

## Isotope and Chemical Composition of Gases from Mud Volcanoes in the Taman Peninsula and Problem of Their Genesis

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**Abstract**—Variations in the carbon isotope composition in gases and waters of mud volcanoes in the Taman Peninsula are studied. The  $\delta^{13}\text{C}$  values in  $\text{CH}_4$  and  $\text{CO}_2$  vary from  $-59.5$  to  $-44.0\text{‰}$  ( $\delta^{13}\text{C}_{\text{av}} = -52.4 \pm 5.4\text{‰}$ ) and from  $-17.8$  to  $+22.8\text{‰}$  ( $\delta^{13}\text{C}_{\text{av}} = +6.9 \pm 9.3\text{‰}$ ), respectively. In waters from most mud volcanoes of the peninsula, this parameter ranges from  $+3.3$  to  $+33.1\text{‰}$ , although locally lower values are also recorded (up to  $-12\text{‰}$ ). Fractionation of carbon isotopes in the  $\text{CO}_2\text{--HCO}_3$  system corresponds to the isotope equilibrium under Earth's surface temperatures. The growth of carbon dioxide concentration in the gaseous phase and increase in the  $\text{HCO}_3$  ion concentration in their water phase is accompanied by the enrichment of the latter with the heavy  $^{13}\text{C}$  isotope. The  $\delta^{13}\text{C}_{\text{TDIC}}$  value in the water-soluble carbon depends on the occurrence time of water on the Earth's surface (exchange with atmospheric  $\text{CO}_2$ , methane oxidation, precipitation of carbonates, and other processes), in addition to its primary composition. In this connection, fluctuations in  $\delta^{13}\text{C}_{\text{TDIC}}$  values in mud volcanoes with stagnant waters may amount to  $10\text{--}20\text{‰}$ . In the clayey pulp, concentrations of carbonate matter recalculated to  $\text{CaCO}_3$  varies from  $1\text{--}4$  to  $36\text{--}50$  wt %. The  $\delta^{13}\text{C}$  value in the latter ranges from  $-3.6$  to  $+8.4\text{‰}$ . Carbonate matter of the clayey pulp represents a mixture of sedimentogenic and authigenic carbonates. Therefore, it is usually unbalanced in terms of the carbon isotope composition with the water-soluble  $\text{CO}_2$  forms.

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For a long time, mud volcanism has attracted the attention of researchers, who propose and discuss different hypotheses and formation models of this remarkable natural phenomenon. Many outstanding Russian researchers have dedicated works to this phenomenon: I.M. Gubkin, G.V. Abikh, P.N. Kropotkin, V.N. Kholodov, N.I. Andrusov, V.I. Vernadsky, A.D. Arkhangel'sky, V.V. Belousov, N.S. Shatskii, V.E. Khain, A.B. Ronov, A.I. Kosygin, A.A. Yakubov, A.A. Aliev, E.F. Shnyukov, and others. Genetic problems of this process are far from being exhausted, which is evident from the current discussion about relations between mud volcanism and degassing of the Earth's interior, i.e., degassing of deep zones ("subcover," according to B.M. Valyaev) of geospheres. Previous investigations revealed that methane in mud volcanic fluids of the Taman Peninsula is close by its carbon isotope composition ( $\delta^{13}\text{C}_{\text{CH}_4}$  from  $-62.8$  to  $-33.4\text{‰}$  relative to PDB) to that from hydrocarbon fields distributed in the same region (Valyaev et al., 1985), while carbon dioxide in these fluids is significantly enriched with the heavy carbon isotope ( $\delta^{13}\text{C}_{\text{CO}_2}$  up to  $+16\text{‰}$ ).

Some researchers explained higher  $\delta^{13}\text{C}$  values in carbon dioxide from mud volcanoes by mantle degassing (Kropotkin and Valyaev, 1981). This conclusion is distinctly inconsistent with recent views on the isotope composition of mantle carbon. In high-temperature

carbon-bearing products of the mantle, such as diamonds from kimberlite pipes, carbonatites, volcanic gases, and vapor inclusions in basalts,  $\delta^{13}\text{C}$  values are usually  $-6 \pm 2\text{‰}$ . Such values are usually considered as characteristic of the mantle (Deines, 1992; Pokrovskii, 2000; and others). Some mantle rocks exhibit low concentrations of reduced carbon forms with lower  $\delta^{13}\text{C}$  values (approximately  $-25\text{‰}$ ), which are thought to be related to the mantle degassing (Pineau Javoy, 1983, 1994; Taylor, 1986) or, less commonly, mantle heterogeneity (Deines, 2002). As far as we know,  $\delta^{13}\text{C}$  values  $> 0\text{‰}$  were never recorded in mantle rocks and high-temperature gases. It is hardly reasonable to consider low-temperature mud volcanic emanations as some peculiar mantle phenomenon, which is clearly confirmed by investigations of the helium isotope composition in gases of the Taman Peninsula (Kikvadze et al., 2010; Lavrushin et al., 1996).

Nevertheless, the factors responsible for variations in some chemical and isotopic parameters of mud volcanic fluids observed in the Taman Peninsula still remain obscure. In this work, we have analyzed relations between the isotope composition of carbon ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{HCO}_3$ ) with other parameters and temperature-dependent properties of fluids from the mud volcanic system of Taman.

## GEOLOGICAL STRUCTURE OF THE TAMAN PENINSULA

In Russia, mud volcanoes are most widespread precisely in the Taman Peninsula, which hoists 38 such structures. Approximately 20 of them expel permanently water and gases. Some of them eject intermittently clayey breccias (Shnyukov et al., 1986). They are confined to the areas characterized by the thick Pliocene–Quaternary sedimentary section being localized in the southwestern peripheral part of the Indol–Kuban foredeep, which borders in the north the eastern segment of the Greater Caucasus mountainous system. The trough is filled with Jurassic–Quaternary sediments up to 11 km thick resting upon the pre-Jurassic basement (Kerimov and Rachinskii, 2011).

The Mesozoic complex in the most part of the region is located at great depths and, thus, is poorly known. Judging from the data on the peripheral areas of the trough recovered by a few boreholes, its Jurassic interval is represented by limestones of the Oxfordian and Kimmeridgian stages. The presumable thickness of the Jurassic section is approximately 3–6 km.

The Lower Cretaceous complex up to 4 km thick is largely composed of clayey rocks with intercalations of compact limestones and siltstones. The Upper Cretaceous interval is represented by carbonate rocks up to 1.5 km thick.

The Eocene complex up to 0.7 km thick is composed of the clayey lithofacies. Its Kuma Horizon (up to 0.4 km thick), which is considered to be one of the most productive formations of the region, is represented by dark bituminous clays, marlstones, and terrigenous flysch. The Oligocene–lower Miocene complex (Maikop Formation) and entire overlying section consists mostly of clays with rare sandstone and siltstone members, which are laterally unsustainable being replaced by clays over relatively short distances. The complex is 6.5 km thick in total.

The Indol–Kuban trough is characterized by the distinctly asymmetrical structure. Its southern slope adjacent to the Greater Caucasus mountainous system is very steep, while the northern slope is gently dipping (Shnyukov et al., 1986). The southern slope is complicated by a system of fold–thrust structures with frontal parts marked by linear extended diapir folds and associated mud volcanoes (Popkov, 2006, *Tektonika ...*, 2009; Yakubov et al., 1980). It is assumed (Marinin and Rastsvetaev, 2008) that the formation of such a system of fold–thrust structures in the northwestern part of the Greater Caucasus Mountains resulted from the movement of rock masses squeezed out from the central part of the orogenic structure (area of maximum pressure and crust contraction) toward its northwestern periclinal part. These processes were most intense in the Neogene. It is believed (Shnyukov et al., 1986) that the peak of mud volcanism in the Taman Peninsula corresponded to the Chokrakian and Sar-

matian time. Now, mud volcanic processes are slowly ceasing.

## MATERIALS AND METHODS

Most of Taman mud volcanoes are characterized by the calm (salse-type) activity regime, which becomes notably weaker in summer. For example, Akhtanizovskii Volcano, which was active last time in 1994 (Lavrushin et al., 1996) and 2001 (Kikvadze et al., 2010) exhibited no indications of the fluid discharge in July 2009. The similar situation was also observed on Sopka Volcano. Powerful ejections of mud breccias intermittently accompanied by methane inflammation are relatively rare and recorded only in Gorelaya Sopka, Karabetovskii, Shugo, Golubitskii, and Miska volcanoes (Shnyukov et al., 1986).

Samples taken from 16 mud volcanoes in July 2009 (Fig. 1) combined with the data published in (Gemp et al., 1970; Lavrushin et al., 1996, 2003, 2005; Valyaev et al., 1985; Voitov, 2001) served as materials for this work.

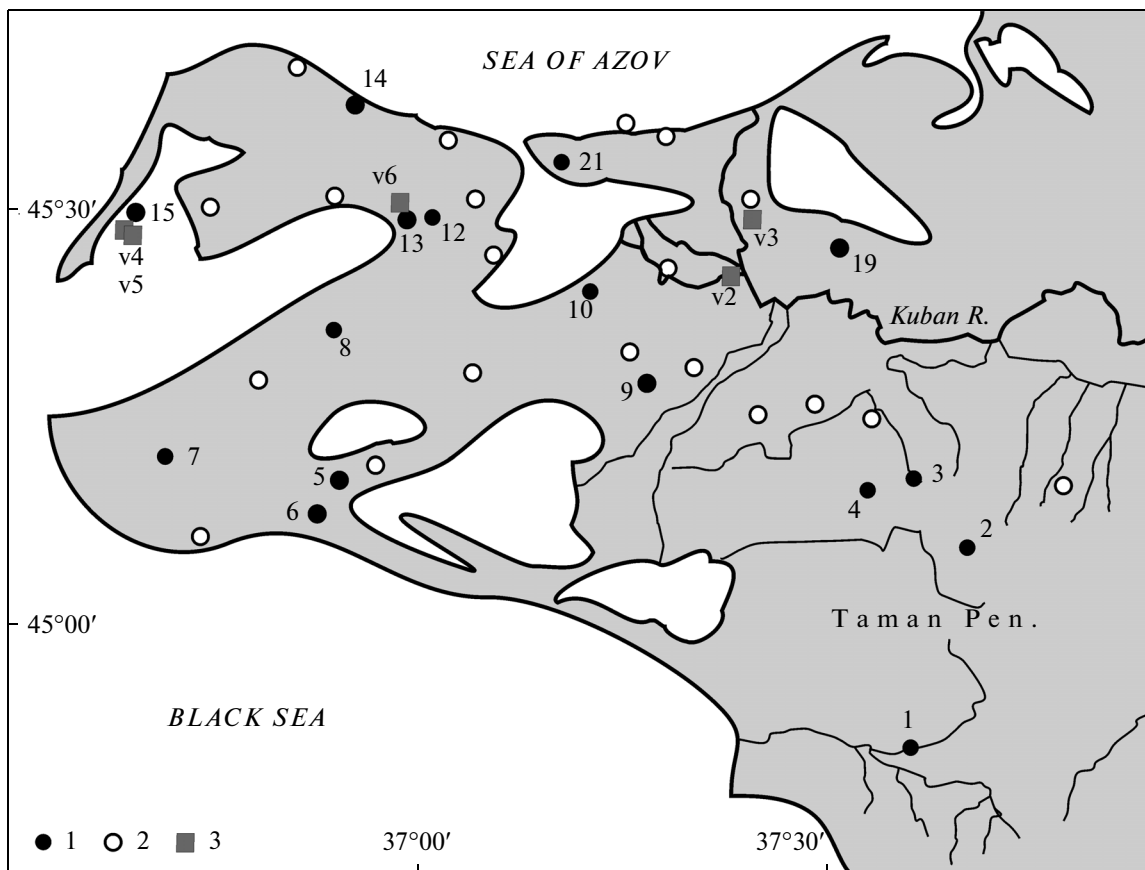
For the analytical investigations, nonassociated gases and water from the central salse, as well as breccias, were sampled in small volcanoes. In large volcanoes, fluids were sampled from several salses.

Nonassociated gases were sampled into glass bottles 220–320 cm<sup>3</sup> in size by the expulsion method. After filling, the bottles were sealed with the rubber stopper. Water was sampled into several plastic vessels for different analytical investigations.

For determining the salt composition by the ICP-AES and ICP-MS methods, water samples were filtered under field conditions through the filter with the mesh of 0.45 μm and then conserved by the nitric acid. Subsequently, they were analyzed at the Institute of Microelectronic Technology and High-Purity Materials of the Russian Academy of Sciences (IPTM RAN, Chernogolovka, Moscow region) using ICAP-61 (Thermo Jarrel Ash, USA) and X-7 ICP MS (Thermo Elemental, USA) equipments. The measurement error for concentrations of individual components was approximately 10–15%, although near the detection limit it could be as high as 50%.

Other analytical investigations of water and gases were performed at the Geological Institute of the Russian Academy of Sciences (GIN RAN, Moscow).

The values of pH, total alkalinity and Cl<sup>−</sup> concentrations, isotope composition of carbon in dissolved forms of carbon dioxide (CO<sub>2diss</sub>, CO<sub>3</sub><sup>2−</sup>, and HCO<sub>3</sub><sup>−</sup>, i.e., in the water-soluble inorganic carbon, (or total dissolved inorganic carbon, TDIC) were measured in water samples filtered through the filter 0.45 μm and kept in the refrigerator without conservation. Inasmuch as waters were characterized by neutral or alkaline pH values, and the content of boric acid in them only occasionally exceeded 10%, we assumed that total alkalinity is mostly determined by HCO<sub>3</sub> ion.



**Fig. 1.** Sampling sites of mud volcanic and surface waters in the Taman Peninsula. (1, 2) Mud volcanoes: (1) sampled, (2) non-sampled; (3) Sampling sites of surface waters. Hereinafter, numbers in figures correspond to numbers in column 1 of Table 1.

The total chemical composition of gas in 20 samples was determined with a Kristall-2000M gas chromatograph by the method of absolute calibration for each component using standard gas mixtures. Concentrations of methane and carbon dioxide were measured with the plasma ionization detector, while contents of hydrogen and oxygen were determined with the thermoconductivity detector (catarometer). Analytical error for each component never exceeded 0.5 vol %.

The carbon isotope composition was determined in  $\text{CH}_4$  and  $\text{CO}_2$  from 23 gas samples and in the dissolved inorganic carbon (TDIC) from 29 water samples. The isotopic composition of hydrogen was also measured in 8 samples of methane and that of carbon and oxygen in dispersed carbonate material in 11 samples of dry mud volcanic pulp. For determining the isotope composition of carbon, hydrogen, and oxygen, we used the complex equipment of the Thermoelectron Corporation. The complex included Delta V Advantage mass spectrometer, Gas-Bench-II device (determination of  $\delta^{13}\text{C}_{\text{TDIC}}$ ,  $\delta^{13}\text{C}_{\text{CARB}}$ , and  $\delta^{18}\text{O}_{\text{CARB}}$ ), and Trace GC Ultra gas chromatograph (determination of  $\delta^1\text{C}_{\text{CH}_4}$ ,  $\delta^1\text{C}_{\text{CO}_2}$ , and  $\delta\text{D}_{\text{CH}_4}$ ). All the  $\delta^{13}\text{C}$  values are given in

promille units (‰) relative to the V-PDB standard;  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values, in promille relative to the V-SMOW standard. The error (reproducibility) in measuring  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values never exceeded  $\pm 0.2\text{‰}$ ; the error for  $\delta\text{D}$  is  $3\text{‰}$ . Table 1 presents all the analytical data obtained by measurements.

Data on the chemical composition of water samples were used for calculating the so-called “basic” temperatures, i.e., temperatures at their formation depths. They were estimated using the Na–Li and Mg–Li geothermometers, i.e., their empirically established ratios (Fouillac and Michard, 1981; Kharaka and Mariner, 1989):

$$T^\circ\text{C} = 1000/(\log(\text{Na}/\text{Li}) - 0.14) - 273, \quad (1)$$

$$T^\circ\text{C} = 2200/(\log((\sqrt{\text{Mg}})/\text{Li}) + 5.47) - 273. \quad (2)$$

These geothermometers were developed for formation waters of petroliferous sedimentary basins, which may be considered as analogs of waters from mud volcanoes of the Taman Peninsula. Comparison of temperature estimates derived from formulas (1) and (2) (Fig. 2, Table 1) reveals their satisfactory consistency. Their general consistency is disturbed only by the data point obtained for Yuzho-Neftyanoi Volcano, which is characterized by the distinctly lowered value  $t(\text{Mg}-\text{Li}) =$

Table 1. Chemical composition and temperature of waters from mud volcanoes of the Taman Peninsula

Number in Fig. 1	Sample	Coordinates		Volcano	T°C meas.	pH	Concentration, g/L		Mineralization g/L	Concentration, mg/L		T°C (geothermometers)		
		N	E				HCO <sub>3</sub>	Cl		Na	Mg	Li*1000	Mg/Li	Li/Na
1	14-1/09	44.901	37.598	Semigorskii	22.3	7.95	5.25	2.1	4.35	2706	28	1.21	87	112
1	14-2/09	44.901	37.598	Semigorskii	23	8.5	4.63	2.1	5.35	—	—	—	—	—
1	14-3/09	44.901	37.598	Semigorskii	23	8.25	5.61	2.1	5.7	3006	28	1.16	86	106
2	2/09BG	45.006	37.724	Gladkovskii	—	6.93	0.61	11.3	—	5836	115	13.3	136	192
2	2-1/09	45.006	37.724	Gladkovskii	23.5	—	0.24	19.6	33.7	—	—	—	—	—
2	2-4/09	45.006	37.724	Gladkovskii	16.6	7.02	0.37	12.6	13	—	—	—	—	—
2	2-8/09	45.006	37.724	Gladkovskii	25.3	—	0.37	14.3	25.3	—	—	—	—	—
2	2-12/09	45.006	37.724	Gladkovskii	18.9	—	0.37	14.2	18	—	—	—	—	—
2	2-13/09	45.006	37.724	Gladkovskii	23.6	—	0.18	13.5	22.4	—	—	—	—	—
3	3-1/09BG	45.070	37.610	Shugo	21	7.73	3.54	7.8	9.16	5725	77	11.2	137	183
3	3-31/09	45.070	37.610	Shugo	24	—	—	—	—	—	—	—	—	—
4	15/09	45.028	37.586	Vostok	—	7.79	3.90	3.2	—	—	43	0.54	63	78
5	4-1/09	45.119	36.898	Bugazskii	20	7.83	6.22	2.6	7.03	3832	102	2.00	83	118
5	4-2/09	45.119	36.898	Bugazskii	23.2	8.1	6.83	3.1	8.44	4411	108	1.83	80	109
5	4-3/09	45.119	36.898	Bugazskii	—	7.79	6.10	3.2	8.68	4409	78	1.58	81	103
6	5/09	45.130	36.921	Polivadina	—	—	4.27	3.2	—	—	—	—	—	—
7	1/09	45.202	36.783	Karabetova Gora	17.9	8.02	9.25	1.5	7.6	3819	63	1.97	89	118
8	6-1/09	45.269	36.963	Shapurskii	21.6	8.48	4.27	5.7	10.2	8013	53	1.09	76	69
8	6-2/09	45.269	36.963	Shapurskii	29.7	8.81	7.93	9.4	20.1	—	—	—	—	—
8	6-3/09	45.269	36.963	Shapurskii	27.2	8.52	6.10	6.8	14.8	—	—	—	—	—
8	6-4/09	45.269	36.963	Shapurskii	31.1	8.91	9.03	12.8	28	—	—	—	—	—
8	6-5/09	45.269	36.963	Shapurskii	—	—	4.64	6.4	—	—	—	—	—	—
9	7/09	45.189	37.184	Yuzhno-Neftyanoi	30.3	—	0.37	0.14	—	108	7.3	0.02	18	84
10	8/09	45.250	37.217	Severo-Neftyanoi	—	—	2.20	3.0	—	—	—	—	—	—
10	9-1/09	45.252	37.439	Gnilaya	—	—	2.20	7.9	—	—	—	—	—	—
12	17/09	45.309	37.039	Tsentral'nye (Vostochnye) Tsimbaly	25	—	3.29	4.5	—	3903	34	1.08	82	94
13	16/09	45.317	37.067	Zapadnye Tsimbaly	23.3	8.1	4.64	2.7	6.1	—	—	—	—	—
14	13-1/09	45.432	36.923	Kuchugurskii	—	6.98	3.78	5.0	—	4814	116	1.02	66	84
14	13-2/09	45.432	36.923	Kuchugurskii	—	—	1.46	5.0	—	—	—	—	—	—
15	12/09	45.354	36.714	Chushka	17.8	7.82	3.05	4.3	7.15	4122	33	1.07	82	91
15	12-1/09	45.354	36.714	Chushka	18.2	7.65	3.90	3.3	7.52	3599	36	0.84	75	87
19	9-2/09BG	45.252	37.439	Gnilaya, central salse near lake	—	8.79	2.44	5.8	—	4597	13.3	0.11	41	20
19	9-3/09	45.252	37.439	Gnilaya, southern group	—	8.66	2.56	5.5	—	4755	5.8	0.12	51	22
21	11/09BG	45.325	37.171	Sopka	25.5	8.55	1.83	3.1	6.63	2903	10.9	0.20	56	49
v1	17-1/09	45.309	37.039	Tsentral'nye Tsimbaly	23	8.5	3.78	3.5	8.56	—	—	—	—	—
v2	8p/09	45.231	37.288	Kazachii Erik River, channel of the Kuban River	—	—	0.05	0.028	—	—	—	—	—	—
v3	10p/09	45.276	37.386	Lake on Miska Volcano	—	7.72	0.24	0.6	—	—	—	—	—	—
v4	12/09BG	45.354	36.714	Limnan, nearby Chushka Volcano	—	—	0.22	11.2	—	—	—	—	—	—
v5	12r/09	45.354	36.714	Limnan, nearby Chushka Volcano	27.6	—	—	—	20.6	—	—	—	—	—
v6	16/09r	45.317	37.067	Lake on Zapadnye Tsimbaly Volcano	—	—	—	—	—	—	—	—	—	—

(—) No data.

18°C. Table 1 also exhibits that Na–Li temperatures appear frequently to be by 10–50°C higher as compared with  $t(\text{Mg–Li})$  values. Such a discrepancy in readouts of these geothermometers may reflect the local geochemical properties of mud volcanic fluids in the Taman Peninsula, which is neglected in empirical Eqs. (1) and (2) developed for other regions. Theoretically, such discrepancies may also result from the recrystallization of magnesian calcite during lithogenesis, owing to which interstitial waters become enriched with Mg.

Another approach for determining formation temperatures of mud volcanic fluids consists in using “isotope” geothermometers, which establishes linkage between the coefficient of isotope equilibrium and temperature in line with the formula in (Bottinga, 1969):

$$\begin{aligned} & 1000 \ln \alpha(\text{CO}_2 - \text{CH}_4) \\ & = 2.28(10^6/T^2) + 15.8(10^3/T) - 8.38, \end{aligned} \quad (3)$$

where  $T$  is absolute temperature.

The following formula is also appropriate:

$$\begin{aligned} & 1000 \ln \alpha(\text{HCO}_3^- - \text{CH}_4) \\ & = 3.38(10^6/T^2) + 15.8(10^3/T) - 12.88. \end{aligned} \quad (4)$$

The latter formula is deduced by the addition of formula (3) and formula, which establishes linkage between the coefficient of isotope equilibrium in the  $\text{HCO}_3^- - \text{CH}_2$  system and temperature (Deines et al., 1974):

$$1000 \ln \alpha \text{HCO}_3^- - \text{CH}_2 = 1.1(10^6/T^2) - 4.5. \quad (5)$$

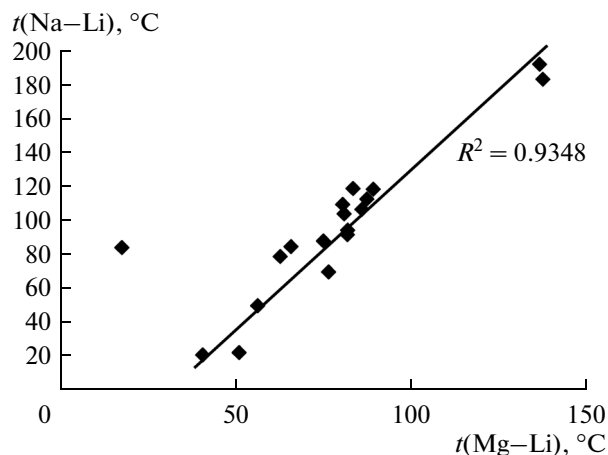
Application of isotope geothermometers is based on the assumption that the geochemical systems under consideration are characterized by isotopic equilibrium.

## RESULTS

### *Composition of Gases from Mud Volcanoes*

*Methane* is the main component of the gaseous phase in mud volcanic fluids (Table 2). In the examined samples, its concentration varies from 73.4 to 96.3 vol % averaging  $87.5 \pm 5.1$  vol % ( $n = 20$ ). In gases from some volcanoes (Shugo, Severno-Neftyanoi, Shapurskii, Polivadina), methane is accompanied by heavy hydrocarbons (HHC) constituting up to 5%. Salses of these volcanoes exhibit occasionally oil films.

The *nitrogen* concentration in most gas samples is below 1.78 vol %. Only samples from the Karabetova Gora, Kuchugurskii, and Chushka volcanoes yielded higher values (3.33, 4.09, and 4.33 vol %, respectively). *Helium* and *argon* are present in insignificant quantities (<0.1 vol %). The *oxygen* concentration never exceeds 0.04 vol %, which means that contamination of gas samples by atmospheric air was insignificant.



**Fig. 2.** Correlation between the calculated formation temperatures of salt composition in the waters from mud volcanoes derived from the hydrochemical geothermometers, according to formulas (1) and (2).

*Carbon dioxide* is also an important component of the gaseous phase being second in significance. Its concentration varies from 0.5 to 22.0 vol % (Table 2) averaging  $7.2 \pm 4.5$  vol % ( $n = 20$ ). In 2009, maximum concentrations of  $\text{CO}_2$  (>15%) were recorded in Karabetova Gora (point 7) (hereinafter, numbers of point correspond to numbers of volcanoes in the first column of Table 1), Polivadina (point 6), Kuchugurskii (point 14), and Semigorskii (point 1) volcanoes.

The tendency for the growth of carbon dioxide concentrations in gases of volcanoes confined to the Kerch Strait, which was assumed by previous researchers (Lagunova and Gemp, 1978; Shnyukov et al., 1986), received no confirmation in our investigations.

Repeated sampling of mud volcanoes in the Taman Peninsula shows that concentrations of carbon dioxide and methane vary both laterally (in neighboring gas occurrences) and temporally. For example, the  $\text{CO}_2$  concentrations in gases from the central salse of Kuchugurskii Volcano is 17 vol %, while in gas from the salse located on the slope of mud volcano edifice, its value is approximately 10 vol %. The  $\text{CO}_2$  concentration in the same mud volcano is usually higher in salses (usually central) with the high yield, while the relatively low-yield peripheral parts are characterized by higher methane and nitrogen concentrations (Table 2). Variations in the gas composition are particularly notable in Semigorskii Volcano. The sampling of its central part in 1994 (Lavrushin et al., 1996), 2001 (Kikvadze et al., 2010), and 2009 revealed that  $\text{CO}_2$  concentrations were substantially different constituting 3, 7, and 17 vol %, respectively. As was previously noted, the  $\text{CO}_2$  concentration in gases from Gnilaya Volcano varies with time within several tens of percents (Gemp et al., 1970; Shnyukov et al., 1986; Valyaev et al. 1985). Temporal variations in relative concentra-

**Table 2.** Chemical composition of nonassociated gases and isotopic characteristics of carbon-bearing compounds in expelled products of mud volcanoes

Number in Fig. 1	Sample	Volcano	Concentration, vol %				$\delta^{13}\text{C}$ , ‰ PDB				wt %	$\delta^{18}\text{O}$ , ‰ PDB
			$\text{CH}_4$	$\text{CO}_2$	$\text{N}_2$	Sum	$\text{CH}_4$	$\text{CO}_2$	$\text{HCO}_3$	$\text{CaCO}_3$		
1	14-1/09	Semigorskii	78.7	17.4	0.76	96.9	-48.8	-3.9	9.1	—	39.5	—
1	14-2/09	Semigorskii	—	—	—	—	—	—	7.9	1.4	—	28.2
1	14-3/09	Semigorskii	88.1	8.0	1.00	97.1	-47.0	0.3	8.9	—	18.3	—
2	2/09BG	Gladkovskii	91.5	1.7	3.33	96.6	—	—	27	1.8	3.8	29.5
2	2-1/09	Gladkovskii	—	—	—	—	-34.6	22.1	7.3	—	—	—
2	2-4/09	Gladkovskii	—	—	—	—	—	—	17.5	—	—	—
2	2-8/09	Gladkovskii	—	—	—	—	—	—	23.7	—	—	—
2	2-12/09	Gladkovskii	—	—	—	—	—	—	6.1	—	—	—
2	2-13/09	Gladkovskii	—	—	—	—	—	—	13.4	—	—	—
3	3-1/09BG	Shugo	91.2	4.5	1.49	97.3	-46.9	-2.1	33.1	3.6	10.3	30.7
3	3-31/09	Shugo	—	—	—	—	—	—	4.1	—	—	—
4	15/09	Vostok	89.5	6.9	0.83	97.3	-52.0	-1.5	7.6	—	15.7	—
5	4-1/09	Bugazskii	89.6	6.4	0.96	97.0	-48.1	22.8	30.8	1.3	14.5	30.4
5	4-2/09	Bugazskii	—	—	—	—	—	—	31.6	—	—	—
5	4-3/09	Bugazskii	—	—	—	—	-44.0	21	30.3	—	—	—
6	5/09	Polivadina	79.6	15.9	0.95	96.4	-50.5	11.6	24.1	—	—	—
7	1/09	Karabetova Gora	73.4	22.0	1.60	97.1	-45.3	12.2	24	0.9	36.2	33.0
8	6-1/09	Shapurskii	—	—	—	—	-45.0	15.5	31.6	—	—	—
8	6-2/09	Shapurskii	—	—	—	—	-47.5	16.8	31.6	—	—	—
8	6-3/09	Shapurskii	—	—	—	—	—	—	30.2	—	—	—
8	6-4/09	Shapurskii	—	—	—	—	—	—	23.7	—	—	—
8	6-5/09	Shapurskii	91.9	4.8	0.80	96.9	-51.5	15.1	27.2	3.1	10.9	29.9
9	7/09	Yuzhno-Neftyanoi	82.4	5.3	0.71	88.5	-52.0	13.7	-12.1	—	12.0	—
10	8/09	Severo-Neftyanoi	85.7	7.2	1.36	94.3	-54.5	16.5	29	—	16.4	—
10	9-1/09	Gnilaya	—	—	—	—	—	—	-4.8	—	—	—
12	17/09	Tsentrallye (Eastern) Tsimbaly	94.7	1.8	0.95	97.4	-59.5	-9	-1.1	—	4.0	—
13	16/09	Zapadnye Tsimbaly	91.2	4.1	1.78	97.1	-53.5	13.5	23.5	—	9.4	—
14	13-1/09	Kuchugurskii	79.1	16.9	0.79	96.8	-54.5	3.2	19.5	8.4	38.4	33.1
14	13-2/09	Kuchugurskii	83.1	9.9	4.09	97.2	-57.5	-17.8	-9.3	—	22.5	—
15	12/09	Chushka	92.4	3.7	1.68	97.8	-56.2	6.7	15.8	-0.5	8.3	28.9
15	12-1/09	Chushka	87.4	5.3	4.83	97.6	-52.5	8.3	17.4	—	11.9	—
19	9-2/09BG	Gnilaya, central salse near lake	95.3	0.8	1.08	97.2	-72.5	-4.4	3.3	—	1.8	28.5
19	9-3/09	Gnilaya, southern group	96.3	0.5	1.02	97.8	-70.0	-4.9	3.3	-3.6	1.0	—
21	11/09BG	Sopka	89.4	6.7	1.05	97.2	-44.0	18.4	5.9	7.9	15.2	31.1
v1	17-1/09	Tsentrallye Tsimbaly	—	—	—	—	—	—	5.7	—	—	—
v2	8r/09	Kazachii Erik River, channel of the Kuban River	—	—	—	—	—	—	-10.2	—	—	—
v3	10r/09	Lake on Miska Volcano	—	—	—	—	—	—	-14.2	—	—	—
v4	12/09BG	Liman, nearby Chushka Volcano	—	—	—	—	—	—	-7.3	—	—	—
v5	12r/09	Liman, nearby Chushka Volcano	—	—	—	—	—	—	-8.2	—	—	—
v6	16/09r	Lake on Zapadnye Tsimbaly Volcano	—	—	—	—	—	—	-9.2	—	—	—

(—) No data.

tions of methane and carbon dioxide indicate that the influx of at least one of these gases to the mud volcanic emanations is variable.

#### *Chemical Composition of Waters from Mud Volcanoes*

Waters from the Taman volcanoes are characterized by neutral and low-alkalinity pH values (6.9–8.8). Their mineralization varies from 4.3 to 33.7 g/L averaging 12.5 g/L. Main components of the salt composition are  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{HCO}_3^-$ . The  $\text{Cl}^-$  concentration is 3–6 times lower as compared with that in seawater, where it averages 19.35 g/L (Horne, 1969). The sole exception is represented by Gladkovskii Volcano, where  $\text{Cl}^-$  concentration in waters is as high as approximately 16 g/L and total mineralization amounts to 33 g/L. This volcano is also characterized by the different composition of fluids with the main cation being represented by  $\text{Ca}^{2+}$  instead of  $\text{Na}^{2+}$ .

In large volcanoes, different salses were sampled. It appeared that, dissimilar to the gaseous phase, variations in the composition of the water phase within a single mud volcano are insignificant and irregular (Table 1). The most significant differences are observable in water samples taken from the closed (or low-yield) and water-expelling salses. Concentration of salts in the first source was usually higher as compared with that from the second one, which likely reflects the different degrees of water evaporation at the surface.

The  $\text{HCO}_3^-$  ion concentration (total alkalinity) in most volcanoes varies from 1.4 to 9.25 g/L averaging 3.4 g/L ( $n = 22$ ). Its maximum concentrations are documented in the western and southwestern parts of the Taman Peninsula: Karabetova Gora (point 7) and Shapurskii (point 8) volcanoes. In the central and northern parts of the peninsula, concentrations of this component are relatively low. The water samples obtained from Gladkovskii Volcano exhibit anomalously low  $[\text{HCO}_3^-]$  values.

As a whole, elevated  $\text{HCO}_3^-$  concentrations are characteristic of salses, which expel gases with high  $\text{CO}_2$  contents (Fig. 3).

#### *Water Formation Temperatures*

At air temperatures ranging from 25 to 32°C, water temperatures in salses varied from 16.6 to 30.3°C. Their maximum values are recorded in low-yield or closed salses, while the lowest temperatures are documented in volcanoes that intensely eject the clayey pulp. It is apparent that their temperatures are distorted by surface factors due to low rates of the fluid discharge: they become cooler in the layer of “neutral” temperatures or warmer at the surface.

Both temperatures of waters at deep levels of the mud volcanic system (formation temperatures of their chemical composition) and depths of fluid generation

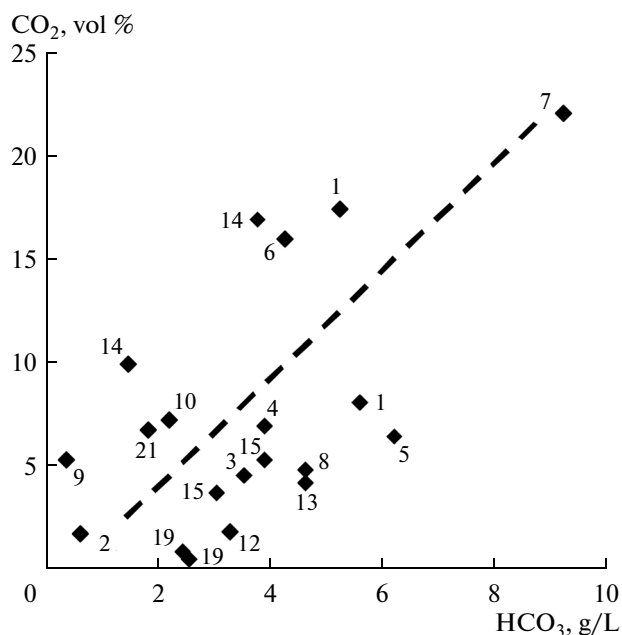


Fig. 3. Correlation between  $\text{CO}_2$  and  $\text{HCO}_3^-$  ion concentrations in the gaseous and water phases, respectively. Dashed line shows the assumed trend.

are unknown. Therefore, they were estimated by indirect methods using the Mg–Li and Na–Li geothermometers (Kharaka and Mariner, 1989). The first estimates of such “basic” temperatures for volcanoes of the Taman Peninsula were derived from chemical analyses of water samples taken in 2001 (Lavrushin et al., 2003). Similar calculations were also performed for water samples obtained in 2009. Their values range from 18 to 137°C and from 20 to 192°C averaging 72 and 91°C, respectively (Table 1). Comparison between the calculated temperature values obtained for water samples of 2001 and 2009 revealed their good consistency: the difference in estimates derived from particular geochronometers never exceeded 5–10°C.

Taking into consideration the value of the geothermal gradient in the Taman Peninsula equal to 40°C/km (Lagunova, 1974), these data allows the formation depth of the chemical composition of waters in mud volcanoes to be estimated as varying from 0.5–1.0 to 4–5 km. Such depths correspond to the interval occupied by Maikop clays. The maximum “basic” temperature values are obtained for the southernmost volcanoes of the Taman Peninsula, which are closest to the Greater Caucasus orogen: Shugo (point 3), Gladkovskii (point 2), and Semigorskii (point 1). It is conceivable that such a distribution of temperatures reflects the increase of heat flow values toward the latter or higher degree of tectonic differentiation, which provides the contribution of deeper aquifers.

*Isotopic Properties of Carbon-Bearing Components  
in Fluids and Breccias*

The isotopic composition of carbon in most *methane* samples (20 of 23) shows insignificant variations:  $\delta^{13}\text{C}$  from  $-59.5$  to  $-44.0\text{‰}$  ( $\delta^{13}\text{C}_{\text{av}} = -52.4 \pm 5.4\text{‰}$ ). Such values reflect the thermocatalytic transformation of organic matter (Galimov, 1973). The anomalously high  $\delta^{13}\text{C}$  values ( $-34.6\text{‰}$ ) are characteristic of methane from Gladkovskii Volcano. According to the sampling of 1980, precisely gases from this volcano are characterized by similarly high  $\delta^{13}\text{C}(\text{CH}_4)$  values equal to  $-33.4\text{‰}$  (Valyaev et al., 1985). The lowest  $\delta^{13}\text{C}_{\text{CH}_4}$  values of  $-72.5$  and  $-70.0\text{‰}$  indicating the microbial synthesis of methane are documented in gases from Gnilaya Volcano.

In carbon dioxide, the  $\delta^{13}\text{C}$  values range from  $-17.8$  to  $+22.8\text{‰}$  ( $\delta^{13}\text{C}_{\text{av}} = +6.9 \pm 9.3\text{‰}$ ).

The  $\delta^{13}\text{C}$  values in methane and carbon dioxide within an individual volcano are slightly variable for different years or its different salses. For example, sampling in Shugo Volcano every 15 min during 2 h revealed insignificant variations in ( $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^{13}\text{C}_{\text{CO}_2}$ : from  $-39.0$  to  $-37.1\text{‰}$  and from  $-4.7$  to  $-1.8\text{‰}$ , respectively (Voitov, 2001). According to sampling of the same volcano in 1977–1981, variations in these parameters amounted to  $\sim 25\text{‰}$  (Valyaev et al., 1985). Even more significant difference in the  $\delta^{13}\text{C}_{\text{CO}_2}$  values were obtained for Yuzhno-Neftyanoi Volcano: up to  $35\text{‰}$ . It should be noted that our data on  $\delta^{13}\text{C}_{\text{CH}_4}$  values are, in general, well consistent with previous values obtained for the same volcanoes (Gemp et al., 1970; Valyaev et al., 1985), being although lower ranging from  $-15.3$  to  $+0.4\text{‰}$  (by  $-6\text{‰}$ , on the average). Dissimilar to  $\delta^{13}\text{C}(\text{CH}_4)$  values, our data on  $\delta^{13}\text{C}_{\text{CO}_2}$  demonstrate no consistency with the previously published data. Variations in the last parameter appear to be more significant: from  $-22.0$  to  $+35.5\text{‰}$  averaging  $+4\text{‰}$ . The cause of such discrepancies is unclear.

By their carbon isotope composition, the samples obtained from different salses of a single volcano show usually insignificant differences. The sole exception is Kuchugurskii Volcano, where the  $\delta^{13}\text{C}(\text{CO}_2)$  value in the sampled peripheral salse appeared to be significantly lower as compared with that in the central one. This example illustrates the complex model of the fluid flow formation in a mud volcanic system. The water sample from the same peripheral salse of Kuchugurskii Volcano is additionally remarkable for the anomalously high concentration of sulfate ion ( $7.9$  g/L), the presence of which is atypical of waters from mud volcanoes in the Taman Peninsulas. This implies mixing with unknown waters from the subsurface zone (Lavrushin et al., 2003, 2005).

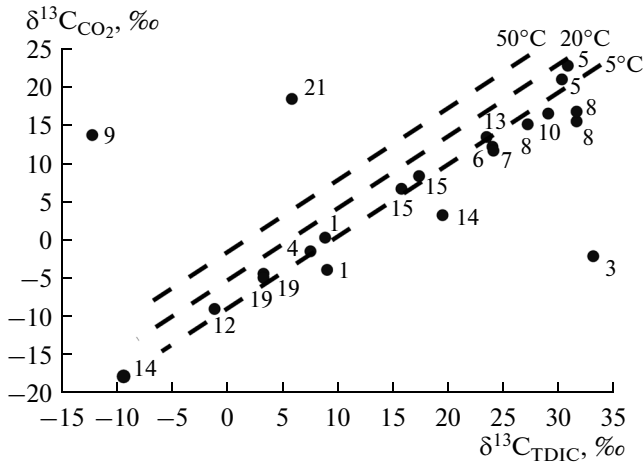
The isotope composition of carbon in *dissolved forms of carbon dioxide* in waters from the Taman volcanoes was never investigated. Our data show that waters from mud volcanoes substantially differ in the carbon isotope composition from their surface counterparts (Table 2). The  $\delta^{13}\text{C}_{\text{TDIC}}$  values in most samples vary from  $+3.3$  to  $+33.1\text{‰}$ . Three samples obtained in the Gnilaya, Yuzhno-Neftyanoi, and Tsentral'nye Tsimbaly volcanoes exhibit negative  $\delta^{13}\text{C}_{\text{TDIC}}$  values:  $-12.1$ ,  $-9.3$ , and  $-1.1\text{‰}$ , respectively. Without these estimates, the average  $\delta^{13}\text{C}_{\text{TDIC}}$  value for 31 samples is  $18.2 \pm 9.7\text{‰}$ . The highest  $\delta^{13}\text{C}_{\text{TDIC}}$  values ( $>29.0\text{‰}$ ) are detected in the Bugazskii, Shapurskii, Severo-Neftyanoi, and Shugo volcanoes. No spatial regularities in variations of the isotope composition of water-soluble inorganic carbon are defined in the examined samples.

In samples taken from different salses of the same volcano, the  $\delta^{13}\text{C}_{\text{TDIC}}$  values differ by not more than  $4\text{‰}$ . At the same time, for some volcanoes (Gladkovskii, Kuchugurskii, and Shugo) the variation range amounts to  $\sim 28\text{‰}$  (Table 2). Such differences may likely be determined by primary geochemical heterogeneities of fluids related to their genesis and influence of processes at the surface such as, for example, evaporation.

Ratio the  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{TDIC}}$  values in fluids of mud volcanoes is controlled by the fractionation of carbon isotopes between the dissolved and nonassociated carbon dioxide reflecting temperature of the isotopic equilibrium (Mook et al., 1974). In the analyzed 21 pairs of the  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{TDIC}}$  values, 18 pairs differ from each other by  $8.5$  to  $12.5\text{‰}$ . This corresponds to the equilibrium temperature below  $20^\circ\text{C}$  (Fig. 4). The total selection demonstrates positive correlation of these values:  $R^2 = 0.48$  ( $n = 21$ ),  $R = 0.69 > R_{\text{crit}}$ . If three data points corresponding to the Yuzhno-Neftyanoi, Shugo, and Sopka volcanoes are excluded from consideration, the dependence between the comparable parameters looks practically as a functional one corresponding to the equilibrium at temperature of approximately  $5^\circ\text{C}$ .

Influence of the surface water evaporation on the isotopic composition of carbon is illustrated by Gladkovskii Volcano. In this structure, several salses (including closed) with variable mineralization and  $\text{HCO}_3^-$  ion concentration (Table 1) were sampled in the area approximately  $\sim 50 \times 50$  m in size. Comparison between the Cl ion concentrations and  $\delta^{13}\text{C}_{\text{TDIC}}$  values reveals the tendency for the increase of the latter with the growth of water mineralization. Such a trend cannot result from degassing, since carbon dioxide at surface temperature is depleted in  $\delta^{13}\text{C}_{\text{TDIC}}$ , relative to bicarbonate ion dissolved in water, by  $8$ – $10\text{‰}$  (Deines et al., 1974). The observed tendency may result from several consistent processes: the isotopic exchange between waters from mud volcanoes and atmospheric





**Fig. 4.** Correlation between  $\delta^{13}\text{C}$  values in the gaseous and dissolved carbon dioxide from fluids of mud volcanoes in the Taman Peninsula.

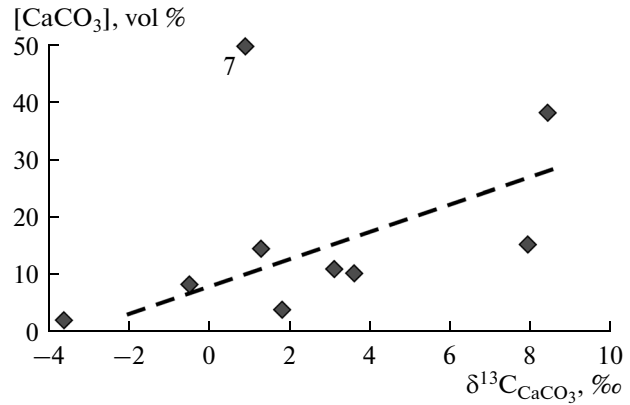
Dashed lines designate isotopic equilibrium for the  $\text{CO}_2(\text{gas})\text{--HCO}_3^-$  system at different temperatures, after (Mook et al., 1974).

$\text{CO}_2$  ( $\delta^{13}\text{C}(\text{CO}_2 \text{atm}) = -7\text{‰}$ ) and/or release of  $\text{CO}_2$  produced due to the microbial oxidation of methane in muddy sediments of salses.

*Clayey pulp* ejected by volcanoes contains from 1 to 50 wt % of carbonate material (Table 2). Its analysis revealed that the  $\delta^{13}\text{C}_{\text{carb}}$  value ranges usually from  $-3.6$  to  $+3.6\text{‰}$ . The higher  $\delta^{13}\text{C}_{\text{carb}}$  values are characteristic of clays from the Sopka and Kuchugurskii volcanoes:  $+7.9$  and  $+8.4\text{‰}$ , respectively.

In most samples, the  $\delta^{13}\text{C}_{\text{carb}}$  values increase with the growth of carbonate material concentrations in breccias (Fig. 5). This trend may be considered as a line indicating the mixing of two different phases, which likely represent genetically different types of carbonate material. The first, background phase (A,  $\delta^{13}\text{C} = -2 \pm 2\text{‰}$ ) corresponds probably to sedimentogenic and authigenic carbonates that are withdrawn from the sediment sequence. The second phase (B,  $\delta^{13}\text{C} > 9\text{‰}$ ) is formed on the volcano surface due to the evaporation of waters from a mud volcano. Participation of the dissolved forms of  $\text{CO}_2$  enriched with the heavy carbon isotope in carbonate mineralization of the clayey pulp from mud volcano is confirmed by the positive correlation between maximum  $\delta^{13}\text{C}_{\text{TDIC}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values (Fig. 6).

The isotope composition of oxygen in carbonate material from the clayey pulp varies from  $+28.2$  to  $+33.0\text{‰}$ . Such concentrations are similar to  $\delta^{18}\text{O}$  values observable in marine carbonates. Nevertheless, taking into consideration the polycomponent composition of analyzed carbonate material and high (from  $+0.7$  to  $+10.0\text{‰}$ )  $\delta^{18}\text{O}$  values in waters from mud volcanoes (Lavrushin et al., 2005), there are no grounds for interpreting the formation conditions of carbonates from the clayey pulp. It should also be noted that the highest  $\delta^{18}\text{O}$  values are frequently characteristic of



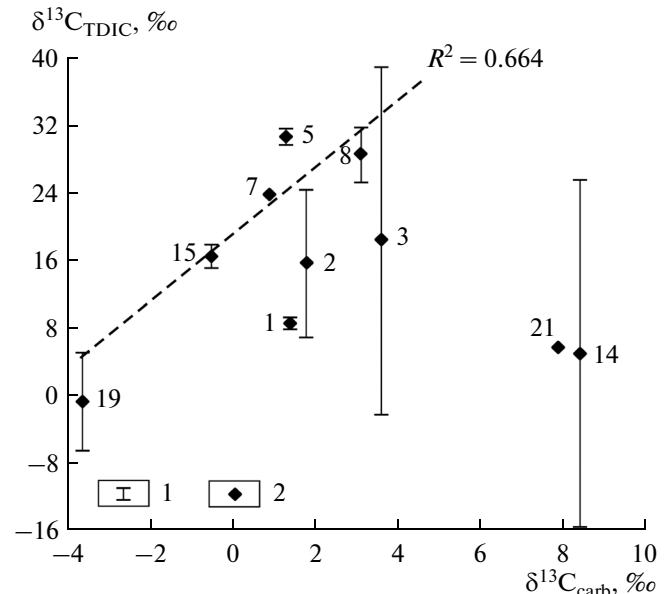
**Fig. 5.** Correlation between the carbon isotope composition and the concentration of carbonate material in mud volcanic breccias.

Dashed line shows the correlation trend ( $R_2 = 0.591$ ,  $n = 8$ ,  $R = 0.769 > R_{\text{crit}}$ ).

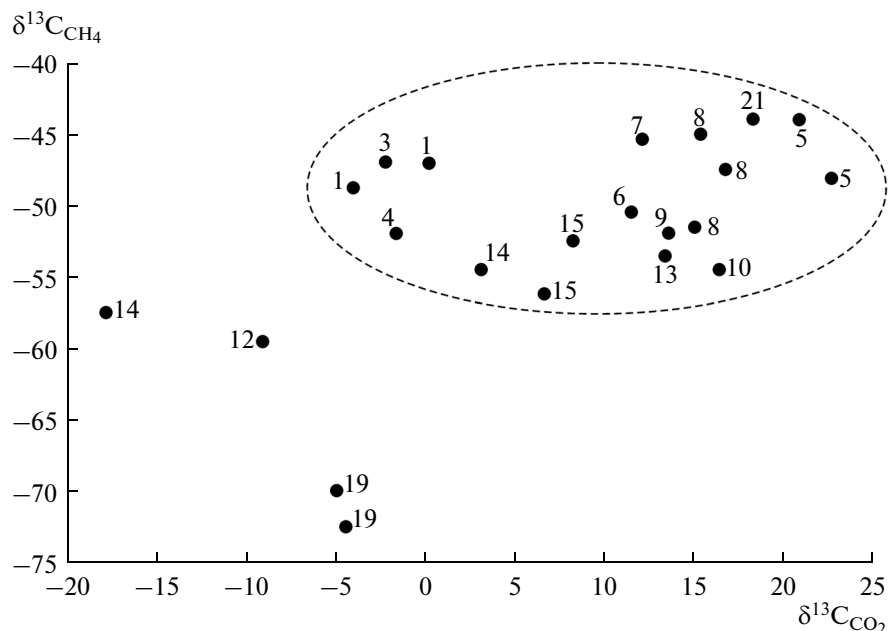
carbonates from volcanoes expelling waters with maximum  $\delta^{18}\text{O}$  values (Karabetova Gora, Shugo, Bugzaskii, and other volcanoes).

## DISCUSSION

Thermodynamic calculations performed more than 50 years ago demonstrated that the isotopic



**Fig. 6.** Correlation between  $\delta^{13}\text{C}$  values in TDIC and  $\text{CaCO}_3$  from the clayey pulp. (1) Interval of values; (2) average. Dashed line shows the correlation trend.



**Fig. 7.** Correlation between  $\delta^{13}\text{C}$  values in the carbon-bearing phases from volcanoes of the Taman Peninsula. Dashed line outlines the area of typical  $\delta^{13}\text{C}$  values in  $\text{CO}_2$  and  $\text{CH}_4$ .

exchange in the  $\text{CO}_2\text{--CH}_4$  system resulted in accumulation of the light ( $^{12}\text{C}$ ) and heavy ( $^{13}\text{C}$ ) carbon isotopes in methane and carbon dioxide, respectively (Bottinga, 1969). Therefore, the frequent co-occurrence of  $^{13}\text{C}$ -depleted methane and  $^{13}\text{C}$ -enriched carbon dioxide never represented a geochemical enigma. Such an association is recorded in natural gas accumulations (Milkov, 2011; Wasserburg et al., 1963), marine sediments enriched in organic matter (Nissenbaum et al., 1972), and hypereutrophic lakes (Gu et al., 2004), in addition to mud volcanoes. The  $^{13}\text{C}$ -enriched diagenetic carbonates are considered as indicators of methane generation in old sediments even in situations, when the latter is missing from them (Murata et al., 1967; Pokrovskii, 1980).

At the same time, significant variations in the isotopic composition of carbon in  $\text{CO}_2$  from mud volcanoes located in a relatively small area and likely related to the source in common is a complex problem. If variations in  $\delta^{13}\text{C}$  values in methane from most mud volcanoes of the Taman Peninsula are within a range of approximately 10‰, their scatter is as much as 40.6‰ in carbon dioxide from the same volcanoes (Fig. 7) and 47.3‰ in the dissolved inorganic carbon (TDIC) with the prevalence of ultrahigh  $\delta^{13}\text{C}$  values exceeding 10‰ (Table 2).

There are four main scenarios for obtaining carbon dioxide significantly enriched with the heavy carbon isotope: (1) isotopic exchange in the  $\text{CO}_2\text{--CH}_4$  system; (2) anaerobic microbial fermentation of organic matter with the formation of  $^{13}\text{C}$ -depleted methane and  $^{13}\text{C}$ -enriched carbon dioxide in the proportion of

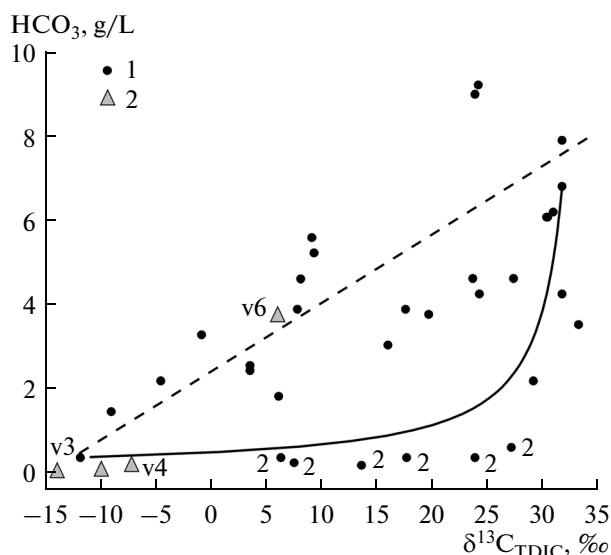
approximately 3 : 1; (3) microbial reduction of  $\text{CO}_2$  up to methane; and (4) degassing of solution oversaturated with carbon dioxide. The last of these scenarios is hardly probable, since, first, fractionation of carbon isotopes in the  $\text{CO}_2$  (gas)–TDIC system is relatively low and, second, the increase of  $\delta^{13}\text{C}_{\text{TDIC}}$  values should be accompanied by the decrease of TDIC concentrations, while these values demonstrate in fact positive correlation (Fig. 8). The choice of the most probable scenario between three others is however difficult.

The scatter of  $\delta^{13}\text{C}$  (TDIC) values comparable with that for mud volcanoes is characteristic of interstitial waters in sediments, diagenesis of which proceeds under the anaerobic conditions and is accompanied by methane generation. In interstitial waters of the Saanich Fiord in Western Canada, this scatter corresponds to the range of  $-37.1$  to  $+17.8$ ‰. Moreover, the  $\delta^{13}\text{C}$  (TDIC) values increase downward almost in all the examined cores up to 35 m thick (Nissenbaum et al., 1972). This allowed the authors to assume that methane in sediments is generated due to the reduction of carbon dioxide, and significant scatter of the  $\delta^{13}\text{C}$  values results from the exhaustion of limited reservoir of isotopically light ( $\delta^{13}\text{C} < -25$ ‰) carbon dioxide produced by the oxidation of organic matter (and, probably, methane) by the sulfate-reducing bacteria. Calculation using the Rayleigh formula shows that the  $\delta^{13}\text{C}$  (TDIC) value equal to 15–20‰ with the fractionation factor  $\alpha = 1.051$  corresponds approximately to 50% exhaustion of the carbon dioxide reservoir. At the same time, no expected decrease in the TDIC concentra-

tion was observed. To the contrary, the  $\delta^{13}\text{C}$  (TDIC) values increased in parallel with the growth of TDIC concentrations (Nissenbaum et al., 1972). It follows from the latter that the isotopic composition of carbon in  $\text{CO}_2$  was controlled in the situation under consideration by the mixing of carbon dioxide from different sources (not by Rayleigh exhaustion): isotopically heavy variety, which was generated (due to the unknown process) at some depth, and isotopically light one, the role of which increased upward. It should be noted that methane generation is not necessarily accompanied by the appearance of significant  $^{13}\text{C}$ -enriched carbon dioxide in sediments. For example, in the methane-rich sediments of the Guatemala Trench, where the thickness of continuous methane hydrates in some holes amounts to 3 m, the isotopic composition of carbon in  $\text{CO}_2$  varies in the range of negative  $\delta^{13}\text{C}$  values ranging from approximately 0 to  $-23\text{‰}$  (Galimov and Shabaeva, 1985).

Se significant variations in the  $\delta^{13}\text{C}$  values may theoretically be determined by different temperatures of the isotopic exchange in the  $\text{CO}_2\text{--CH}_4$  system or temperature of the fermentative methane genesis at different levels. Average temperatures measured by the hydrochemical and isotopic thermometers are sufficiently close to each other:  $77 \pm 28^\circ\text{C}$  (formula 1);  $67 \pm 39^\circ\text{C}$  (formula 3);  $55 \pm 41^\circ\text{C}$  (formula 4). They are well consistent with the data on borehole gases of Azerbaijan, according to which the  $^{13}\text{C}$ -enriched (isotopically heavy) carbon dioxide is formed due to the biodegradation of hydrocarbons at the upper boundary of oil generation zone at temperatures ranging from 30 to  $70^\circ\text{C}$  (Feizulaev and Movsumova, 2010; Milkov, 2011). The paradox consists in the fact that correlation of  $\delta^{13}\text{C}$  (TDIC) values is positive with temperatures derived from the hydrochemical thermometers and negative with temperatures calculated from the "isotopic" thermometer (Figs. 9a, 9b). This paradox is difficult for solving. Therefore, it is reasonable to consider both situations.

The negative correlation of the  $\delta^{13}\text{C}$  (TDIC) values and temperature of isotopic fractionation in the TDIC– $\text{CH}_4$  system is trivial: positive correlation between these parameters is excluded. Proceeding from this dependence, it may be assumed that the lower levels of the mud volcanic system are characterized by the formation of carbon dioxide depleted (not enriched) in  $^{13}\text{C}$ . The carbon dioxide becomes mixed during its upward migration with the isotopically heavy carbon dioxide that is formed at lower temperatures. Nevertheless, degassing and gradual  $\text{CO}_2$  reduction to methane may be excluded from the list of factors responsible for the enrichment of carbon dioxide with  $^{13}\text{C}$ , since the TDIC concentration cannot increase under the partial reduction of degassing (Fig. 8). As a whole, this scenario seems less probable, since the isotopically light carbon dioxide in mud volcanoes associates more readily with the  $^{13}\text{C}$ -depleted "microbial" methane, which is generated at shallow depths.

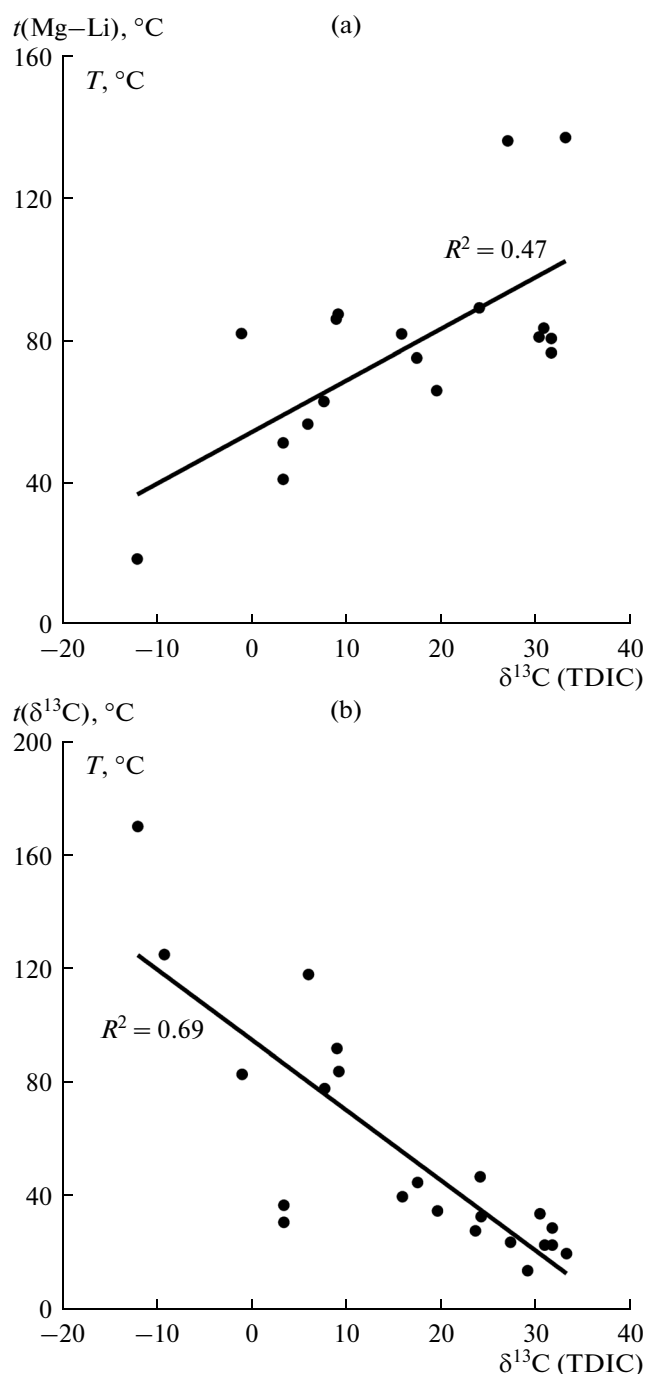


**Fig. 8.** Correlation between  $\text{HCO}_3^-$  concentrations and  $\delta^{13}\text{C}$  (TDIC) values in waters from mud volcano (1) and surface waters (2).

Dashed line shows the trend (without data points obtained for Gladkovskii Volcano); the solid line is the calculated line of mixing of the isotopically heavy and  $\text{HCO}_3^-$ -rich waters from mud volcanoes and surface waters with low  $\text{HCO}_3^-$  concentrations and negative  $\delta^{13}\text{C}_{\text{TDIC}}$  values.

Positive correlation between the Mg–Li temperature and  $\delta^{13}\text{C}$  (TDIC) values cannot result from the temperature dependence of the value of isotopic fractionation between carbon dioxide and methane. In such a situation, the effect should be opposite, since the isotopic composition of methane (dominant phase) varies insignificantly, while isotopic fractionation between carbon dioxide and methane increases with the temperature fall according to formulas (3) and (4). At the same time, temperature may indirectly indicate the depth of fluid generation: carbon dioxide maximally enriched with  $^{13}\text{C}$  should be considered in such a situation as representing a deeper component, which becomes mixed during its upward migration with  $^{13}\text{C}$ -depleted carbon dioxide that is generated by oxidized methane and/or organic matter.

Indeed, as follows from Fig. 8, the observable correlation between  $\text{HCO}_3^-$  and  $\delta^{13}\text{C}_{\text{TDIC}}$  values (dashed line) resembles the line of mixing of waters from mud volcanoes enriched in the isotopically heavy dissolved hydrocarbonate with waters depleted in  $\text{HCO}_3^-$ , TDIC of which is characterized by negative  $\delta^{13}\text{C}$  values. By their isotopic characteristics, the latter are close to surface waters. Nevertheless, the obtained dependence significantly differs by its configuration from the theoretical line of mixing of extreme water types (solid line in Fig. 8). Thus, mixing responsible for the diversity of  $\delta^{13}\text{C}$  (TDIC) values and  $\text{HCO}_3^-$



**Fig. 9.** Correlation between  $\delta^{13}\text{C}$  (TDIC) values and temperatures of fluid generation derived from the hydrochemical (Mg–Li) (a) and “isotope”  $\delta^{13}\text{C}$  ( $\text{CH}_4\text{--CO}_2\text{--HCO}_3$ ) (b) geothermometers.

Lines show the functional dependences of parameters.

concentrations cannot be described by the simple model of two-component mixing of fluid systems.

In fact, differences in the above-mentioned two interpretation variants are reduced to choice of the preferable geothermometer: carbon isotope or hydrochemical Mg–Li and Na–Li. We believe that the

hydrochemical geothermometers characterize more adequately relative variations in fluid generation temperatures in the mud volcanic systems, as compared with the carbon isotope geothermometer. This conclusion supports the previous analysis of relations between Mg–Li temperatures and different geochemical parameters of fluids from mud volcanoes (Lavrushin et al., 2003, 2006). For example, positive correlation between the  $\delta^{18}\text{O}$  values in water and the Mg–Li temperatures reflects the trend of temperature-dependent reactions of the oxygen isotope exchange in the water–rock system that controls the formation of waters with high  $\delta^{18}\text{O}$  values in the mud volcanic systems (up to +10‰).

Therefore, the concept of correlation between the isotopically heavy carbon dioxide and the high-temperature fluid systems seems more persuasive, although we cannot define unambiguously the formation mechanism for such  $\text{CO}_2$ . It is likely that the temperature range of the “oil window” (~60–120°C) includes the stage of organic matter transformation with the release of significant volume of the isotopically heavy  $\text{CO}_2$ .

## CONCLUSIONS

Localization in the relatively small area and similarity in the morphology, geological structure, and activity mode imply the roots in common and single formation mechanism for mud volcanoes of the Taman Peninsula. At the same time, variations in the chemical and isotope compositions of fluids in the mud volcanic systems are too large for explaining them in the scope of simple models. Estimates of the formation temperatures derived from the Mg–Li and Na–Li geothermometer calculations provide grounds for assuming that the water phase of fluids was formed in the temperature range of ~20–140°C and up to 192°C, respectively. It remains unclear, however, what factors are responsible for these difference—the presence of roots of mud volcanoes at different depths (from a few hundreds of meters to 5 km or more) or the gradual cooling of fluids in the intermediate reservoirs during their upward migration.

The last scenario cannot be ruled out. At the same time, the question arises as to what components of fluid are inherited from the generation zone and to what degree its composition was transformed during its upward migration? Methane representing the main component of the gaseous phase ( $87.5 \pm 5.1\%$ ) is characterized in most volcanoes by rather uniform  $\delta^{13}\text{C}$  values ( $-52.4 \pm 5.4\%$ ) typical of most economic gas fields. It may be assumed that it is generated by the thermocatalytic way during catagenesis. At the same time, gases from Gnilaya Sopka Volcano contain substantially lighter methane ( $\delta^{13}\text{C}_{\text{CH}_4}$   $-72.5$  and  $-70.0\%$ ), which indicates its microbial formation near the surface.

Scatter in  $\delta^{13}\text{C}$  values in the oxidized carbon forms is substantially wider than in methane: it is 40.6 and 47.3‰ in  $\text{CO}_2$  and TDIC, respectively. The highest  $\delta^{13}\text{C}$  (TDIC) values are documented in waters with maximum Mg–Li temperatures. Such a correlation indicates that the  $^{13}\text{C}$ -enriched carbon dioxide is formed at the relatively deep levels, probably along with methane, while the  $^{13}\text{C}$ -depleted  $\text{CO}_2$  represents a product of organic material and/or methane oxidation in the intermediate reservoirs located at shallower depths. It should be emphasized that the depletion of carbon dioxide in the heavy carbon isotope during its upward migration cannot result from changes in the temperature conditions of isotopic fractionation in the  $\text{CO}_2$ – $\text{CH}_4$  system: in such a situation, the effect should be opposite. The assumption that waters and gases of mud volcanoes are formed at different depths cannot also be ruled out.

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