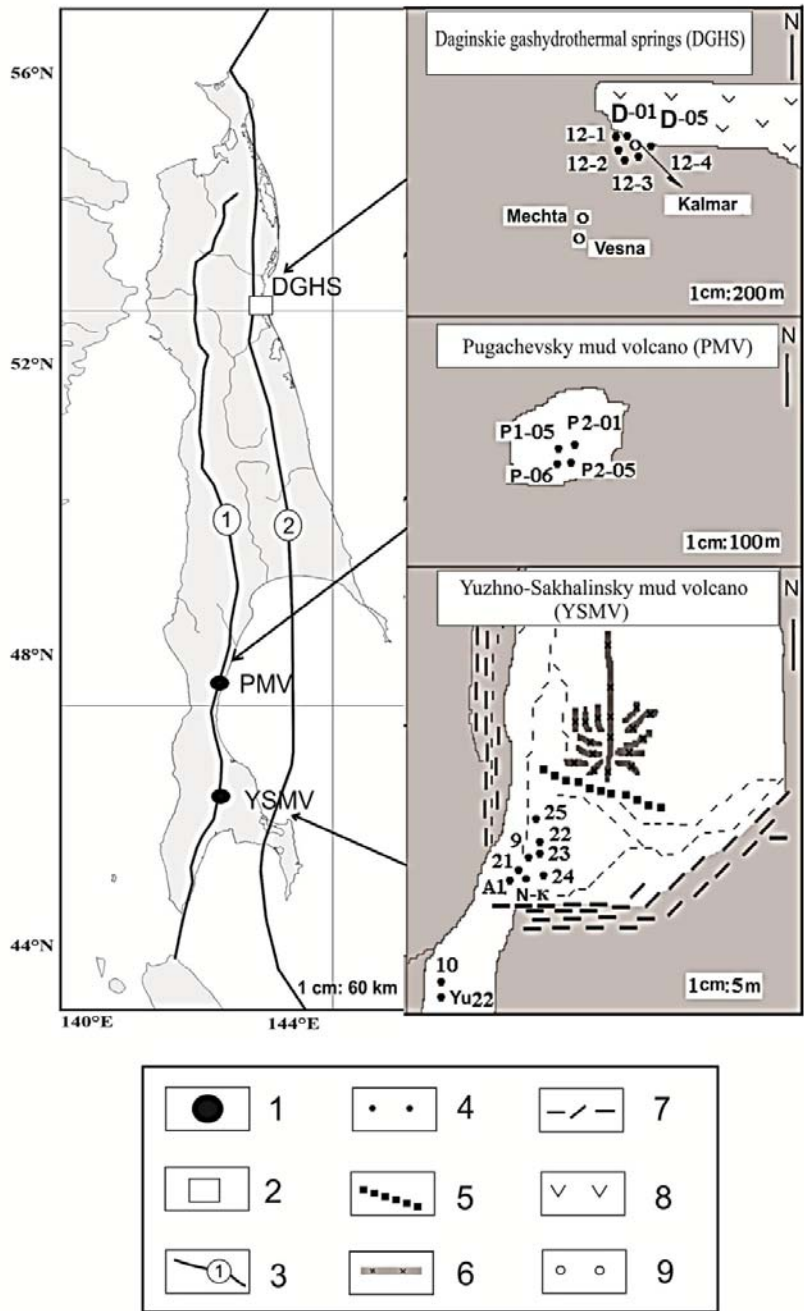


Figure 1. Scheme of mud volcanic sampling sites on Sakhalin Island: 1 - mud volcanoes; 2 - area of Daginsky geo-thermal system; 3 - faults (in brackets: 1 - Central Sakhalin fault, 2 - Hokkaido-Sakhalin fault); 4 - sampling sites and sample number; 5 - Zones of uplifting - subsidence of the mud field; 6-7 - fissures in mud field; 8 - area, flooded with sea tidal water; 9 - thermal springs. N-κ -gryphon 'Naparnik'. Remark: The abbreviations are explained in the text



Figure 2. YSMV: a) general view of YSMV from satellite (google-earth); b) view to northern part of YSMV, gryphonYu-9



Figure 3. PMV: a) general view of PMV from satellite; b) passive gryphon at PMV, August 2005

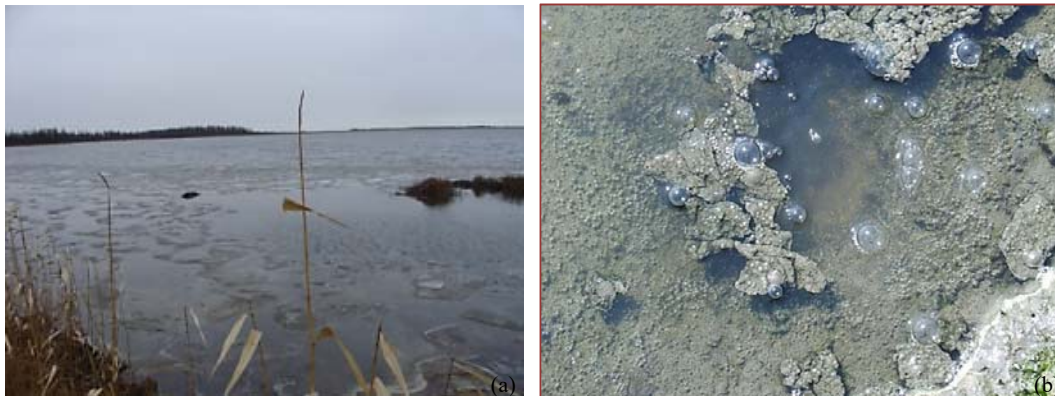


Figure 4. DGHS: a) view to Daginsky bay; b) output of gases from DGHS, in 2005

3. Study methods

Analysis of hydrocarbon gases, nitrogen and carbon dioxide was carried out in the gas

geochemistry laboratory of POI FEB RAS using a two-channel gas chromatograph 'CrystalLux4000M' equipped with ionization and

thermal conductivity sensors having a sensitivity of 10-5%. For the analysis of helium and hydrogen, a portable gas chromatograph “Khromatek-Gasochrom 2000” was used with a sensitivity of 1-2 ppm for helium and hydrogen.

The elemental composition (gross content) in samples of recent mud volcano breccias was determined at an analytical chemistry laboratory in the Far Eastern Geological Institute, FEB RAS. The major (matrix) elements were measured using an inductively coupled plasma atomic emission spectrometry (ICP-AES), whereas the trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) method. The analytical error for the major elements is ±1 - 2%, for the trace elements is not higher than ±15%. The results of REE contents are interpreted in the form of chondrite normalization (Dubinin, 2006) and following the criteria for estimating the compositions of lanthanides, as follows:

$$Eu_{an} = Eu/Eu^* = Eu_N / (Sm_N + Gd_N/2);$$

$$Ce_{an} = Ce/Ce^* = Ce_N / (La_N + Pr_N)/2$$

$$L_L/L_H = (La_N + 2Pr_N + Nd_N) / (Er_N + Tm_N + Yb_N + Lu_N)$$

The mineral composition of the mud breccia was studied in thin sections and immersion method prepared according to a conventional procedure (Petelin, 1957). Silicate analysis of carbonates was performed also at the analytical chemistry laboratory of the Far Eastern Geological Institute, FEB RAS. The trace el-

ement composition of carbonates is acquired using an IXA-8100 microscopic analyzer. The isotopic compositions of carbon and oxygen of authigenic carbonates, as well as carbon of methane and carbon dioxide, were determined at the laboratory of stable isotopes of the Far Eastern Geological Institute, FEB RAS, using a Finnigan MAT-252 mass spectrometer.

The sample processing for diatom analysis was carried out using heavy potassium-cadmium liquid chemical-technical technique (Diatomic algae of the USSR, 1974).

4. Study results and discussions

4.1. Gasgeochemical features

According to the gas specialization, YSMV and PMV belong to the carbonic-methane type of mud volcanoes. The predominant gas component for YSMV is CO₂ (up to 74%), while methane (CH₄) can reach as high as 24%. The Pugachevsky group of mud volcanoes is characterized by a low emission intensity of free gases. In terms of quantitative ratio, the composition of PMV gases differs from the free gases of YSMV where the relative contents of CO₂ and CH₄, respectively, are ~ 25% and ~ 70% (with variations). Both mud volcanoes are characterized by the presence of heavy hydrocarbon gases to pentane inclusively, which indicate their common genesis (Table 1).

Table 1. Component compositions of free gases from YSMV, PMV, DGHS

Object	CO ₂ , %	O ₂ +Ar, %	N ₂ , %	CH ₄ , %	C ₂ H ₆ , ppm	C ₃ H ₈ , ppm	i-C ₄ H ₁₀ , ppm	n-C ₄ H ₁₀ , ppm	n-C ₅ H ₁₂ , ppm	He, ppm	H ₂ , ppm	Year of sampling
YSMV	69.2-83.9	0.2-7.4	2-5.2	12.4-28.4	1.6-371	7.5-426	6.9-90.5	0.6-108.7	nd	-	-	2001
	58.6-86.7	0.1-0.9	1.2-6.9	11.8-33.3	0.16-2855	0.04-581	0.005-128	0.005-125	nd	-	-	2005
	68.3-78.8	0.1-3.2	1.1-3.3	12.7-35.6	0.07-0.2	0.02-0.05	0.005-0.01	0.006-0.01	13.16-22.78	11.8-40.9	6.3-15	2007
	67.3-84.1	0.2-1.2	1.5-4.6	13.3-29.8	0.1-0.25	0.03-0.1	0.005-0.1	0.005-0.1	15-22	-	-	2009
	68.4-92.5	0.1-0.3	1.24-2	6.6-29.5	0.06-0.27	0.01-0.06	0.003-0.01	0.005-0.01	7.5-15.2	16.8-43.7	0.2-1.6	2011
DGHS	72.2-87.0	0.15-4.8	1.4-17.5	10.0-23.5	0.12-0.24	0.02-0.05	0.0007-0.009	0.0009-0.002	3.1-7.6	12-31.7	0.4-5.7	2013
PMV	8.6	18.4	60.4	12.6	92.8	nd	nd	nd	-	-	-	2001
	6.4-27	2.7-21.8	-	63.0-83.0	0.5-5.6	0.3-0.9	nd	nd	-	-	-	2005
	18.8	5.3	12.6	63.3	0.02-0.03	nd	nd	nd	0.32	-	-	2009
DGHS	0.3-1.0	0.3-2.0	6.0-9.0	89.0-93.2	nd	nd	nd	-	-	-	-	2005

Remark: Data were acquired at the Laboratory of Gasgeochemistry at POI FEB RAS, nd: not determined

The Pugachevsky and Yuzhno-Sakhalinsky volcanoes are similar in many respects: they have similar mud field dimensions and the character of activity; they are situated in the field of gas-bearing, highly plastic Upper Cretaceous aleurolite-argillite formation and are confined to the Central Sakhalin fault of upthrust-overthrust type. Mud volcanoes are local gas drainage systems in the Earth's crust, but they are considered in the system of controlling linear structures. In this case, this is a deep-seated active fault with nearly north-south strike. This means that the fault zone is a single fluid-dynamic system, in some parts of which (especially, in the zone of fault crossing or near intrusion bodies), specific conditions appear for the formation of flows of gases with certain composition. In the southern part of the Central-Sakhalin fault, the source of carbon dioxide for both YSMV and PMV, on the one hand, and in Sinegorskies mineral water springs, on the other hand, likely the same. Within these boundaries, the concentrations of CH₄ and CO₂ show characteristic variations: a considerable portion of methane in mud volcanoes (up to 60%) is replaced sometimes by the predominance of carbon dioxide in Sinegorskies springs. This difference is determined by the different water filling in the mud volcanic channel: YSMV more saturated by water because its location is near freshwater spring. Carbon dioxide dissolves in the water in large portions. In opposite, the PMV has low content of water in the mud flow. Therefore, methane dominates in this PMV as compared to the YSMV. Taken into account the equal water saturation of the both mud volcanoes, we could expect similar proportion between the methane and carbon dioxide. But this study needs additional methods. Remarkably, basic rock diapirs (diabas) located close to the YSMV could also be source of the carbon dioxide.

It should be noted that, in terms of component composition, the PMV gases match with the gases of the Northern Sakhalin oil fields (Siryk, 1968). The peculiarities of the geological development of formation area of the mud

volcanoes definitely indicate a greater probability of finding hydrocarbon deposits in the sedimentary thickness at the Pugachevsky volcano region (Veselov et al., 2012). For YSMV, the isotopic composition of carbon of carbon dioxide $\delta^{13}\text{C}$ is from -2.8 to -2.7 ‰ PDB and $\delta^{13}\text{C}$ of methane is -27 ‰ PDB; for the Pugachevsky mud volcanic group, $\delta^{13}\text{C}$ of methane is -24.9 ÷ -20.9 ‰ PDB, for carbon dioxide $\delta^{13}\text{C}$ is -4.1 ‰ PDB.

The main component of the spontaneous DGHS gas is methane (up to 93% by volume) with $\delta^{13}\text{C}\text{-CH}_4\text{-54}\div\text{-57 ‰ PDB}$. The methane concentration from DGHS is genetically close to the methane in oil and gas-bearing fields of Sakhalin Island and the nearest shelf, where concentrations are up to 10,000 n/l (Shakirov et al., 2012).

As a result of long-term observations (from 2001 to 2013), the average chemical composition of free gases of Sakhalin mud volcanoes was established during passive periods and shown in Table 1.

The idea of a deep gas source in the Pugachevsky and Yuzhno-Sakhalinsky mud volcanoes is in good agreement with the opinion of a number of researchers (Veselov et al., 2012; Ershov et al., 2011) that mud volcanoes are generated in sedimentary strata at depths about 7-8 km (calculated using isotope geothermometers), where thermobaric conditions are favorable for the formation of large volumes of gases.

There is an empirical dependence of methane carbon isotope composition on temperature and its generation (Prasolov, 1990). According to this dependence the average value of $\delta^{13}\text{C}$ methane of the Yuzhno-Sakhalinsky mud volcano corresponds to temperature of methane genesis of about 320-340°C. The average geothermal gradient in the southern part of Sakhalin Island calculated according to work of Veselov and Soinov (1997), shows about 41.1°C/km. Therefore, we believe that a methane source depth for the volcano is located between 7.8 and 8.3 km.

Extent of isotope division of carbon in the CO₂-CH₄ system depends on temperature conditions of gas generation. The range of

temperature of isotope balance in this system calculated for average values $\delta^{13}\text{C-CH}_4$ and $\delta^{13}\text{C-CO}_2$ by formulas from work of Horita (2001), is 330–350°C, corresponding to the range of generation depths between 8.0 and 8.5 km.

4.2 Geochemical features of the mud breccias

Collected samples of recent mud volcano breccias from YSMV and PMV were dark gray liquid silt-pelitic sediment containing a small

amount of sand. The mineralogical study of the samples identified two classes of minerals belonging to carbonates or sulphides. Carbonates are represented by well-formed crystals of beige-brown and red-brown color which constitute 92-97% of the heavy fraction. The chemical and microprobe analytical results shown in, respectively, Table 2 and Table 3, suggest their compositions corresponding to the magnesian-feric variations of siderite-sideroplexites (Sorochinskaya et al., 2008).

Table 2. Chemical and isotopic compositions of YSMV major natural gases

CH ₄ , %	$\delta^{13}\text{C}_{\text{pdb-CH}_4}$, ‰	CO ₂ , %	$^{13}\text{C}_{\text{pdb-CO}_2}$, ‰	He, ppm	H ₂ , ppm	Year of sampling
13.6 – 29.9	–29.8 – 27.3	67.5 – 84.1	–6.3 – 4	-	-	2009
23.9(49)	–28.8(49)	73(49)	–5.3(49)	-	-	
17.9 – 23.9	–29.3 – 28.9	74 – 80.4	–5.4 – 4.7	-	-	2010
21.5(5)	–29.06(5)	76.5(5)	–5.1(5)	-	-	
6.6 – 29.5	–27.6 – 30.3	65.8 – 80.3	–4.7 – 6.7	16.8 – 32.4	0.2 – 1.6	2011
23.1(15)	28.7(15)	74.9(15)	–5.6(15)	28.3(15)	0.7(15)	
10.9 – 24.2	-	72.2 – 87	-	12 – 30.2	0.4 – 24.6	2013
18.9(24)	-	77.9(24)	-	23.8(24)	2.9(24)	

Remark: In numerator - minimum/maximum values, in denominator – an average, in () - the number of the analysed samples

Table 3. Chemical composition of major components in authigenic carbonates from YSMV and PMV (in mass%)

Object	Components												
	SiO ₂	Al ₂ O ₃	TiO ₂	FeO	Fe ₂ O ₃	MnO	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	H ₂ O	*
YSMV	8.4	2.65	0.056	32.45	5.73	0.52	6.60	5.34	0.34	0.47	0.07	0.64	36.4
PMV	8.8	2.65	0.056	32.21	5.86	0.14	6.53	5.80	0.37	0.39	0.09	0.37	36.3

(*): loss on ignition

The maximal contents of Mn (4.68%), Hg (0.59%) and Sr (0.25%) are in carbonates collected in YSMV from an active gryphon (sample Yu-9 / 17.08). The isotope composition of carbon ($\delta^{13}\text{C}$) of authigenic carbonates from YSMV and PMV varies within narrow limits, from -0.3 to -0.7 ‰ PDB, $\delta^{18}\text{O}$ values varying from 2.6 to 4.4 ‰ PDB (Table 4).

Samples from DGHS are represented by pelite - aleurite sediment of dark gray color with up to 70% organic remains (spicules of

sponges, diatoms). The main authigenic mineral is framboidal pyrite (up to 90% of the heavy fraction) in the form of nonmagnetic pseudomorphs by organic residues and dark gray globules. The main lines on the X-ray diffraction pattern of sample D-1: 2.729 (10); 2.428 (7); 2.226 (5); 2.044 (2); 1.636 (6). Single crystals of red-brown sideroplexites are noted, which are similar in composition to those previously described in the samples from YSMV and PMV (Table 4).

Table 4. Compositions of trace elements in individual crystals in authigenic carbonates determined by microscopic analysis

Object	Sample	Elemental content, wt.%						
		Mn	Ni	Cu	Zn	Sr	Ba	Hg
YSMV	Yu-22(1)	0.77	nd	nd	0.19	0.16	0.14	0.49
	Yu-22(2)	0.82	nd	0.13	0.1	nd	nd	nd
	Yu-22(3)	0.43	0.09	0.09	0.03	0.17	nd	0.14
	Yu-22(4)	0.93	0.16	0.16	0.1	0.08	0.08	nd
	Yu-22(5)	1.92	nd	0.09	0.06	0.11	0.11	nd
	Yu-9/17.08(6)	0.59	0.15	0.13	0.11	0.21	nd	0.38
	Yu-9/17.08(8)	0.41	0.13	0.19	nd	0.23	nd	nd
	Yu-9/17.08(11)	4.68	0.1	0.02	nd	nd	nd	0.59
	Yu-9/17.08(12)	1.55	nd	nd	nd	0.25	0.1	nd
PMV	P-06(13)	0.31	0.14	0.17	0.12	0.16	0.13	nd
	P-06(14)	0.15	nd	nd	nd	0.17	nd	0.44
	P-06(15)	0.18	nd	nd	nd	0.29	0.07	0.45
DGHS	D1/1(16)	0.81	0.11	nd	0.03	0.13	0.05	nd.
	D1/1(19)	0.72	nd	0.04	0.07	nd	0.11	nd
	D1/1(21)	0.55	nd	0.11	0.09	0.13	nd	0.08
	D1/1(22)	0.54	nd	0.03	nd	0.24	0.2	nd
	D1/1(23)	0.61	0.13	0.04	nd	0.12	nd	nd
	D1/1(23)	0.63	nd	0.02	0.05	0.19	0.15	nd

Remarks: Yu-22(1) - Yu-22(5) - individual crystals of sideropiezites selected from the sample

Yu-22; Yu-9/17.08(6) - Yu-9/17.08(12) - individual crystals of sideropiezites selected from the sample Yu-9/17.08;

P-06(13) - P-06(14) - crystals of sideropiezites selected from the sample P-06; D1/1(16) - D1/1(16) - crystals of sideropiezites selected from the sample D1/1; nd- not determined

Analysis of diatom flora in samples from DGHS showed the prevalence of marine and brackish-water species, among which the marine plankton-benthic species *Paralia sulcata* (Ehrenberg) Cleve, characteristic of shelf waters, dominates (Diatoms eic algae of the USSR, 1974; Hasle and Syvertsen, 1996). A significant number of freshwater diatoms (up to 32%) and an admixture (up to 5.5%) of marine species, extinct in the Neogene, (*Actinocyclus ingens* Rattray, *Ikebea tenuis* (Brun) Akiba, *Cosmiodiscus insignis* (Brun) Jousé, *Eupyxidicula zabelinae* (Jousé) Blanco & Wetzel Pyxidicula zabelinae (Jousé) Makarova et Moisseeva et al.), supposedly introduced from the clay strata of the Okobykai and Nutovsky Neogene formations distributing lower at a relatively shallow depth (Gladenkov (Editor), 1998; Lobodenko, 2010; Zharov et al., 2013). This indicates the existence of an active fluid dynamic system, which drains oil and gas bearing complexes (Table

5). Elemental compositions of mud volcanic breccias from YSMV, PMV, and DGHS.

The chemical compositions of the mud volcanic breccias (Table 5) were normalized to their average contents (Clarke: C) in clays and shales (Vinogradov, 1962; Grigoriev, 2008). Most of the elemental contents in the YSMV breccia are in the range of 0.8-1.2 xC, which is comparable to the Clark content (C) of each element. Elevated concentrations in the mud volcanic breccia presented by the Na (2.9-5.2 xC), Li (1.5-2.0), Zn (1.4-1.9) and Sn (1.6-2.4), although the contents of Mn, Ca, Zr, Mo, Cd, Hf, U are lower than their Clarke values (<0.5 xC).

A similar feature is observed in the mud volcanic breccia from PMV that, the content of most elements is close to their Clarke concentrations. The samples contain rather high Na (2.9 xC), Li (1.7 xC), Zn (1.6 xC), Sn (1.9-4.3 xC); whereas Mn, Ca, Zr, Mo, Cd, Hf, Ta and U concentrations are lower than their Clarke values (<0.5 xC).

Table 5. Elemental compositions of mud volcanic breccia from YSMV, PMV, DGHS

Element	YSMV										PMV						DGHS					
	Yu-9 17_08	Yu-9 17_08	Yu-10	Yu-10 17_08	Yu-10 22_01	N-k	A-1	E-21	E-22	E-23	E-24	E-25	P2/2-01	P-1-05	P-2-05	P-06	D-01	D-05	D-12-1	D-12-2	D-12-3	D-12-4
	Weight %																					
Ti	0.37	0.36	0.36	0.36	0.37	0.36	0.35	0.36	0.35	0.35	0.3	0.36	0.36	0.36	0.36	0.37	0.22	0.26	0.27	0.27	0.20	0.31
Al	8.72	8.64	8.62	7.92	8.72	8.45	8.27	8.51	8.41	8.62	8.59	8.58	8.58	8.30	8.15	8.29	6.05	6.63	6.48	6.13	5.14	6.49
Fe	3.58	3.09	3.84	2.77	3.78	3.56	3.78	3.92	3.95	3.44	3.80	3.85	3.72	3.75	4.60	3.60	1.08	1.11	2.00	2.19	1.75	1.89
Ca	0.51	0.39	0.54	0.50	0.82	0.54	0.63	0.58	0.68	0.55	0.63	0.70	0.46	0.68	0.63	0.50	0.52	0.55	0.74	0.66	0.51	0.65
Mg	1.01	0.95	1.03	1.20	1.03	1.01	1.06	1.04	1.05	0.99	1.05	1.04	0.91	0.89	0.95	0.88	0.38	0.47	0.45	0.47	0.43	0.57
K	2.49	2.49	2.42	2.41	2.47	2.44	2.37	2.43	2.40	2.48	2.44	2.44	2.43	2.38	2.33	2.40	2.51	2.32	2.33	2.29	2.42	2.32
Na	1.93	1.97	1.89	3.40	2.05	1.96	2.15	2.01	2.00	2.24	2.18	2.14	1.94	1.91	1.90	1.87	2.03	2.03	2.15	2.08	1.67	1.94
Mn	0.04	0.03	0.05	0.02	0.06	0.04	0.05	0.05	0.05	0.04	0.04	0.05	0.02	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.01
P	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.01	0.02	0.01	0.01	0.01	0.02
	g/t																					
Li	52.54	49.91	50.28	65.13	52.25	53.94	51.96	51.69	50.03	54.70	53.15	53.03	54.24	55.87	54.35	57.73	17.98	22.03	20.80	19.90	17.40	23.70
Be	1.72	1.70	1.59	1.48	1.52	1.68	1.71	1.61	1.68	1.69	1.66	1.52	1.67	1.75	1.84	1.80	1.11	1.27	1.26	1.19	0.93	1.30
Sc	16.50	15.00	17.20	12.70	17.30	16.20	16.90	17.40	18.90	16.40	17.20	17.00	15.40	15.30	17.50	15.00	6.70	8.20	6.65	6.27	4.82	7.39
V	98.60	96.00	97.10	93.70	99.80	96.80	95.20	101.60	102.90	97.70	98.50	97.50	86.30	83.90	86.10	83.10	30.10	37.60	47.90	47.10	34.30	56.00
Cr	47.33	46.78	45.34	43.18	46.28	45.97	44.83	45.53	46.00	46.08	45.60	64.26	46.72	46.04	46.23	46.00	30.76	41.70	36.80	36.10	28.50	46.60
Co	18.40	15.10	17.30	16.00	17.50	17.20	16.50	16.60	17.40	17.50	16.90	16.80	15.80	16.00	16.00	15.80	7.30	9.00	5.38	4.98	4.60	5.54
Ni	28.90	25.80	28.30	27.30	30.20	29.70	31.50	29.20	31.40	28.80	30.50	33.90	26.60	27.70	28.50	26.30	17.80	20.90	17.70	18.30	16.40	20.00
Cu	38.50	40.50	36.50	36.60	37.70	37.70	38.80	36.60	37.30	38.10	35.80	35.50	27.30	27.30	27.70	26.50	6.30	6.30	8.90	6.52	6.40	7.96
Zn	85.70	87.10	85.80	70.70	86.30	83.00	98.90	83.40	83.00	80.20	82.70	87.10	85.80	83.30	83.20	81.50	35.40	32.70	42.50	43.60	37.20	49.20
Ga	16.99	17.38	16.25	15.77	16.64	16.97	16.27	16.43	16.07	16.92	16.36	16.52	16.09	16.22	15.75	16.79	10.63	11.77	14.80	14.50	11.10	15.60
As	7.72	7.34	8.06	6.06	8.16	8.72	8.07	8.03	7.62	8.54	8.50	9.01	10.16	10.95	10.73	11.50	4.32	4.20	5.49	7.35	5.73	7.40
Rb	104.64	102.56	100.39	79.22	100.60	103.72	98.98	98.58	98.39	104.97	98.58	99.92	103.52	105.4	100.8	106.6	83.51	84.62	110.0	106.0	101.0	112.0
Sr	219.70	193.10	220.40	247.60	234.30	230.60	227.10	222.40	220.40	224.80	221.30	233.10	233.7	220.9	253.7	214	221.6	219.8	271.0	240.0	191.0	224.0
Y	19.00	18.10	18.90	10.70	20.20	19.20	19.10	20.00	20.30	18.70	19.10	18.80	19.1	18	19.9	18.5	11.4	13.2	12.00	12.50	9.95	13.80
Zr	93.83	90.06	91.06	86.70	91.86	123.48	88.17	90.52	90.67	90.67	91.02	87.13	78.07	71.07	77.65	81.65	42.79	52.03	66.70	67.70	45.10	74.40
Nb	8.08	7.99	7.62	7.50	7.67	7.95	7.67	7.57	7.56	7.82	7.63	7.53	8.55	8.51	8.47	8.86	5.40	6.40	7.98	8.15	6.01	8.98
Mo	0.38	0.39	0.42	0.33	0.45	0.36	0.42	0.70	0.51	0.57	0.39	0.50	0.43	0.49	0.69	0.40	0.71	1.03	1.11	1.47	1.22	1.78
Ag	0.15	0.15	0.16	0.16	0.15	0.21	0.23	0.17	0.16	0.17	0.16	0.15	0.16	0.15	0.16	0.18	0.16	0.14	0.19	0.19	0.19	0.19
Cd	0.13	0.17	0.09	0.11	0.13	0.13	0.14	0.14	0.13	0.13	0.11	0.13	0.16	0.10	0.09	0.09	0.26	0.24	0.22	0.29	0.35	0.25
Sn	7.45	6.42	8.41	6.39	5.67	7.01	6.69	6.88	7.23	6.57	7.51	6.31	15.00	7.77	6.69	6.68	0.01	0.25	1.70	1.61	1.28	1.89
Cs	8.00	7.37	7.70	7.48	7.77	8.05	7.19	7.57	7.51	8.08	7.58	7.61	7.29	7.47	7.21	7.56	4.19	4.47	6.27	5.68	5.03	6.84
Ba	446.70	455.50	449.40	537.50	454.50	457.00	466.90	444.40	438.10	499.80	451.00	458.30	510.90	512.80	515.00	482.90	659.90	568.50	543.10	508.90	521.20	497.00
La	20.90	20.88	20.20	9.62	20.88	20.13	19.80	19.96	19.43	19.75	18.99	19.05	19.58	19.49	18.95	20.13	16.03	17.57	22.80	26.40	19.70	28.60
Ce	47.94	47.53	46.74	23.96	48.10	47.02	45.35	47.05	45.69	46.0	44.89	44.5	45.45	46.28	45.75	47.17	34.00	37.79	48.30	55.60	42.0	59.90
Pr	5.27	5.13	5.10	2.93	5.27	4.97	5.06	5.15	4.93	5.06	4.84	4.97	5.05	5.25	4.99	5.27	3.85	4.33	5.57	6.26	4.75	6.89
Nd	19.70	19.85	20.07	11.78	20.19	19.74	19.04	19.98	19.62	19.21	18.96	19.33	20.02	20.88	20.45	20.77	14.79	16.97	20.10	22.60	17.60	24.90
Sm	3.90	3.83	3.85	2.47	3.84	3.70	3.68	3.93	3.98	3.74	3.74	3.72	3.89	4.13	3.93	4.10	2.66	2.93	3.84	4.43	3.293	4.77
Eu	0.80	0.73	0.80	0.50	0.81	0.81	0.79	0.82	0.81	0.79	0.79	0.78	0.83	0.83	0.81	0.84	0.63	0.69	0.91	0.92	0.72	0.96
Gd	3.86	3.65	3.79	2.43	3.99	3.70	3.74	3.92	3.88	3.73	3.63	3.72	4.08	4.03	3.92	4.11	2.54	2.96	3.68	4.10	3.19	4.43
Tb	0.50	0.50	0.54	0.34	0.54	0.52	0.51	0.5	0.54	0.51	0.50	0.55	0.55	0.56	0.55	0.55	0.33	0.40	0.50	0.54	0.43	0.59
Dy	2.97	2.96	3.0	1.95	3.19	3.02	3.08	3.07	2.96	2.90	3.03	3.08	2.99	2.95	3.07	3.11	1.85	2.07	2.68	2.84	2.26	3.15
Ho	0.58	0.55	0.57	0.38	0.61	0.60	0.59	0.61	0.59	0.58	0.57	0.58	0.54	0.56	0.60	0.57	0.35	0.41	0.53	0.57	0.44	0.61
Er	1.76	1.79	1.90	1.18	1.91	2.03	1.77	1.76	1.83	1.80	1.82	1.75	1.68	1.66	1.70	1.65	1.06	1.18	1.56	1.60	1.28	1.77
Tm	0.25	0.26	0.26	0.16	0.2	0.24	0.26	0.25	0.24	0.25	0.26	0.24	0.24	0.22	0.23	0.25	0.14	0.15	0.23	0.23	0.19	0.26
Yb	2.55	2.53	2.61	1.95	2.68	2.54	2.51	2.66	2.76	2.51	2.63	2.5	2.51	2.33	2.65	2.34	1.29	1.4	1.51	1.53	1.23	1.68
Lu	0.28	0.27	0.25	0.17	0.25	0.25	0.25	0.27	0.26	0.26	0.26	0.24	0.25	0.21	0.22	0.24	0.15	0.15	0.23	0.22	0.18	0.24
Hf	2.70	2.71	2.81	2.48	2.79	2.73	2.63	2.74	2.64	2.63	2.57	2.63	2.35	2.29	2.36	2.44	1.40	1.50	1.81	2.06	1.47	2.09
Ta	0.53	0.52	0.51	0.50	0.51	0.52	0.53	0.52	0.50	0.52	0.51	0.48	0.59	0.58	0.59	0.62	0.32	0.41	0.65	0.68	0.50	0.85
W	2.32	1.98	2.2	1.96	2.26	2.55	1.72	2.27	2.19	2.53	2.28	2.36	3.23	3.60	3.50	3.57	0.97	1.25	1.38	1.45	0.98	1.69
Pb	16.06	16.46	15.84	13.77	16.63	17.01	17.05	15.86	15.91	16.19	18.49	16.57	15.75	17.14	17.00	16.56	10.24	9.44	20.70	19.60	18.40	19.00
Th	9.62	9.83	9.47	7.31	9.62	9.51	9.37	9.46	9.15	9.41	9.26	9.22	9.79	9.64	9.60	9.99	5.10	6.05	7.99	9.29	6.27	11.00
U	1.86	2.04	1.78	1.55	1.88	1.78	1.81	1.81	1.79	1.86	1.79	1.85	1.92	1.82	1.87	1.91	1.24	1.44	1.98	2.08	1.60	2.49
Σ REE	111.2	110.4	109.7	59.8	112.5	109.3	106.4	110.0	107.5	107.1	104.9	105.1	107.7	109.4	107.8	111.1	79.7	89.0	112.4	127.8	97.5	138.7
La _y /Y _{bn}	5.53	5.56	5.22	3.33	5.25	5.34	5.32	5.06	4.75	5.31	4.87	5.02	5.26	5.64	4.82	5.80	3.88	8.46	10.18	11.63	10.80	11.48
Gd _y /Y _{bn}	1.22	1.16	1.17	0.74	1.01	1.18	1.20	1.19	1.13	1.20	1.11</											

$\times C$) and $Pb = 0.7-1.5 \times C$. The concentrations of other elements such as Cr, Zn, Sr, Ag and Ba are comparable with their Clark concentrations of about $0.7-1.3 \times C$. The increase in the content of Cd and Pb in the sediment is obviously associated with the processes occurring at the river-sea geochemical barrier, where the precipitation of suspended and dissolved forms of metals increases sharply (Oreshkin and Gordeev, 1983). Also, the human economic activity can also increase the concentration of these metals in the sediment.

A comparison was made of the activity of individual gryphons in their passive and active phases. It was found that with an active gryphon, the output volume of spontaneous gases increases sharply (from 0.5 to 7l/min), and the temperature of the water-mud mixture increases (from $+10^{\circ}C$ to $+16^{\circ}C$) (Astakhov et al., 2001). The content of a number of chemical elements in mud breccias also changes (Astakhov et al., 2001; Sorochinskaya et al., 2008). During the activation of the Yu-9 and Yu-10 gryphons (samples Yu-9 / 17.08 and Yu-10 / 17.08), the contents of many elements such as Fe, Na, Mg, Mn, Sc, Rb, As, V, Cr, Co, Ni, Zn, Zr, Y, Sn, Cs, W, Pb are decreased, while the contents of Ba, Li, Na are increased. A more contrasting feature is observed for the Yu-10 gryphon (Figure 5). Activation of gryphons is accompanied by a decrease in the content of REE, in the sample Yu-9/17.08, for example, from 111.25 g/t decreasing to 110.45 g/t, and in the sample Yu-10/17.08, the content being from 109.71 g/t decreasing to 59.83 g/t (Figure 6). The most significant decrease is observed in the content of light lanthanides (La and Ce), where the ratio of LREE/HREE for gryphon Yu-10 during the activation is reduced from 4.89 to 3.91. The europium anomaly (Eu/Eu*) in the breccia is also reduced when the gryphon is activated, for example, for Yu-9 gryphon from 0.62 to 0.59, for Yu-10 gryphon from 0.64 to 0.62.

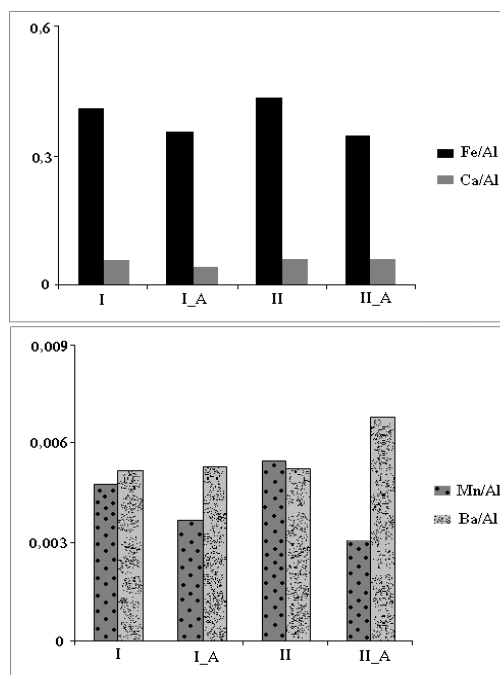


Figure 5. Changes in chemical compositions of mud volcanic breccia in active and passive eruptive mud; I, II- Fe/Al, Ca/Al, Mn/Al, Ba/Al in samples selected from passive gryphons Yu-9 and Yu-10 respectively, I_A, II_A - Fe/Al, Ca/Al, Mn/Al, Ba/Al in samples selected with activation of gryphons (samples Yu-9/17.08 and Yu-10/17.08)

Since YSMV refers to the carbonic-methane-type mud volcanoes, under activation, the rate of CO_2 , CH_4 and N_2 increases sharply (Shakirov, 2016). This promotes the formation and migration of soluble hydrocarbonate complexes of many elements, in particular iron, calcium, manganese and REE, etc. This is associated with a decrease in the content of these cations in the mud volcanic breccia during the activation of a gryphon. But an increase in the contents of a number of elements such as Na, Li, Ba, Hg, B, characterized by the mud breccia, is associated with endogenous supply along with the deep hydrocarbon gases (Aliyev et al., 2009; Shnyukov et al., 1992; Yakubov et al., 1980).

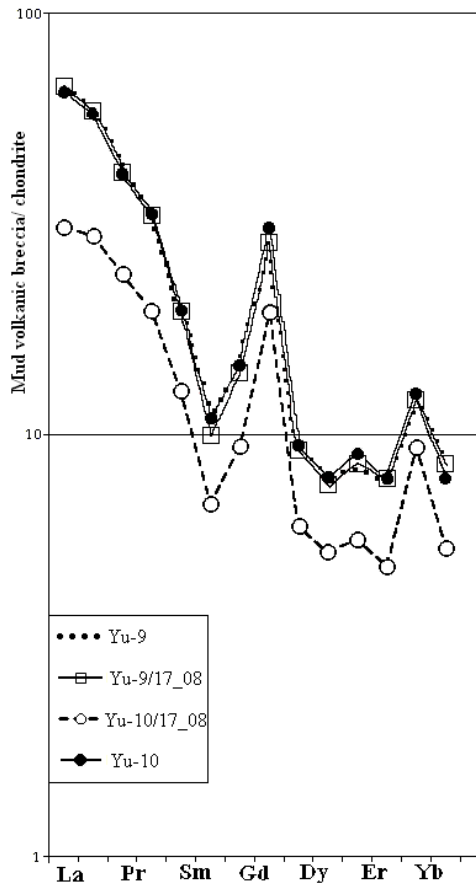


Figure 6. Rare earth element chondrite normalized of samples collected at active and passive gryphons of YSMV

5. Conclusions

The chemical and isotope compositions of free gases, and the chemical composition of the mud breccia including complex of authigenic minerals, indicate the genetic relationship of the Yuzhno-Sakhalinsky and Pugachevsky mud volcanoes. YSMV and PMV are located in the field of the sedimentary sequence (Bykovskaya suite), and are confined to one tectonic structure (Central-Sakhalin deep fault) and are of the carbonic-methane-type mud volcanoes. The carbon isotope composition of carbon dioxide ($\delta^{13}\text{C} = -2.8$ to -2.7% PDB) and methane ($\delta^{13}\text{C} = -27.1\%$

PDB) indicates the formation of these gases as a result of deep thermogenic transformation of organic matter. The contents of the most chemical elements in the mud breccia of YSMV and PMV are comparable to the Clarke contents of these elements ($0.8-1.2 \times C$). For Na, Li, Zn, Sn, the C_{sample}/C ratio varies from 1.4 to $5.2 \times C$. Elevated contents of Na and Li are due to the ascending endogenous fluid.

The study of the chemical composition of the mud breccia during the change in the explosive activity of YSMV under the seismic activity allowed to clarify: when the gryphons are under activation against the background of an increase in the temperature of the water mud mixture and the volumes of spontaneous gases, the content of a number of elements (iron, calcium, manganese, rare earths, etc.) is decreased. This is explained by the formation of soluble hydrocarbonate complexes. When excess CO_2 is removed, the above cations are precipitated from the solution in the form of iron - sideroplezite carbonates. The resulting carbonates are enriched with trace elements, which saturate the associated water during the activation period and inherit the carbon isotope composition of carbon dioxide.

For the Daginsky geothermal system, the main component of the spontaneous gas is methane having an isotopic composition of $\delta^{13}\text{C}$ from -58.8 to -57.0% PDB. This methane resulted from the mixture: a result of anaerobic decomposition of organic matter (thermogenic) and involving methane-forming bacteria (microbial). In such physicochemical conditions, the ferrous iron is bound to sulfides, and the main authigenic mineral on the DGHS is pyrite. Ooze samples from DGHS are depleted with trace elements compared to samples from YSMV and PMV, and C_{sample}/C values for the majority of the elements are $0.6 \times C$. In DGHS ooze samples, only Cd ($2.2-3.4 \times C$) and Pb ($0.7-1.5 \times C$) are higher than the Clarke content.

Deep shears are the supply channels for both fluids from sedimentary basins (hydrocarbons) and magmatic rock fluids (helium, hydrogen, carbon dioxide). The mud volcanic gas emission from sedimentary basins is enhanced during seismic activity. The presence of active mud volcanoes and mineral springs proves the activity of deep faults, through which deep fluids migrate. The factors determining the 'weighting' of the methane carbon isotope composition in southern Sakhalin are probably the increased seismic activity of deep-seated faults, as well as the presence of intrusions and hydrothermally altered rocks.

Yuzno-Sakhalinsky and Pugachevsky mud volcanoes are sharply varied from the Darginskie gas-geothermal springs. This difference is related to the gasgeochemical zoning of the Sakhalin Island: mud volcanoes are located in the 'carbon dioxide-methane zone', while Darginskie gas-geothermal springs located in the 'methane zone'.

The same research pattern may be proposed to geothermal springs in Viet Nam along the Red River deep seated faults and geothermal-mud manifestations in the Central Vietnam.

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