

# Waters from Mud Volcanoes of Azerbaijan: Isotopic–Geochemical Properties and Generation Environments

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**Abstract**—New data on chemical and isotopic properties of waters from 35 mud volcanoes of Azerbaijan show that they are represented by two contrasting types characterized by different mineralization: Cl–Na (M = ~30–80 g/L) and HCO<sub>3</sub>–Cl–Na (M = ~8–15 g/L). Waters of the last type are usually enriched with alkaline metals, B, and Br. Waters of the Cl–Na type are similar in their Cl/Br coefficient with seawater. According to Mg–Li and Na–Li geothermometers, waters were formed at temperatures varying from ~20 to ~140°C. Taking into consideration these estimates, “roots” of the volcanoes under consideration should be located at depths of 6.0–7.5 km. The fluid generation temperatures exhibit a tendency for their growth toward the Greater Caucasus orogen. The δD, δ<sup>18</sup>O, and δ<sup>13</sup>C (TDIC) values in dissolved inorganic carbon vary from –32 to –12 and –0.6 to +10.4‰ (V-SMOW) or –12.9 to +37.3‰ (V-PDB), respectively. The highest δD, δ<sup>18</sup>O, and δ<sup>13</sup>C values are typical of HCO<sub>3</sub>–Na waters. It is shown that the growth of formation (Mg–Li) temperatures is accompanied by a significant increase of the δ<sup>18</sup>O(H<sub>2</sub>O) and δ<sup>13</sup>C(HCO<sub>3</sub><sup>–</sup>) values along with HCO<sub>3</sub><sup>–</sup> concentrations. The degree of water enrichment with Br, B, and alkaline metals also increases. This allows the formation of soda waters from mud volcanoes with elevated <sup>18</sup>O and <sup>13</sup>C contents to be attributed to relatively high-temperature transformations of mineral and organic matter during the catagenic alteration sedimentary rocks.

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Mud volcanoes are usually formed in large sedimentary basins associated with accretionary structures such as subduction or intracontinental collision zones. Two prerequisites required for their development are observed in such zones (Kopf, 2002): accumulation of many kilometers thick sedimentary sequences with the high hydrocarbon potential and high degree of tectonic fracturing that provides vertical permeability of confining beds. Mud volcanic regions are often associated with zones of neomagmatic (mantle) activity. Therefore, conditions of the formation and genesis of hydrocarbon fluids in mud volcanic systems remain a debatable issue so far. Mud volcanism is usually thought to be related to the sedimentary cycle of organic and mineral matter transformation and lithostatic compaction of clayey sequences (Gubkin and Fedorov, 1938; Braunstein and O’Brien, 1968; Kholodov, 2002). There is also a concept of deep (magmatogenic) nature of mud volcanism (Kovalevskii, 1940; Valyaev et al., 1985; Kropotkin, 1986), although the available data on helium isotope composition in gases from mud volcanoes of the Caucasus region argue against this hypothesis (Aliev and Kabulova, 1980; Yakubov et al., 1980; Lavrushin et al., 1996, 2009).

According to geophysical data, the “roots” of mud volcanoes in the South Caspian Basin, which is filled with sediments over 20–25 km thick, are presumably located at a depth of 8 or 9 km (Yakubov et al., 1980; Rakhmanov, 1987; Guliev et al., 1988; *Geologiya ...*, 2008). Therefore, the investigation of mud volcanic emanations helps to specify geochemical properties of deep fluid systems inaccessible now for borehole sampling. In addition, some problems, such as mechanisms responsible for the formation of a thinned clayey pulp at great depths and the degree of hydrodynamic isolation of mud volcanic channels from aquifers located in the upper part of the sedimentary section, remain unsolved. The water phase represents one of the components of mud volcanic products. It investigation allows the thermal conditions and probable mechanism responsible for the formation of mud volcanic fluids to be reconstructed.

## MATERIALS AND METHODS

In total, 35 mud volcanoes of Azerbaijan were investigated in October 2010 (water discharge was missing in Zaakhtarma Volcano) and 42 water samples

were taken (Fig. 1). Water from the flowing but abandoned production well located at the Neftechala Volcano foothill was also sampled. These samples were subjected to analyses of chemical and isotopic ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) compositions in water, as well as isotopic composition of carbon ( $\delta^{13}\text{C}$ ) in dissolved carbon dioxide. For comparison, six samples were taken from freshwater streams and the Caspian Sea (Tables 1, 4).

Despite moderate air temperatures (day temperature varied from 15 to 24°C) and absence of heavy rains, it was assumed that the salt composition in waters from nonflowing salses can be modified notably due to evaporation or admixture of atmospheric precipitation. In addition, the chemical composition of water in such salses can be modified owing to the dissolution of salt exudation on the volcanic surface. In this connection, preference during sampling was given to small water seepages (from a few tens of centimeters to 1 m in diameter) with intense effusions of water and mud. If possible, salses were selected in the central part of the volcanic breccia field. In addition, mineralization in different water seepages was qualitatively estimated by the salometer prior to water sampling from large mud volcanoes. It was established that the salometer underestimated mineralization in waters with a significant admixture of clayey emulsion (1.08–1.59 kg/L).

In field conditions, only some chemical characteristics of water (pH, Eh,  $\text{HCO}_3$ ) were determined. The Eh measurements were conducted using the platinum electrode. The results were corrected for the “hydrogen” electrode ( $\text{Eh} = E_{\text{meas}} + 200 \text{ mV}$ ). The total alkalinity was determined by titration of the water aliquot by 0.1 HCl solutions with pH control using the glass electrode.

Other investigations of water samples were carried out in laboratory conditions. The F and Cl ion concentrations were determined in the chemical laboratory of GIN. The samples to be analyzed for concentrations of microcomponents were passed through the 0.45  $\mu$  filter and fixed by nitric acid. Subsequently, they were analyzed by the ICP-AES and ICP-MS methods at the Analytical Center of the Institute of Microelectronics Technology Problems and High Purity Materials of the Russian Academy of Sciences (Chernogolovka, Moscow region). The measurements were conducted with the ICAP-61 (Thermo Jarrel Ash, USA) and X-7 ICP-MS (Thermo Elemental, USA) devices. Error in the measurement of concentrations of individual components was approximately 10–15%, although it could be as high as 50% near the detection limit.

Water samples taken for isotopic investigations were passed through the 0.45  $\mu$  filter and kept without any fixing in the refrigerator. The  $\delta^{13}\text{C}$  values in the dissolved  $\text{CO}_2$ , as well as the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in water, were determined at GIN using a Finnigan DELTA<sup>plus</sup> mass spectrometer (ThermoQuest Company). Error in the measurement of was not worse than

$\pm 0.2\text{‰}$  for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values and  $\pm 0.2\text{‰}$  for  $\delta\text{D}$ . All the  $\delta^{13}\text{C}$  values are given relative to the V-PDB standard;  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values, relative to the V-SMOW standard.

The water temperature was measured under field conditions with an electron thermometer accurate to  $\pm 0.1^\circ\text{C}$ .

The formation or “basic” temperatures of generation of the water salt composition were estimated based on the hydrochemical geothermometers ( $\text{SiO}_2$ , Na–Li, Mg–Li, Na–K). For this purpose, the results of the chemical analysis—Na, Li, K, Mg, and  $\text{SiO}_2$  concentrations (in mg/L)—were used.

The **Na–Li geothermometer** was developed for estimating temperatures of slightly and moderately mineralized formation waters of sedimentary basins ranging from 20 to 340°C:

$$T^\circ\text{C} = 1000/(\log(\text{Na}/\text{Li}) - 0.14) - 273.15$$

(Fouillac and Michard, 1981).

The **Mg–Li geothermometer** is applied for measuring the formation and oil waters of sedimentary basins with temperatures up to 300°C:

$$T^\circ\text{C} = 2200/(\log((\sqrt{\text{Mg}})/\text{Li}) + 5.47) - 273.15$$

(Kharaka and Mariner, 1989).

Temperatures based on **Si and Na–K geothermometers** were calculated using the following formulas:

$$T^\circ\text{C} = 1522/(5.75 - \log\text{SiO}_2) - 273.15$$

(Fournier, 1977),

$$T^\circ\text{C} = 777/\log(\text{Na}/\text{K}) + 0.7) - 273.15$$

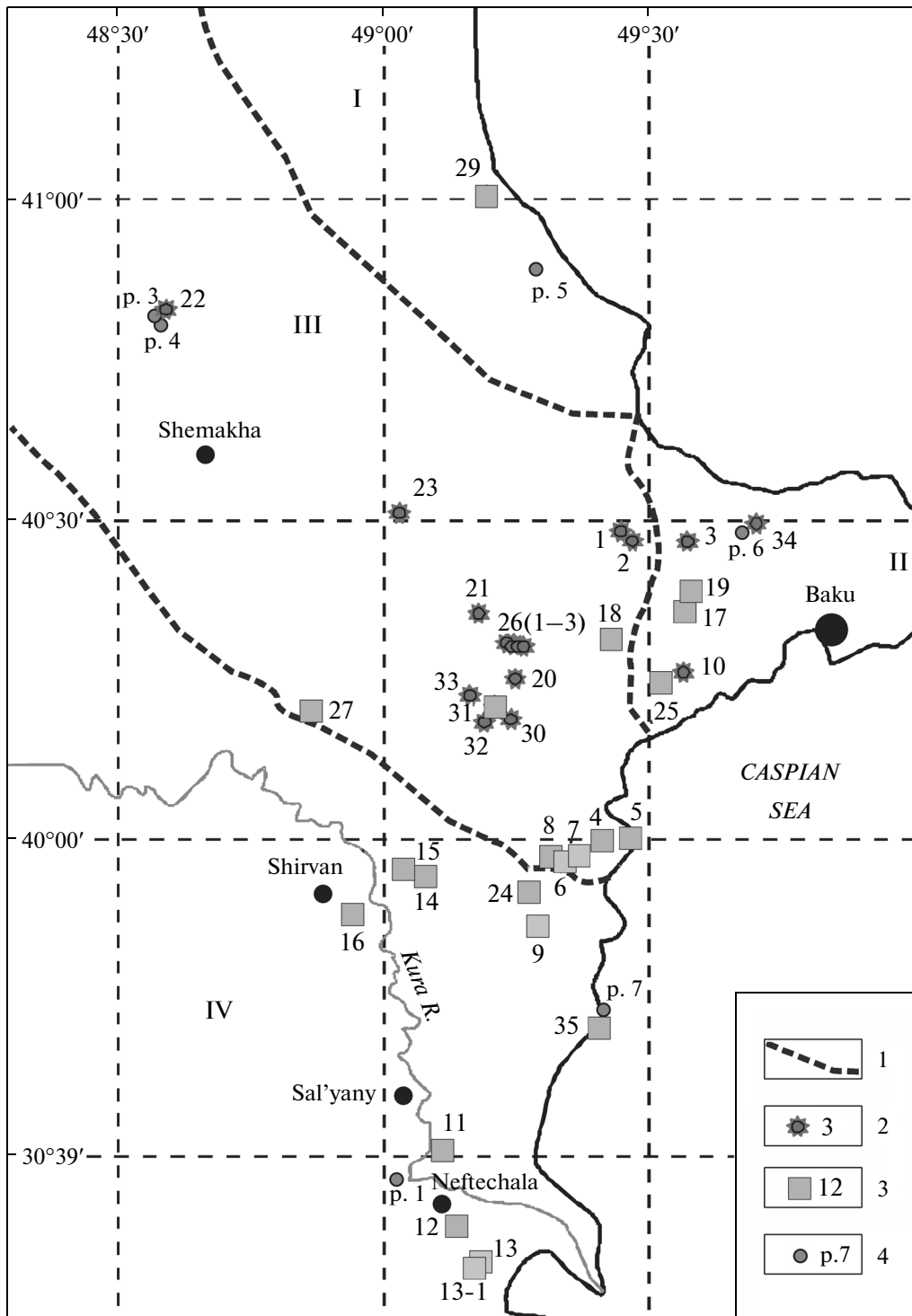
(Fournier and Truesdell, 1973).

The last two geothermometers were developed for hydrothermal systems of areas with recent volcanism.

Comparison of temperatures calculated with different formulas shows that the values derived from Mg–Li and Na–Li geothermometers are most consistent (Fig. 2). They are also correlated with Na–K temperatures, although with a higher dispersion. No correlation of  $t(\text{SiO}_2)$  with values obtained by other geothermometers is observable.

As compared with temperatures determined by the Mg–Li geothermometer, its Na–Li counterpart yields usually similar ( $\pm 5^\circ\text{C}$ ) or slightly lower (up to  $\sim 15^\circ\text{C}$ ) temperatures in mineralized waters of the Cl–Na type ( $M = 20\text{--}80 \text{ g/L}$ ). In soda water, its estimates are, to the contrary, mostly higher by 20–40°C. Such a phenomenon can hardly be explained by the influence of high  $\text{HCO}_3$  concentrations on the carbonate equilibrium, since the removal of Mg ion from the solution due to carbonate precipitation should, in contrast, result in the growth of Mg–Li temperature values. It is conceivable that the estimates yielded by geothermometers in soda water are affected by carbon dioxide leaching, i.e., selective Na removal (relative to Li and Mg) from the exchange complex of clays during their interaction with waters enriched in the  $\text{HCO}_3$  ion.

As a whole, the Mg–Li geothermometer seems to be most universal among all analytical formulas. It is developed for sedimentation waters with a wide spec-



**Fig. 1.** Schematic sampling map of Azerbaijan mud volcanoes. (1) Boundaries of mud volcanic regions: (I) Caspian, (II) Absheron, (III) Shemakha–Gobustan, (IV) Kura; (2) water sampling sites; (2) mud volcanoes with  $\text{HCO}_3^- > 25$  mg-equiv %, (3) the same with  $\text{HCO}_3^-$ , 25 mg-equiv %, (4) surfaces waters (rivers, springs, Caspian Sea). Numbers in the figure correspond to sample numbers in Tables 1–4.

trum of mineralization found in petroliferous basins. Waters of mud volcanoes likely represent analogs of such waters. The Na–Li geothermometer can be used as an alternate.

It should also be noted that the data on absolute values of temperatures of fluid generation obtained by such methods should be taken with caution. All the above-mentioned empirical formulas were developed

**Table 1.** Coordinates of sampling sites

Sample no.*	Name of volcano/sampling site	Latitude, N	Longitude, E	Altitude, m
<b>I. Caspian region</b>				
29/10	Zarat (Khydyrzyndy-2)	41°00'11.4"	049°11'51.8"	4
<b>II. Absheron region</b>				
3/10	Uchtepe	40°27'44.6"	049°34'27.2"	131
10/10	Pel'pelya-Garadag	40°15'27.6"	049°33'02.0"	23
17/10	Shorbulag	40°21'17.1"	049°33'34.0"	84
19/10	Davaboinu	40°22'54.8"	049°35'03.0"	141
25/10	Otman-Bozdag	40°14'24.1"	049°30'23.8"	396
34/10	Chegeldag	40°29'34.6"	049°42'10.9"	65
<b>III. Shemakha–Gobustan region</b>				
1/10	Pirekyashkyul, northern group	40°28'49.9"	049°26'53.2"	322
2/10	Pirekyashkyul, southern group	40°27'58.5"	049°28'10.2"	275
4-1/10	Dashgil, large salse 15 m across	39°59'43.8"	049°24'23.1"	83
4-2/10	Dashgil, central mud breccia field	39°59'46.2"	049°24'10.0"	95
5/10	Bakhar	39°59'55.0"	049°28'27.9"	29
5-1/10	Bakhar, northern group	40°00'03.6"	049°28'13.1"	29
6/10	Saryboga, western group	39°58'12.7"	049°20'50.3"	97
7/10	Goturdag	39°58'24.9"	049°21'35.2"	189
8/10	Airantekyan	39°59'40.3"	049°18'32.8"	279
18/10	Shakhigaya, salse 8 m across	40°18'45.6"	049°26'14.0"	140
20/10	Galendarakhtarma	40°15'02.8"	049°14'43.3"	348
21/10	Nardaran-Akhtarma Vostochnaya	40°21'09.3"	049°10'52.4"	371
22-1/10	Demirchi (brown-colored pulp)	40°49'39.2"	048°35'08.1"	1441
22-2/10	Demirchi (gray-colored pulp)	—	—	—
23/10	Malyi Merezze	40°30'36.7"	049°01'55.5"	682
26/10	Cheildag	40°17'54.6"	049°15'15.3"	265
26-1/10	Cheildag, northern group	40°18'03.2"	049°15'51.1"	267
26-2/10	Cheildag, western group	40°18'27.0"	049°14'00.9"	264
26-3/10	Cheildag, southern group	40°18'07.5"	049°14'24.0"	239
30/10	Gylych	40°11'10.0"	049°14'22.4"	234
31/10	Agdam group	40°12'22.2"	049°12'36.2"	330
32/10	Arzani	40°10'51.0"	049°11'22.6"	353
33/10	Shekikhan	40°13'14.7"	049°09'44.6"	368
<b>IV. Kura region</b>				
9/10	Khydyrly	39°51'40.6"	049°17'45.3"	−14
11/10	Durovdag	39°30'43.6"	049°06'27.8"	9
12/10	Duzdag, small salse ejecting water	39°22'53.8"	049°08'46.0"	−6
12-1/10	Duzdag, central salse 5 m across	—	—	—
13/10	Neftechala Yuzhnaya	39°18'53.1"	049°11'03.9"	−16
13-1/10	Oil well, near Neftechala Yuzhnaya Volcano	39°19'06.0"	049°11'13.6"	−18
14/10	Malyi Mishovdag	39°56'49.3"	049°04'39.5"	292
15/10	Bol'shoi Mishovdag	39°57'11.1"	049°03'07.4"	249
16/10	Yandere	39°53'03.5"	048°57'00.5"	138
24/10	Kalmaz	39°55'15.5"	049°15'53.3"	191
27/10	Akhtarma-Pashaly	40°11'45.8"	048°52'13.8"	298
28/10	Zaakhtarma	40°14'19.3"	048°50'57.0"	379
35/10	Bindovan	39°42'15.0"	049°24'42.2"	30
<b>Surface waters</b>				
1p/10	Kura River near the Garemanly Sett.	39°47'38.8"	049°01'30.8"	−21
3p/10	Freshwater spring near Demirchi Volcano (22/10)	40°49'05.4"	048°34'17.5"	1552
4p/10	River, near Demirchi Volcano (22/10)	40°48'17.6"	048°34'49.0"	1438
5p/10	Water conduit from the Samur River	40°53'01.1"	049°20'20.8"	−5
6p/10	Water reservoir in Baku near Chegeldag Volcano (34/10)	40°29'28.5"	049°42'01.5"	27
7p/10	Caspian Sea, near the shore, Shirvan reserve area	39°42'43.7"	049°24'43.8"	−31

(\*) Number in the numerator corresponds to the number in Fig. 1.

for other regions and, therefore, cannot in full take into consideration the regional specific features of water composition and their host rocks of the area in question. The thermometric and hydrochemical investigations in wells of the Kura depression could solve this problem, but such data are unfortunately unavailable. Nevertheless, we believe that hydrochemical geothermometers provide quite objective information at least on relative differences in temperatures of fluid generation for the comparative investigation of mud volcanoes in the region under consideration.

Sampling of different salses within a single volcano or closely spaced group of volcanoes allows to estimate the error in temperature measurements. In Dashgil and Duzdag volcanoes, the Mg–Li temperature in largest salses is 18–20°C higher than in their smaller counterparts (Table 3, samples 4/1-10, 4-2/10, 12/10, 12-1/10). The same trend is also noted for temperatures obtained by the Na–Li, Na–K, and SiO<sub>2</sub> geothermometers. Sampling of salses with the brown and gray pulps at Demirchi Volcano (samples 22-1/10, 22-2/10) revealed that the temperature estimates differ only by 13°C (temperature was lower in the brown pulp,). In groups of mud volcanoes (Pirekyashkyul and Cheildag, samples 1/10, 2/10, 26/10–26-3/10) located several kilometers away from each other, the amplitude of Mg–Li temperature variations was 7 and 24°C, respectively. Proceeding from these data, we estimate the error in calculation of Mg–Li temperatures at ±11°C.

Tables 1–4 present all the obtained results.

#### CHEMICAL PROPERTIES OF MUD VOLCANIC WATERS

The investigation of waters from mud volcanoes of Azerbaijan has a long history (Gulyaeva, 1939; Kovalenskii, 1940; Buniat-Zade, 1964; Aliev and Buniat-Zade, 1964, 1967; Yakubov et al., 1971, 1980; Lagunova and Gemp, 1978; Rakhmanov, 1987; Guliev et al., 2004; Aliev et al., 2009; and others). It is known that their mineralization varies from ~8 to ~80 mg/L (Yakubov et al., 1971, 1980).

Two main groups of waters are definable based on the interrelation of anion concentrations and mineralization (Tables 2, 4). The first group includes waters with a high share of the HCO<sub>3</sub><sup>-</sup> ion in the anion composition (25–62 mg-equiv %) and mineralization below 13–15 g/L. They belong usually to the HCO<sub>3</sub>–Cl or Cl–HCO<sub>3</sub> types. The second group is represented by waters belonging exclusively to the Cl type (Cl > 75 mg-equiv %) with mineralization of 15–80 g/L. Hereafter, waters of the first group characterized by high HCO<sub>3</sub><sup>-</sup> concentrations are designated for short as “soda” waters or waters of the HCO<sub>3</sub> type, while the highly mineralized varieties are designated as chloride or Cl-type waters.

Distribution of such waters is characterized by spatial regularity. The area with chloride waters comprises

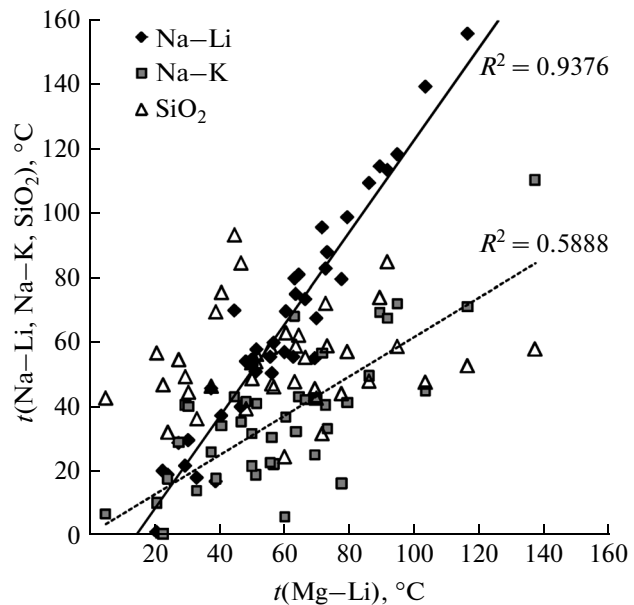


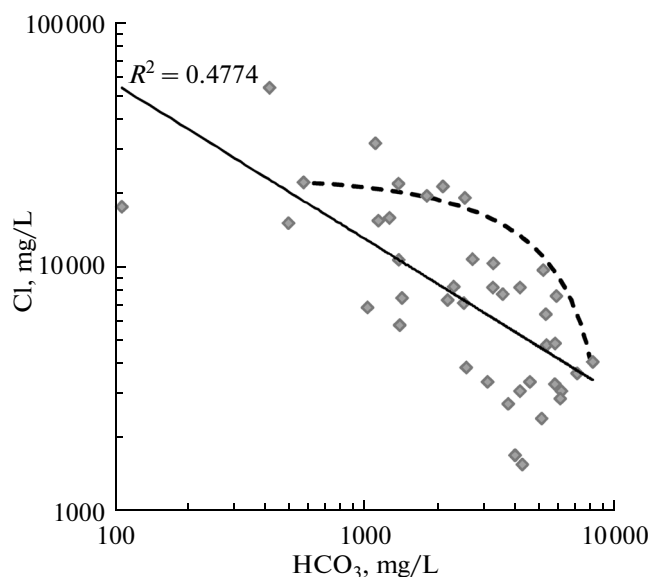
Fig. 2. Correlation of formation temperatures of fluid generation derived from Mg–Li, Na–Li, and SiO<sub>2</sub> geothermometer data. Lines show trends of correlation with Mg–Li (solid) and Na–K (dashed) temperatures.

the entire Kura region and partly the Absheron and Caspian domains, where they are observable in volcanoes confined to the Caspian Sea coast. Waters of this type are also documented in southern areas of the Shemakha–Gobustan region adjacent to the Kura depression (Fig. 1). Waters of the soda type are localized exclusively in the central Shemakha–Gobustan and northwestern Absheron regions.

The HCO<sub>3</sub><sup>-</sup> content in waters varies from ~100 to 8000 mg/L ( $\text{HCO}_3^-_{\text{av}} = 3300 \text{ mg/L}$ ,  $n = 40$ ) (Table 4). Concentrations of HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> ions exhibit the opposite correlation (Fig. 3). The minimum HCO<sub>3</sub><sup>-</sup> concentrations are characteristic of the Cl-type waters distributed in the Kura region. In waters from small volcanoes (Khydyrly and Neftechala Yuzhnaya, samples 9/10 and 13/10), the HCO<sub>3</sub><sup>-</sup> content (~110–420 mg/L) is notably lower than in the adjacent larger edifices such as, for example, Kalmaz and Duzdag volcanoes ( $\text{HCO}_3^- = 1100\text{--}2260 \text{ mg/L}$ , Table 4, samples 24/10 and 12/10).

The SO<sub>4</sub><sup>2-</sup> concentration in waters of mud volcanoes is usually insignificant (lesser than 10–50 mg/L), although can be as high as 500–3000 mg/L in waters from some volcanoes of the Absheron and Shemakha–Gobustan regions. Its high concentrations associate with the exposed gypsum-bearing Paleogene sequences.

By their cation composition, all the waters belong to the Na type (Na<sup>+</sup> > 80 mg-equiv %). They are characterized by the prevalence of Mg over Ca (Ma/Ca =



**Fig. 3.** Correlation of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  concentrations in mud volcanic waters of Azerbaijan. The solid line corresponds to the correlation line; dashed line corresponds to the theoretical line of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  water mixing (the data on Khydyrly and Pirekyashkyul volcanoes are used as extreme members).

0.4–14.4,  $\text{Mg}/\text{Ca}_{\text{av}} = 4.7$ ,  $n = 40$ ). In the Shemakha–Gobustan region, average  $\text{Mg}/\text{Ca}$  values are notably higher (5.8,  $n = 23$ ) as compared with the Absheron (3.2,  $n = 5$ ) and Kura (3.3,  $n = 11$ ) regions.

The mud volcanic waters are characterized by neutral or slightly alkaline properties: pH value varies from 6.50 to 8.65 ( $\text{pH}_{\text{av}} = 7.75$ ,  $n = 40$ ); Eh value ranges from  $-95$  to  $+180$  mV (Table 2). Waters exhibit high concentrations of some microcomponents, alkaline and alkaline-earth metals, boron (up to 477 mg/L), and bromine (up to 124 mg/L). The B, K, Rb, and Cs concentrations in them demonstrate no dependence from the Cl ion content and, correspondingly, general mineralization. To the contrary, the Br, Na, Ca, Mg, and Sr contents increase proportionally to  $[\text{Cl}^-]$ . At the same time, analysis of the  $[\text{Cl}^-]$ -normalized concentrations of alkaline metals, B, and Br in soda waters reveals the reversed correlation. In less mineralized soda waters, normalized concentrations of these elements are substantially higher than in waters with high Cl ion concentrations.

The Ba concentration in solution is determined by the solubility of barite ( $\text{BaSO}_4$ ). Correspondingly, water with the high  $\text{SO}_4$  ion content is characterized by minimum Ba concentrations. The growth of the sulfate sulfur content in the solution is accompanied by the increase in uranium concentrations (up to 28  $\mu\text{g}/\text{L}$ ). Such a correlation implies its secondary nature in water of mud volcanoes:  $\text{SO}_4^{2-}$  is formed during the oxidation of sulfides in the surface zone, which stimulates uranium mobilization.

The fluorine concentrations vary from 0.1 to 3.0 mg/L ( $F_{\text{av}} = 0.92$  mg/L,  $n = 40$ ). No correlation of  $[\text{F}^-]$  contents with  $[\text{HCO}_3^-]$ ,  $[\text{Br}^-]$ , and  $[\text{Cl}^-]$ , as well as with concentrations of alkaline metals, is established. The  $[\text{F}^-]$  concentrations demonstrate negative correlation with  $[\text{Ca}^{2+}]$ ,  $[\text{Mg}^{2+}]$ ,  $[\text{Ba}^{2+}]$ , and  $[\text{Sr}^{2+}]$  contents. The F concentration in mud volcanic waters increase only with the growth of B and Zr contents.

The Cl/Br values vary from 81 to 370. Their ratio similar to that in seawater ( $\text{Cl}/\text{Br} \approx 290$ ) is characteristic of highly mineralized waters distributed in the Kura depression ( $\text{Cl}/\text{Br}_{\text{av}} = 243$ ). In the Absheron and Shemakha–Gobustan regions,  $\text{Cl}/\text{Br}_{\text{av}}$  is substantially lower: 150 and 136, respectively.

The Cl/Br value exhibits negative correlation with  $\text{HCO}_3^-$  concentrations. Such a trend is likely common for mud volcanoes of the entire Caucasus region. It was previously established for waters in mud volcanoes of the Taman Peninsula (Lavrushin et al., 2003). The enrichment of waters with Br (relative to Cl) results most likely from postsedimentary transformations in the water–rock system and is genetically related to the formation of soda waters. An important role in this process can belong to smectite illitization, which stimulates a significant decrease in the exchange capacity of clay minerals and, consequently, transfer of absorbed Br into interstitial solutions (Krasintseva, 1968).

Therefore, we believe that low values of the Cl/Br coefficient provide no information on the primary genesis of mud volcanic waters. It should also be noted that the maximum value of this parameter ( $\text{Cl}/\text{Br} = 370$ ) is recorded in the most mineralized waters from Neftechala Yuzhnaya Volcano (Table 2, Sample 13/10,  $\text{Cl} = 54.8$  g/L). It is conceivable that this value reflects the contribution of waters, which leach rock salt deposits, to their composition in the southernmost volcanoes of the Kura region.

The comparative analysis of waters discharged from different salses or synonymous groups of volcanoes involved the Dashgil, Demirchi, Cheildag, and Duzdag edifices (Table 2). In Duzdag Volcano (samples 12/10 and 12-1/10), water mineralization in the large central salse (approximately 5 m in diameter) with the low water discharge appeared to be 1.5 times lower as compared with that in a small, but more active salse located  $\sim 25$ –25 m away. In the less mineralized water, concentrations of almost all components were lower, although the degree of their dilution relative to the more mineralized water was variable. For example, the Cl, B, Na, Ca, and Mg concentrations in the mineralized water were 2.1, 1.6, 1.5, 1.9, and 4.1 times, respectively, higher, while the difference in the sum of salts was 1.5 times. Moreover, concentrations of some components ( $\text{HCO}_3^-$ , F, Si, As, Li, Rb, Mo, and  $\text{SO}_4$ ) in freshwater appeared to be similar or even higher than in waters with higher mineralization.

In Dashgil Volcano, one sample (4-1/10) was taken from the central part of a small salse (0.3 m across)

Table 2. Chemical composition of mud volcanic waters of Azerbaijan

Sample no.	Mud volcano	Eh	pH	Min.	Cl	F	B	Na	Mg	Al	Si	S	K	Ca	Mn	Fe	Cu	Zn	
		mV	—	g/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>I. Caspian region</b>																			
29/10	Zarat (Khydyrzyndy-2)	-45	7.42	29.9	21560	0.3	113	10918	123	n.d.	6.6	4.8	186.4	123	0.013	n.d.	n.d.	n.d.	
<b>II. Absheron region</b>																			
3/10	Uchtepe	-65	7.77	9.9	2411	0.5	194	2919	28.3	0.044	6.8	3.4	8.3	15.3	0.015	0.97	0.0023	0.0090	
10/10	Pel'pelya-Garadag	—	8.65	19.7	7659	1.2	297.8	6556	66.9	0.07	2.0	19.9	7.8	18.8	n.d.	0.13	n.d.	n.d.	
17/10	Shorbulag	-110	7.82	12.7	5815	0.8	90.6	4382	75.3	0.045	3.5	320.6	15.8	107	0.031	0.30	n.d.	n.d.	
19/10	Davaboynu	-175	7.65	18.9	10780	0.4	74.9	6730	215	n.d.	7.6	4.5	25.3	94.0	0.010	0.30	n.d.	n.d.	
34/10	Chegeldag	-70	8.27	8.8	3901	1.2	104	2976	11.5	0.037	4.0	2.6	11.1	8.5	0.084	n.d.	0.0023	0.0078	
25/10	Otman-Bozdag	—	—	—	10850	—	—	—	—	—	—	—	—	—	—	—	—	—	
<b>III. Shemakha—Gobustan region</b>																			
1/10	Pirekyashkyl, northern group	-265	8.00	18.4	4113	2.0	79.8	5670	81.3	0.038	6.1	151.5	20.9	13.0	0.094	1.8	n.d.	n.d.	
2/10	Pirekyashkyl, southern group	-175	8.00	12.5	3120	0.6	97	3802	37.3	0.039	10.2	4.5	13.3	6.3	0.008	0.65	n.d.	0.0068	
4-1/10	Dashgil, mud breccia field	—	7.45	21.4	15247	0.4	59.4	7500	362	n.d.	4.5	3.1	17.2	217	0.067	0.85	n.d.	0.033	
4-2/10	Dashgil, large saise (lake)	-20	7.49	33.1	19715	0.4	183	11702	352	n.d.	4.5	1056.0	24.0	83.2	0.014	0.75	n.d.	n.d.	
5/10	Bakhar	-150	7.84	13.5	7163	0.7	86.4	4833	14.0	0.089	4.4	9.8	10.8	13.2	0.0030	0.091	n.d.	n.d.	
5-1/10	Bakhar, northern group	—	7.92	32.0	19361	0.7	180	11776	159	n.d.	3.2	155.3	18.4	18.2	n.d.	0.09	n.d.	0.047	
6/10	Saryboga, western group	-220	7.88	14.4	7517	0.5	79.8	5267	65.3	n.d.	5.8	1.7	9.7	25.0	0.011	0.76	n.d.	n.d.	
7/10	Goturdag	—	7.58	16.5	8298	0.3	62.0	5548	111	n.d.	6.8	28.2	15.4	31.7	0.012	1.1	n.d.	n.d.	
8/10	Airantekyan	-220	7.58	17.1	8298	0.3	62.1	5908	120	n.d.	5.8	78.8	11.8	29.0	0.015	1.5	n.d.	n.d.	
18/10	Shakhigaya	-205	7.60	26.6	22411	0.8	98.1	9406	392	0.07	4.6	184.3	9.3	244	0.083	4.4	n.d.	n.d.	
20/10	Galendarakhtarma	-205	7.99	13.9	3688	3	94.3	4233	25.4	0.029	4.2	24.1	7.1	6.3	0.022	0.47	n.d.	n.d.	
21/10	Nardaran-Akhtar-ma Vostochnaya	-215	7.52	15.5	4823	2.5	258	4860	80.3	0.076	7.8	216.7	15.3	43.7	0.202	0.18	0.018	0.010	
22-1/10	Demirchi (brown-colored pulp)	-45	8.02	8.2	1702	2.7	374	2384	22.8	0.13	4.7	22.3	9.4	9.2	0.005	0.24	n.d.	0.0119	

Table 2. (Contd.)

Sample no.	Mud volcano	Eh mV	pH	Min. g/L	Cl mg/L	F mg/L	B mg/L	Na mg/L	Mg mg/L	Al mg/L	Si mg/L	S mg/L	K mg/L	Ca mg/L	Mn mg/L	Fe mg/L	Cu mg/L	Zn mg/L	
22-2/10	Demirchi (gray-colored pulp)	-95	7.60	8.3	1560	2.9	371	2362	18.1	0.13	5.6	1.1	17.9	13.8	0.001	0.18	n.d.	0.0083	
23/10	Malyi Mereze	-185	7.98	9.8	3404	1.6	149	3231	31.8	0.036	4.9	19.9	8.8	11.3	0.010	0.79	n.d.	n.d.	
26/10	Cheildag	-235	8.46	13.1	3333	0.6	133	4030	59.1	0.039	4.8	10.6	18.1	10.6	0.0066	0.87	n.d.	n.d.	
26-1/10	Cheildag, northern group	-295	8.12	11.5	2908	1.9	109	3353	65.2	0.041	2.6	0.8	18.0	14.1	0.012	1.09	n.d.	n.d.	
26-2/10	Cheildag, western group	-180	7.82	9.7	3120	0.4	113	3014	32.7	0.041	6.4	22.9	10.8	9.5	0.023	2.27	n.d.	0.0056	
26-3/10	Cheildag, southern group	-215	7.82	11.4	3404	0.8	65.3	3618	37.9	0.024	6.8	15.2	28.0	18.3	0.0026	0.51	n.d.	n.d.	
30/10	Glych	-218	7.48	16.8	6454	0.3	91.0	5447	108	n.d.	10.8	2.1	39.6	49.8	0.007	1.2	n.d.	n.d.	
31/10	Agdam group	-220	8.10	20.9	9787	0.8	477.0	6975	113	0.11	5.0	62.5	24.5	15.8	0.015	1.4	n.d.	n.d.	
32/10	Arzani	-175	7.66	14.9	4893	0.4	127	4738	64.6	0.031	14.7	2.9	33.0	19.8	0.011	1.0	n.d.	n.d.	
33/10	Shekikhan	-175	8.00	9.6	2766	0.8	128	2966	43.5	0.042	4.7	42.7	21.0	42.3	0.013	0.21	0.0015	0.0067	
<b>IV. Kura region</b>																			
9/10	Khydyrly	-220	7.47	26.5	17801	0.2	81.2	8777	259	n.d.	2.7	3.0	15.6	1085	1.1	0.78	n.d.	n.d.	
11/10	Durovdag	-205	7.89	34.8	22127	2.2	139	13231	84.0	n.d.	4.0	4.3	16.2	20.3	0.017	0.09	n.d.	n.d.	
12/10	Duzdag, small salse ejecting water	-	7.61	35.2	32410	0.7	167	13208	170	n.d.	6.4	1.1	18.2	82.1	0.037	0.57	n.d.	n.d.	
12-1/10	Duzdag, central salse	-	7.41	22.7	15602	1.6	102	8592	41	n.d.	9.4	2.2	15.2	43.0	0.012	0.22	n.d.	n.d.	
13/10	Neftechala Yuzh- naya	-145	6.51	75.2	54750	0.2	64.3	24294	981	n.d.	14.6	4.2	73.5	3326	0.80	20.4	n.d.	n.d.	
13-1/10	Neftechala, well	-	-	40.2	-	-	78	13710	465	n.d.	11.3	2.7	40.1	1195	0.443	n.d.	n.d.	n.d.	
14/10	Malyi Mishovdag	-155	7.46	18.1	10425	0.4	45.9	6275	145	n.d.	6.3	n.d.	22.3	36.1	n.d.	0.34	0.0032	n.d.	
15/10	Bol'shoi Mishovdag	-155	7.60	13.6	7376	0.4	57.0	4789	92.3	n.d.	4.2	2.0	16.6	31.2	0.0078	n.d.	n.d.	n.d.	
16/10	Yandere	n.d.	7.69	11.3	6879	0.5	73.7	4046	86.0	0.028	5.9	n.d.	10.2	43.1	0.011	0.42	n.d.	n.d.	
24/10	Kalmaz	-210	7.97	15.8	8369	0.3	123.6	5622	66.7	n.d.	6.7	8.7	11.6	37.0	0.008	0.26	n.d.	n.d.	
27/10	Akhtarma Pashaly	-175	7.29	15.5	7801	0.1	59.8	4781	359.5	0.027	18.4	n.d.	18.0	133.2	0.026	4.8	n.d.	n.d.	
35/10	Bindovan	-135	7.76	20.0	16028	0.2	98.7	7422	78.4	n.d.	4.6	n.d.	19.5	72.7	0.005	0.14	n.d.	n.d.	



Table 2. (Contd.)

Sample no.	Mud volcano	As mg/L	Br mg/L	Sr mg/L	Ba mg/L	Pb mg/L	Li µg/L	Rb µg/L	Zr µg/L	Mo µg/L	Sb µg/L	Cs µg/L	Th µg/L	U µg/L
<i>I. Caspian region</i>														
29/10	Zarat (Khydyrzyndy-2)	n.d.	86.4	45.1	11.4	0.0027	14081	117.4	14.9	8.2	1.36	n.d.	n.d.	1.3
<i>II. Absheron region</i>														
3/10	Uchtepe	0.0053	11.7	2.8	3.9	0.0018	688	3.2	11.6	2.7	0.36	n.d.	n.d.	0.19
10/10	Pel'peya-Garadag	0.065	47.0	5.0	2.3	n.d.	595	2.0	63.6	187.7	7.78	n.d.	n.d.	10.3
17/10	Shorbulag	0.002	48.3	2.2	0.57	n.d.	360	4.8	3.3	91.1	3.1	n.d.	n.d.	15.7
19/10	Davaboynu	0.051	53.9	18.0	19.6	n.d.	1298	10.2	3.6	69.7	0.67	n.d.	n.d.	1.3
34/10	Chegaldag	0.0012	21.3	1.7	0.86	0.00043	381	5.8	7.1	21.7	0.62	0.098	0.012	4.4
25/10	Otman Bozdag	—	—	—	—	—	—	—	—	—	—	—	—	—
<i>III. Shemakha—Gobustan region</i>														
1/10	Pirekyashkyl, northern group	0.034	22.2	0.6	0.22	n.d.	873	6.9	113	74.0	0.48	n.d.	0.046	28.0
2/10	Pirekyashkyl, southern group	0.025	15.9	1.6	0.58	0.00043	775	5.4	16.5	21.2	0.32	0.07	n.d.	0.6
4-1/10	Dashgil, mud breccia field	n.d.	69.7	32.5	13.4	0.0014	459	7.4	2.9	129.0	0.36	n.d.	n.d.	1.4
4-2/10	Dashgil, large salse (lake)	n.d.	94.7	16.1	0.1	n.d.	1170	6.6	13.1	33.9	n.d.	n.d.	n.d.	1.8
5/10	Bakhar	0.024	37.7	5.1	4.0	0.0022	411	3.9	3.9	90.2	0.96	0.060	n.d.	0.59
5-1/10	Bakhar, northern group	0.032	93.6	9.2	1.0	n.d.	240	5.8	27.6	246	1.06	n.d.	n.d.	12.0
6/10	Saryboga, western group	0.033	59.2	9.2	6.1	n.d.	388	2.6	2.0	25.3	n.d.	n.d.	n.d.	0.26
7/10	Goturdag	n.d.	59.2	10.4	4.2	n.d.	896	4.5	10.4	21.7	n.d.	n.d.	n.d.	0.81
8/10	Airantekyan	0.026	63.5	8.7	0.79	n.d.	495	4.0	9.0	76.1	n.d.	n.d.	n.d.	2.9
18/10	Shakhigaya	n.d.	78.5	30.7	0.58	0.00088	210	2.3	2.9	77.5	n.d.	n.d.	n.d.	1.0
20/10	Galendarakhtarma	0.023	27.9	0.5	0.27	n.d.	783	1.1	24.0	318.0	0.80	n.d.	0.081	2.0
21/10	Nardaran-Akhtarma Vostochnaya	0.0035	32.7	1.0	0.63	n.d.	666	5.7	13.1	209.3	1.6	0.10	0.021	7.9
22-1/10	Demirchi (brown-colored pulp)	0.008	9.3	4.0	0.56	0.00058	1996	5.5	7.1	11.7	1.8	0.12	n.d.	1.3
22-2/10	Demirchi (gray-colored pulp)	0.029	8.9	5.2	3.4	0.00030	2783	15.4	4.4	1.6	1.3	0.52	n.d.	0.2
23/10	Malyi Mereze	0.0065	23.0	1.8	0.24	0.00042	256	3.2	7.2	38.5	0.48	0.040	n.d.	2.2

Table 2. (Contd.)

Sample no.	Mud volcano	As	Br	Sr	Ba	Pb	Li	Rb	Zr	Mo	Sb	Cs	Th	U
		mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
26/10	Cheildag	n.d.	22.9	2.6	3.9	n.d.	1683	10.6	11.3	36.1	n.d.	0.39	n.d.	0.69
26-1/10	Cheildag, northern group	n.d.	23.6	0.68	0.53	0.00033	977	4.5	13.3	143	0.07	0.060	0.021	3.1
26-2/10	Cheildag, western group	0.017	17.8	2.4	3.6	0.00039	956	3.1	5.8	27.7	0.12	0.056	n.d.	1.1
26-3/10	Cheildag, southern group	0.025	30.0	1.2	2.3	n.d.	1880	17.2	8.7	60.5	n.d.	0.96	n.d.	2.6
30/10	Gylych	n.d.	45.8	5.8	4.5	n.d.	2585	19.6	16.2	2.1	n.d.	0.337	n.d.	0.28
31/10	Agdam group	0.020	76.3	2.2	1.6	n.d.	167	7.6	48.9	68.3	3.69	i.i.	0.089	3.4
32/10	Arzani	0.041	41.9	4.5	3.4	n.d.	2186	9.8	9.6	16.2	0.13	0.090	n.d.	0.58
33/10	Shekikhan	0.013	20.6	1.3	1.1	0.00062	553	8.0	14.9	50.3	1.6	0.11	n.d.	6.7
<i>IV. Kura region</i>														
9/10	Khydyrly	0.0045	63.9	42.5	12.7	n.d.	186	6.3	3.2	35.6	0.73	n.d.	n.d.	1.0
11/10	Durovdag	0.039	71.9	17.0	7.9	n.d.	32.8	6.4	12.0	95.3	n.d.	n.d.	n.d.	1.6
12/10	Duzdag, small salse ejecting water	0.036	77.5	27.5	11.8	n.d.	124	6.9	12.0	29.8	n.d.	n.d.	n.d.	0.65
12-1/10	Duzdag, central sals	0.068	46.6	12.2	4.8	n.d.	167	6.8	10.4	41.0	0.67	n.d.	n.d.	0.29
13/10	Neftechala Yuzhnaya	n.d.	124	154	24.2	n.d.	1204	90.3	20.5	10.1	n.d.	1.7	1.5	2.8
13-1/10	Neftechala, well	0.011	80.8	52.3	10.2	n.d.	612	20.6	11.0	4.6	n.d.	0.760	n.d.	n.d.
14/10	Malyi Mishovdag	0.015	43.4	25.0	16.4	n.d.	586	9.3	4.5	4.5	0.76	0.36	n.d.	0.15
15/10	Bol'shoi Mishovdag	0.008	30.9	14.1	6.5	n.d.	159	7.5	3.8	21.1	1.3	0.16	n.d.	0.88
16/10	Yandere	0.047	32.2	7.2	2.0	n.d.	130	3.8	1.0	17.7	0.39	n.d.	n.d.	0.38
24/10	Kalmaz	0.026	34.4	18.3	9.0	n.d.	485	3.7	3.4	17.5	n.d.	n.d.	n.d.	0.38
27/10	Akhtarma-Pashaly	0.039	52.4	16.3	4.8	n.d.	660	2.5	1.7	6.3	n.d.	n.d.	n.d.	0.25
35/10	Bindovan	0.0072	47.5	25.8	15.1	n.d.	538	6.7	3.7	40.1	0.58	0.142	n.d.	0.56

(n.d.) not detected; (–) component was not measured.

Table 3. Temperatures of mud volcanic waters

Sample no.	Mud volcano	Measured $t$ , °C		Formation $t$ values calculated from hydrochemical geothermometer data, °C				Fluid generation depths calculated from hydrochemical geothermometer data, km		
		air	water	soil (10 cm)	Mg-Li	Na-Li	Na-K	Si	Mg-Li	Na-Li
29/10	Zarat (Khydyrzyndy-2)	19.5	13.1	—	137	160	110	58	6.52	7.64
3/10	Uchtepe	—	18.9	—	73	88	33	59	3.48	4.18
10/10	Pel'peya-Garadag	—	—	—	60	57	6	24	2.85	2.70
17/10	Shorbulag	17.5	14.2	—	48	54	41	39	2.29	2.57
19/10	Davaboinu	16.5	15.6	—	64	81	43	62	3.06	3.85
34/10	Chegeldag	14.2	13.7	13.6	70	67	43	43	3.32	3.21
<b>I. Caspian region</b>										
1/10	Pirekyashkyl, northern group	17.0	15.0	—	66	73	42	55	3.16	3.49
2/10	Pirekyashkyl, southern group	—	16.0	—	73	83	40	72	3.46	3.94
4-1/10	Dashgil, mud breccia field	18.0	19.0	—	37	46	26	46	1.78	2.17
4-2/10	Dashgil, large salse (lake)	18.5	19.6	—	57	60	22	46	2.69	2.84
5/10	Bakhar	—	20.0	—	69	55	25	45	3.30	2.61
5-1/10	Bakhar, northern group	—	19.0	—	33	18	14	36	1.57	0.84
6/10	Saryboga, western group	—	18.5	—	51	51	19	54	2.43	2.41
7/10	Goturdag	—	19.6	—	63	75	32	59	3.02	3.57
8/10	Airantekyan	16.8	17.5	—	50	54	21	54	2.37	2.59
18/10	Shakhigaya	18.5	14.7	—	23	20	0	47	1.07	0.95
20/10	Galendarakhtarma	21.5	13.9	—	77	79	16	44	3.69	3.78
21/10	Nardaran-Akhtarma Vostochnaya	21.0	13.0	—	60	69	37	63	2.88	3.31
22-1/10	Demirehi (brown-colored pulp)	17.0	10.0	—	103	139	45	48	4.91	6.64
22-2/10	Demirehi (gray-colored pulp)	—	9.0	—	116	156	71	53	5.53	7.42
23/10	Malyi Mereze	20.0	11.1	10.4	50	53	32	49	2.38	2.52
26/10	Cheildag	17.1	16.1	14.3	86	109	50	48	4.09	5.21
<b>III. Shemakha-Gobustan region</b>										
<b>II. Absheron region</b>										

Table 3 (Contd.)

Sample no.	Mud volcano	Measured $t$ , °C			Formation $t$ values calculated from hydrochemical geothermometer data, °C					Fluid generation depths calculated from hydrochemical geothermometer data, km	
		air	water	soil (10 cm)	Mg-Li	Na-Li	Na-K	Si	Mg-Li	Na-Li	
26-1/10	Cheildag, northern group	—	15.4	—	71	96	57	31	3.40	4.55	
26-2/10	Cheildag, western group	17.5	14.5	—	79	99	41	57	3.77	4.70	
26-3/10	Cheildag, southern group	—	14.8	—	95	118	72	59	4.50	5.63	
30/10	Gylych	16.1	15.9	13.1	89	115	69	74	4.25	5.45	
31/10	Agdam group	16.0	14.8	13.5	29	21	40	49	1.40	1.02	
32/10	Arzani	14.7	16.8	14.8	92	113	67	85	4.36	5.40	
33/10	Shekikhan	15.5	14.4	—	63	80	68	48	3.00	3.79	
<b>IV. Kura region</b>											
9/10	Khydyrly	19.1	17.9	—	24	19	18	32	1.60	1.24	
11/10	Durovdag	18.5	19.9	—	5	—24	7	43	0.33	—	
12/10	Duzdag, small salse ejecting water	18.9	20.3	—	21	1	10	57	1.37	—	
12-1/10	Duzdag, central salse	—	—	—	39	17	17	69	2.59	1.10	
13/10	Nefechala Yuzhnaya	12.3	19.0	—	47	40	35	84	3.10	2.65	
13-1/10	Nefechala, well	—	22.6	—	41	37	34	75	2.70	2.47	
14/10	Malyi Mishovdag	14.7	17.5	—	51	58	41	56	3.42	3.84	
15/10	Bol'shoi Mishovdag	14.1	16.0	—	30	29	40	44	2.03	1.96	
16/10	Yandere	18.9	17.5	—	27	29	29	55	1.83	1.90	
24/10	Kalmaz	13.4	16.0	15.6	56	55	22	58	3.70	3.69	
27/10	Akhtarma-Pashaly	17.8	15.5	—	45	70	43	93	2.97	4.65	
35/10	Bindovan	17.7	15.5	15.0	56	50	30	47	3.73	3.35	

(—) Temperature was not measured.

Table 4. Isotopic parameters of the dissolved mud volcanic waters

Sample no.	Sampling site	HCO <sub>3</sub> , mg/L	$\delta^{13}\text{C}(\text{HCO}_3)$ , ‰	$\delta^{18}\text{O}$ , ‰	$\delta\text{D}$ , ‰	$\Delta\delta\text{O}^*$ , ‰
<b>I. Caspian region</b>						
29/10	Zarat (Khydyrzyndy-2)	2044	21.7	7.2	-25	12
<b>II. Absheron region</b>						
3/10	Uchtepe	5063	37.3	7.4	-21	11
10/10	Pel'pelya-Garadag	5795	28.6	3.1	-19	7
17/10	Shorbulag	1373	7.6	2.1	-22	6
19/10	Davaboinu	1360	32.2	3.2	-24	7
34/10	Chegaldag	2532	16.5	6.2	-13	9
25/10	Otman Bozdag	2684	13.2	3.8	-18	7
<b>III. Shemakha—Gobustan region</b>						
1/10	Pireyashkyul, northern group	8104	34.2	3.1	-12	6
2/10	Pireyashkyul, southern group	6070	35.7	2.8	-21	7
4-1/10	Dashgil, mud breccia field	494	10.6	2.0	-17	5
4-2/10	Dashgil, large salse (lake)	1763	-11.7	2.5	-29	7
5/10	Bakhar	2474	27.2	4.1	-26	9
5-1/10	Bakhar, northern group	2501	3.8	2.5	-23	7
6/10	Saryboga, western group	1403	25.7	3.2	-31	8
7/10	Goturdag	4148	27.2	2.3	-31	7
8/10	Airantekyan	3233	27.6	1.2	-24	5
18/10	Shakhigaya, salse (lake)	567	-12.9	1.9	-22	6
20/10	Galendarakhtarma	7015	33.1	5.6	-14	9
21/10	Nardaran-Akhtarma Vostochnaya	5301	18.3	5.4	-15	9
22-1/10	Demirchi (brown-colored pulp)	3965	13.7	10.4	-23	15
22-2/10	Demirchi (gray-colored pulp)	4240	9.7	10.3	-23	14
23/10	Malyi Mereze	3081	9.1	7.0	-21	11
26/10	Cheildag	5719	34.7	4.9	-20	9
26-1/10	Cheildag, northern group	6009	36.6	4.7	-12	7

Table 4 (Contd.)

Sample no.	Sampling site	HCO <sub>3</sub> , mg/L	δ <sup>13</sup> C (HCO <sub>3</sub> ), ‰	δ <sup>18</sup> O, ‰	δD, ‰	ΔδO*, ‰
26-2/10	Cheildag, western group	4148	36.5	6.6	-14	10
26-3/10	Cheildag, southern group	4545	29.1	5.4	-22	9
30/10	Gylych	5261	31.8	4.8	-22	9
31/10	Agdam group	5139	22.8	2.7	-29	8
32/10	Arzani	5734	22.7	5.1	-20	9
33/10	Shekikhan	3721	24.7	8.2	-24	12
<b>IV. Kura region</b>						
9/10	Khydyrly	107	-8.5	1.0	-30	6
11/10	Durovdag	1357	-3.9	1.2	-23	5
12/10	Duzdag, small salse ejecting water	1098	-2.6	2.0	-16	5
12-1/10	Duzdag, central salse	1129	5.8	3.3	-21	7
13/10	Neftechala Yuzhnaya	415	17.3	-0.6	-32	5
13-1/10	Neftechala, well	122	0.6	0.0	-32	5
14/10	Malyi Mishovdag	3248	28.1	2.3	-23	6
15/10	Bol'shoi Mishovdag	2135	30.1	2.5	-16	6
16/10	Yandere	1022	22.5	3.0	-18	7
24/10	Kalmaz	2257	29.0	4.4	-16	8
27/10	Akhtarma-Pashaly	3538	30.8	1.5	-21	5
35/10	Bindovan	1251	29.2	3.7	-25	8
<b>Surface waters</b>						
1p/10	Kura R.	207	-8.2	-10.2	-59	-
3p/10	Spring near Demirchi Volcano	200	-9.7	-9.8	-57	-
4p/10	Demirchi R.	256	-8.5	-9.6	-55	-
5p/10	Canal from the Samur R.	159	-4.0	-11.5	-67	-
6p/10	Water reservoir in Baku	122	-3.1	-10.2	-60	-
7p/10	Caspian Sea, near the shore, Shirvan reserve area	256	-0.5	-3.4	-27	-

(ΔδO\*) Deviation of the δ<sup>18</sup>O value from the line of meteoric waters (Craig) calculated in accordance with the formula ΔδO = δ<sup>18</sup>O - (δD - 10)/8.

with the high water and gas discharge; another sample (4-2/10), from a large salse (~15 m in diameter) with a very low water discharge. The latter salse is locally characterized by intense gas discharge, which is documented by one of the previously deployed station of automatic control over gas emanations. Dissimilar to Duzdag Volcano, water mineralization in the large salse of Dashgil Volcano (Sample 4-2/10) appeared to be 1.5 times higher as compared with that in the mud breccia field (Sample 4-1/10). This water was also characterized by the higher  $\text{SO}_4$  concentration (3.1 g/L) and elevated (2.53–3.6 times) Li,  $\text{HCO}_3$ , and B concentrations. In contrast, the Ca, Mg, Sr, and Ba concentration were almost equal or slightly lower as compared with the less mineralized waters.

There is information in some publications on the discharge of waters characterized by a different composition within some mud breccia fields: Kyrykh, Duzdag, Malyi and Bol'shoi Kharami (Aliiev and Buniat-Zade, 1967). At the same time, our data concede the possibility of supergene alteration of the salt composition in waters of isolated or large salses. This can be caused by different factors: admixture of rain water or intense evaporation and washout of salts from the exposed dry mud breccia flows. The elevated general mineralization and high sulfate ion concentrations in waters of Dashgil Volcano can be explained by the supergene alteration related to water evaporation at the surface; the presence of sulfate ion, by the oxidation of sulfides contained in mud breccias.

At first glance, the lowered mineralization of water in the large salse in Duzdag can be explained by the recent rain. However, the degree of water dilution in Cl and  $\text{HCO}_3$  ions is significantly different. It is conceivable that we are dealing in the situation under consideration with the discharge of waters characterized by different compositions within the same volcano, which was noted in previous publications. In our opinion, this explanation needs additional arguments.

In Demirchi Volcano, water was also sampled from salses ejecting the color-variable clayey pulp: brown (Sample 22-1/10) and gray (Sample 22-2/10) (Table 2). The distance between these water seepages is ~25–30 m. Their water is almost identical by the general salt composition, although the Eh value in the gray-colored pulp is slightly lower (+105 mV) as compared with that in the brown one (+155 mV). Correspondingly, concentrations of elements with the variable valence, such as S, Mn, Fe, Zn, Ge, As, Pb, Mo, Ce, and U, were also different. Water from the gray-colored pulp was also characterized by higher Ba, Ca, K, and Rb concentrations.

As a whole, judging from the main components (Cl,  $\text{HCO}_3$ , Na, B, Br, F, Si), waters of Demirchi Volcano are delivered most likely from a single reservoir. The observable variations in microcomponent concentrations can be explained by different compositions of the clayey pulp mobilized by the ascending flow of mud volcanic fluids. The salses ejecting brown-

colored emulsion are located closer to the base of the landslide slope, while outcrops of the gray pulp are located away from the latter. It is conceivable that the ascending flow of the mud volcanic fluid mobilizes partly brown-colored slope sediments developed in the zone of supergene rock alteration.

Thus, waters from mud volcanoes of Azerbaijan are characterized by the sufficiently variable composition, which likely indicates their belonging to different aquifers and/or different degrees of postsedimentary alteration.

## GEOTHERMAL GENERATION CONDITIONS OF MUD VOLCANIC WATERS

The thermal conditions and depths of the formation of mud volcanic fluids in the Caucasus region and Kura depression are discussed in (Lagunova, 1975; Feizulaev et al., 1999; Guliev et al., 2001, 2004; Aliiev et al., 2009). It is assumed that "roots" of mud volcanoes are located at depths of approximately 6–10 km. These concepts are supported by the seismic profiling data on the South Caspian Basin that recorded the regionally thinned (fluid-saturated) members at depths of 8–12 km (Guliev et al., 1988). These layers presumably feed mud volcanic systems.

The influx of fluids from such depths should theoretically form the thermal anomaly in areas of their discharge. At the same time, direct measurements of temperatures conducted in October 2010 revealed that mud volcanic waters are characterized by relatively low values:  $t = 9.0\text{--}22.6^\circ\text{C}$ . They correspond approximately to the air temperature or its average values.

The sampling was performed during calm periods in volcanic activity. The thermal anomaly related to the migration of these waters to the surface becomes apparently dispersed due to their low discharge. Theoretically, the cooling effect can also provoke adiabatic expansion of gas during its ascent from deep zones.

Thus, the direct measurements of temperature at the surface of volcanoes provide no information on conditions of the water formation in a bed.

No direct measurements of temperatures of mud volcanic fluid generation at depths exceeding 6–7 km are yet available. Therefore, they can be estimated only by indirect methods, for example, using hydrochemical geothermometers (Mg–Li, Li–Na, Na–K,  $\text{SiO}_2$ ).

Table 3 presents the calculated generation temperatures of the water salt composition. Their analysis provides grounds for preferring the Mg–Li geothermometer (see comments to Fig. 2). The Mg–Li temperature values vary from 21 to  $137^\circ\text{C}$  ( $t_{\text{av}} = 60.5^\circ\text{C}$ ,  $n = 40$ ). The minimum temperature value was obtained for Durovdag Volcano ( $t(\text{Mg–Li}) = 5^\circ\text{C}$ ). It is of interest that the Na–Li and Na–K geothermometers yielded minimum and even negative temperature values for waters of this volcano, suggesting that these estimates represent an artifact. Therefore, they were omitted

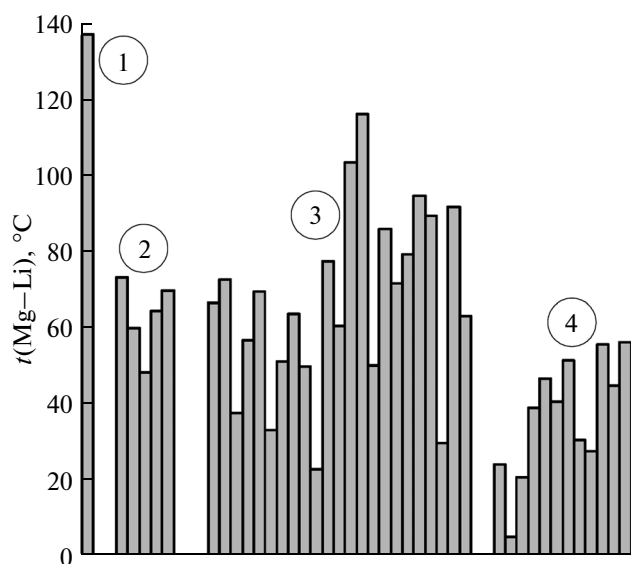


Fig. 4. Fluid generation temperatures estimated for mud volcanic waters in the Caspian (1), Absheron (2), Shemakha–Gobustan (3), and Kura (4) regions according to the Mg–Li geothermometer data.

from calculations of minimum and maximum values of formation temperatures. It is conceivable that they are explained by the influence of recent rain that provided the influx of salts from the volcanic surface to the salses. Noteworthy is the fact that the Si temperature obtained for Duzdag Volcano is close to  $t(\text{SiO}_2)$  values in other volcanoes of the Kura region (Table 3). This provides grounds for an assumption that the true temperature of fluid generation in Duzdag Volcano is generally similar to that in other volcanoes of the region.

Thermal conditions of water formation in different areas of Azerbaijan are notably different (Fig. 4). These differences are evident from comparison of the average  $t(\text{Mg-Li})$  values. For example,  $t(\text{Mg-Li}) = 39.6^\circ\text{C}$  ( $n = 11$ ) determined for volcanoes of the Kura region appeared to be notably lower than in the Shemakha–Gobustan and Absheron regions, where  $t_{\text{av}}$  values are similar:  $t_{\text{av}} = 68^\circ\text{C}$  ( $n = 22$ ) and  $t_{\text{av}} = 63^\circ\text{C}$  ( $n = 5$ ), respectively.

Thus, there is a tendency for the growth of temperatures of fluid generation toward the Greater Caucasus orogen.

#### DEPTHS OF MUD VOLCANIC FLUID GENERATION

The thermal investigations in wells reveal that temperature gradients in mud volcanic domains of Azerbaijan vary from 13–17°C/km in the Kura region and Baku Archipelago to 20–22°C/km in the Shemakha–Gobustan and Absheron regions (Aliiev, 1985; Guliev et al., 2004). Keeping these data in mind, we accepted the temperature gradient of 15°C/km for the Kura

region and 21°C/km for other mud volcanic regions of Azerbaijan. Table 3 presents the depth estimates.

It follows from the table that the depth of volcanic “roots” varies from 2.3 to 3.5 km in the Absheron region, from ~1 to 4.9 km in the Shemakha–Gobustan region, and from 0.3 to 3.7 km in the Kura region. The maximum depth of 6.5 km is obtained for the sole volcano sampled in the Khydyrzyndy group of the Caspian region. Probably, this estimate is not artefact, since other geothermometers (Na–Li and Na/K) also yielded maximum temperature values (Table 3).

According to the Na–Li geothermometer data, the maximum depth in these regions is approximately 1 km greater. Thus, with an allowance for errors in estimating formation temperatures by the Mg–Li and Na–Li geothermometers ( $\pm 11^\circ\text{C}$ ) and differences in their readings, the depths of mud volcanic reservoirs in the onshore part of Azerbaijan likely vary from ~1 to ~6–7.5 km.

Comparison of average depths of fluid generation obtained for different regions demonstrates that they differ less notably than average values of formation temperatures. In the Kura region, the average depth ( $h_{\text{av}} = 2.4$  km,  $n = 11$ ) is only slightly shallower as compared with that in the Absheron and Shemakha–Gobustan regions, where  $h_{\text{av}} = 3.0$  and 3.2 km ( $n = 5$  and 23), respectively. The temperature differences between these regions become smoothed during estimation of fluid generation depths due to lowered values of temperature gradients in wells drilled in the Kura region

#### PECULIARITIES OF THE ISOTOPIC COMPOSITION OF MUD VOLCANIC WATERS

In the Caucasus region, the isotopic composition of mud volcanic waters has been investigated for a long period (Erokhin and Titkov, 1982; Esikov, 1995; Seletskii, 1991; Guliev et al., 2004; Lavrushin et al., 2005; *Geologiya ...*, 2008).

Additional measurements of the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values (Table 4) revealed the following fact: in terms of isotopic composition ( $\delta\text{D} = -32$  to  $-12\text{‰}$ ,  $\delta^{18}\text{O} = -0.6$  to  $+10.4\text{‰}$ ), mud volcanic waters of Azerbaijan significantly differ from both surface (sea and river) and oil waters (Guliev et al., 2004). Their main difference consists in high  $\delta^{18}\text{O}$  values (Fig. 5). However, comparison with well waters is likely improper, since mud volcanic fluids are frequently formed at deeper levels as compared with waters recovered by wells.

By their average  $\delta^{18}\text{O}$  values, waters of Azerbaijan volcanoes are generally similar to their counterparts in the Taman Peninsula (+3.7 and +3.9‰, respectively), although the  $\delta D_{\text{av}}$  value in them is slightly higher ( $\delta D_{\text{av}} = -22\text{‰}$ ) than in waters of the peninsula, where it amounts to  $-27\text{‰}$  (Lavrushin et al., 2005). Dissimilar to Taman mud volcanic waters, their Azerbaijan counterparts do not form well-expressed trend (Fig. 5) observed in the Kura region, although it is character-



ized by a less notable inclination (relative to meteoric waters) than in the Taman Peninsula.

Difference between the isotopic compositions of mud volcanic waters and meteoric waters (Fig. 5) is attributed by some researchers to underground evaporation/condensation in gas pools (Seletskii, 1991). However, it was subsequently shown for mud volcanic waters of the Taman Peninsula (Lavrushin et al., 2005) that their isotopic and chemical properties are better consistent with the formation due to their interaction in the rock–water and water–methane systems at different temperatures during fluid generation.

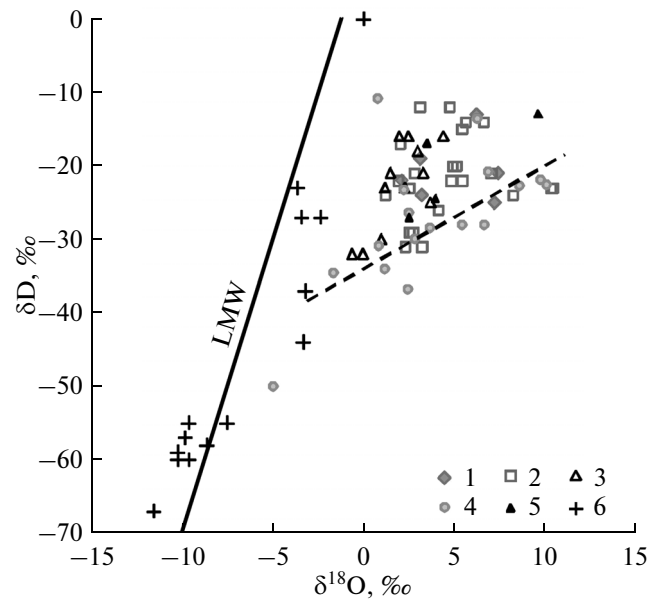
Indeed, mud volcanic waters of Azerbaijan are characterized by the positive correlation of  $\Delta\delta^{18}\text{O}$  values (deviation of data point of volcano from the line of meteoric waters, i.e., “oxygen shift”) with temperatures calculated from Mg–Li geothermometer data (Fig. 6). Moreover, this trend is likely universal for all mud volcanic waters of the region (Azerbaijan, Kakhetia, and Taman Peninsula).

It means that mud volcanic waters become enriched with the heavy oxygen isotope due to the isotopic exchange with host rocks, and variations in the  $\delta^{18}\text{O}$  values reflect differences in temperatures of the water formation.

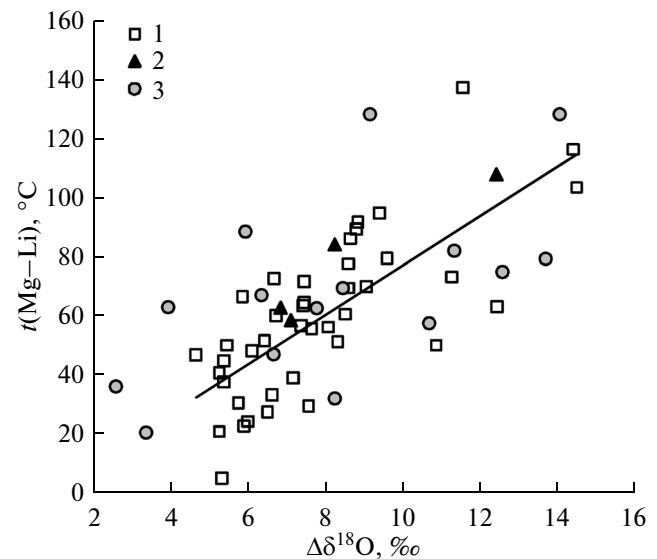
Soda waters differ from their chloride counterparts by the higher  $\delta^{18}\text{O}$  values (Figs. 7, 8). Hence, the isotopic composition of mineralized waters of the Cl–Na type, which are widespread in the Kura region, are less modified during lithogenesis as compared with desalinated waters of the soda type. The lower degree of postsedimentary transformation of Cl–Na waters is also evident from the lowered values of Mg–Li temperatures (Table 3, Fig. 4). As a whole, the negative correlation between the oxygen isotope composition in water and contents of Cl ion in the latter (Fig. 8) indicates that Cl–Na waters are formed at shallower depths as compared with waters of the  $\text{HCO}_3\text{--Na}$  type. Moreover, increase in the contribution of residual brines of the evaporite type to mud volcanic waters plays a subordinate role in the growth of  $^{18}\text{O}$  concentrations.

Comparison of isotopic and chemical properties of Cl–Na waters reveals heterogeneous sources of their feeding (Fig. 8). For example, data points obtained for waters of the Kura region with the Cl ion concentration of ~20 mg/L are located near the data point of seawater ( $\text{Cl} = 19 \text{ g/L}$ ,  $\delta^{18}\text{O} \sim 0\text{‰}$ ). At the same time, water from Neftechala Yuzhnaya Volcano with the highest concentration of Cl ion ( $[\text{Cl}^-] = 54.7 \text{ g/L}$ ) is characterized by the lowest  $\delta^{18}\text{O}$  values ( $-0.6\text{‰}$ ).

The **carbon isotope composition** in the dissolved  $\text{CO}_2$  was previously available only for six mud volcanoes of Azerbaijan (Feizulaev and Movsumova, 2010). We have additionally measured  $\delta^{13}\text{C}$  values in 42 water samples from 34 volcanoes and 1 well (Table 4). Inasmuch as all the water samples are characterized by



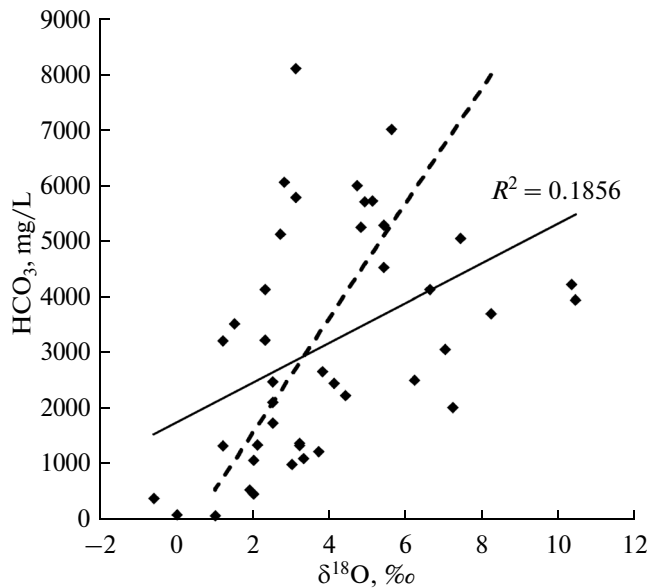
**Fig. 5.** Oxygen and carbon isotope compositions in mud volcanic waters of the Caucasian region. Mud volcanoes: (1–3) Azerbaijan: (1) Absheron, (2) Shemakha–Gobustan, (3) Kura; (4) Taman Peninsula; (5) Georgia, after (Lavrushin et al., 2005); (6) surface waters of Azerbaijan. The dashed line shows the position of the assumed trend obtained for waters of the Taman Peninsula according to data in Table 4 (Lavrushin et al., 2005); (LMW) line of meteoric waters.



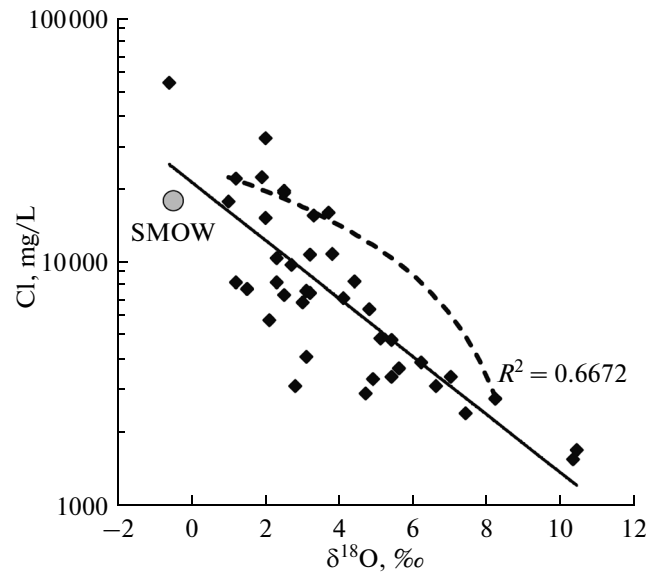
**Fig. 6.** Correlation of Mg–Li temperatures and “oxygen shift” (deviation of  $\delta^{18}\text{O}$  from the line of meteoric waters) values for mud volcanic waters of the Caucasian region: Azerbaijan (1), Kakhetia (2), Taman Peninsula (3).

neutral and slightly alkaline pH values, the  $\text{HCO}_3$  ion is the main  $\text{CO}_2$  form dissolved in water.

In our collection of mud volcanic water samples, the  $\delta^{13}\text{C}(\text{HCO}_3^-)$  is highly variable ranging from  $-12.9$



**Fig. 7.** Correlation between the  $\delta^{18}\text{O}$  values and  $\text{HCO}_3^-$  concentrations in mud volcanic waters of Azerbaijan. For line designations, see Fig. 3.



**Fig. 8.** Correlation between the  $\delta^{18}\text{O}$  values and  $\text{Cl}^-$  concentrations in mud volcanic waters of Azerbaijan. For line designations, see Fig. 3.

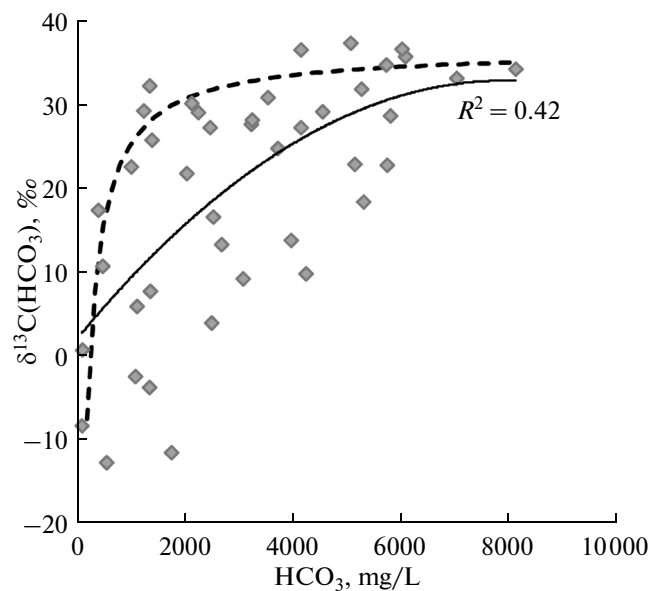
to  $+37.3\text{‰}$  (Table 4), although most samples are characterized by high  $\delta^{13}\text{C}$  values ( $\delta^{13}\text{C}_{\text{av}} = +20.1 \pm 14\text{‰}$ ,  $n = 41$ ), which is well consistent with the presence of isotopically heavy  $\text{CO}_2$  ( $\delta^{13}\text{C}(\text{CO}_2)$  up to  $+22\text{‰}$ ), genesis of which is debatable for a long time (Valyaev et al., 1985; Feizulaev and Movsumova, 2010).

The  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values increase in parallel with the growth of the  $\text{HCO}_3^-$  concentration (Fig. 9). It means that the enrichment of carbon dioxide with the heavy carbon isotope is not related to its degassing or reduction of  $\text{CO}_2$  to  $\text{CH}_4$  during migration of the fluid toward the surface. In the last situation, the correlation should be reverse. Figure 9 also shows that the highest  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values are typical precisely of soda waters. In this connection, the average  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values in the Kura region ( $\delta^{13}\text{C}_{\text{av}} = +16.2\text{‰}$ ,  $n = 11$ ), where waters of the Cl type are widespread, appeared to be lower than in the Absheron ( $\delta^{13}\text{C}_{\text{av}} = +24.4\text{‰}$ ,  $n = 6$ ) and Shemakha–Gobustan ( $\delta^{13}\text{C}_{\text{av}} = +21.3\text{‰}$ ,  $n = 23$ ) regions.

Differences between the hydrocarbonate (soda) and chloride ( $[\text{Cl}^-] > 75$  mg-equiv/L) types are even more contrasting:  $\delta^{13}\text{C}(\text{HCO}_3^-)_{\text{av}} = +26.6$  and  $14.9\text{‰}$ , respectively ( $n = 17$  and  $25$ , respectively). All the negative  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values (up to  $-12.9\text{‰}$ ) are documented only for waters of the Cl type. In soda waters, the  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values below  $+9.1\text{‰}$  have never been recorded. It should be noted that maximum  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values obtained for waters of both types

are almost identical:  $+37.3$  and  $+32.2\text{‰}$  for  $\text{HCO}_3^-$ - and Cl types, respectively).

Sampling in different salses of an individual volcano (Demirchi, Duzdag, Dashgil) or mud breccia fields in synonymous groups (Pirekyashkyul, Cheildag, Bakhar) yielded different  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values. Variations in the  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values amounted to



**Fig. 9.** Correlation between  $\text{HCO}_3^-$  concentrations and  $\delta^{13}\text{C}$  value in the dissolved inorganic carbon. For line designations, see Fig. 3.

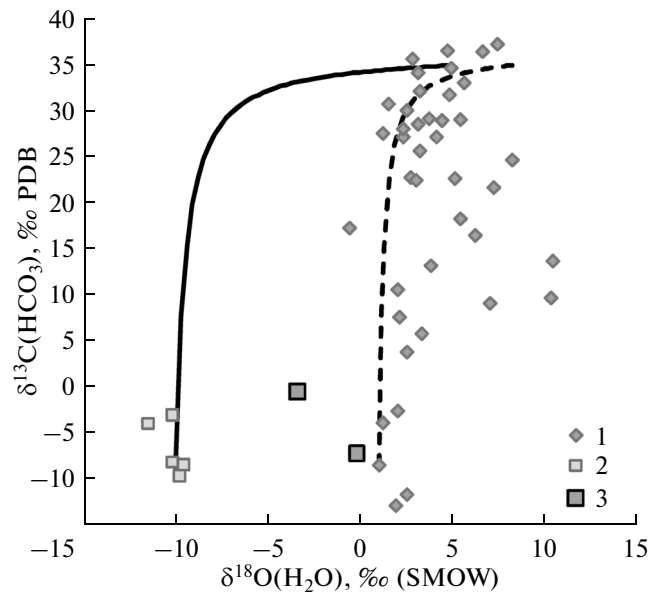
~22–24‰ in some cases (Bakhar and Dashgil volcanoes) and were below 1.5–8.4‰ in others (Cheildag, Demirchi, Pirekyashkyul, Duzdag volcanoes). Although the number of observations is relatively insignificant, there is an impression that the maximum dispersion of  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values is characteristic of areas with the Cl-type waters.

No correlation between the isotope composition of carbon dissolved in carbon dioxide and that of oxygen is observable (Fig. 10). The figure also demonstrates that mud volcanic waters with low  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values (<0‰) are similar by this parameter to waters of rivers, which originate in mountainous areas of the Caucasus, and waters of the Black and Caspian seas. At the same time, mud volcanic waters differ significantly from river waters by the  $\delta^{18}\text{O}$  values. The calculated line reflecting the mixing of river and mud volcanic waters presented in the last figure shows that waters from volcanoes with lowered  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values (<0‰) are not related to the mixing of formation and river waters.

At the same time, the influence of near-surface oxidation of methane on the carbon isotope composition in  $\text{HCO}_3^-$  cannot be ruled out. In highly mineralized chloride waters, admixture of the isotopically light  $\text{CO}_2$  should have a stronger influence on the  $\delta^{13}\text{C}(\text{HCO}_3^-)$  value, since concentrations of hydrocarbonate ion in them is minimal. This likely also explains highly variable  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values in water samples taken from different salses of the same volcano or group of volcanoes.

Data presented in the diagram (Fig. 10) do not exclude the possibility of the formation of waters depleted in  $^{13}\text{C}$  due to the seawater admixture. By their  $\delta^{18}\text{O}$  values, these waters are analogous with their counterparts from the Caspian and Black seas and differ from them by the chemical composition, for example, the content of sulfate ion. Notable concentrations of the latter are recorded only in waters from some volcanoes of the Shemakha–Gobustan region located at significant distance from the sea coast. In other mud volcanic areas of Azerbaijan, no sulfate sulfur is recorded in waters or is present in insignificant concentrations ( $S < 20$  mg/L). Such a property can be explained by sulfate reduction, although lowered  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values are characteristic of waters with high concentrations of Cl ion ( $\text{Cl} = 15\text{--}32$  g/L), which also makes them different from water of the Caspian Sea ( $\text{Cl} = \sim 3\text{--}6$  mg/L).

Correlation of  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values with Mg–Li temperatures (Fig. 11) allows to define a statistically significant trend. Only three data points corresponding to Khydryzindy (Zarat) and Demirchi (brown- and gray-colored pulps) volcanoes are located above the trend. The temperature growth is accompanied by increase in the  $\text{HCO}_3^-$  ion concentration (Fig. 12).

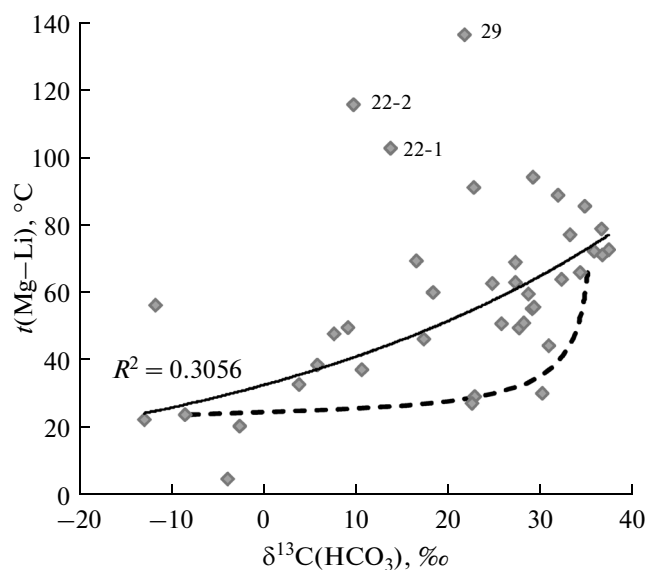


**Fig. 10.** Isotope characteristics of carbon and oxygen in the dissolved forms of  $\text{CO}_2$  and waters, respectively. (1) Mud volcanoes of Azerbaijan; (2) rivers of Azerbaijan; (3) Caspian and Black seas. Solid line corresponds to the theoretical line of mixing of river ( $\delta^{18}\text{O} = -10\text{‰}$ ,  $\delta^{13}\text{C}(\text{HCO}_3^-) = -10\text{‰}$ ,  $\text{HCO}_3^- = 200$  mg/L) and mud volcano ( $\delta^{18}\text{O} = +5\text{‰}$ ,  $\delta^{13}\text{C}(\text{HCO}_3^-) = +35\text{‰}$ ,  $\text{HCO}_3^- = 6000$  mg/L) waters; dashed line corresponds to the calculated line of mixing of Cl and  $\text{HCO}_3^-$  mud volcanic waters with the extreme member values corresponding to compositions of waters from Khydryly and Pirekyashkyul volcanoes.

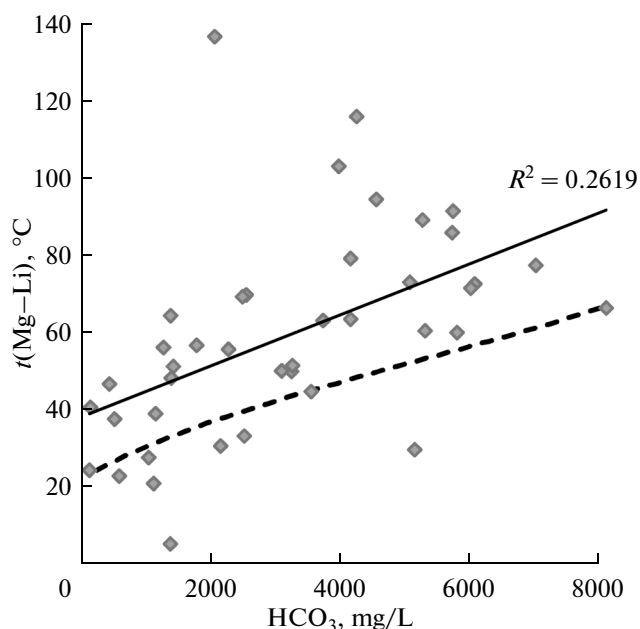
## DISCUSSION

Distribution patterns of different (Cl–Na and  $\text{HCO}_3^-$ –Na) mud volcanic waters demonstrate that the traditional zoning of mud volcanic domains of Azerbaijan based on the geomorphological principle (Yakubov et al., 1971) is inconsistent with the observable geochemical zonality. For example, the domain dominated by Cl-type waters includes both the Kura and Caspian regions that also comprises southern areas of the Shemakha–Gobustan and Absheron regions. The soda ( $\text{HCO}_3^-$ –Na) waters are developed over a substantially lesser area and localized only in the central part of the last two regions.

The thorough analysis of correlation between the chemical composition of mud volcanic waters and geological structure of the region under consideration reveals that waters of the  $\text{HCO}_3^-$ –Na type associate with the zone characterized by maximum activity of tectonic processes confined to the southern slope of the Greater Caucasus (Aliiev and Bairamov, 2007; *Geologiya ...*, 2008; Kerimov and Rachinskii, 2011; Kadirov et al., 2012; Kadirov and Safarov, 2013). This zone exhibits significant retardation of horizontal movements recorded by GPS measurements, elevated background seismicity, intense dislocations, and



**Fig. 11.** Correlation of the  $\delta^{13}\text{C}$  values in the dissolved inorganic carbon and Mg–Li temperatures obtained for the formation of salt composition in mud volcanic waters of Azerbaijan. Numbers in the figure correspond to sample numbers in Table 1 and Fig. 1. For line designations, see Fig. 3



**Fig. 12.** Correlation between  $\text{HCO}_3^-$  ion concentrations and Mg–Li temperatures obtained for fluid generation in mud volcanic waters of Azerbaijan.

large-scale systems of tectonic thrusts (Guliev et al., 2002; Relinger et al., 2006; Aliev and Bairamov, 2007; *Geologiya ...*, 2008). Thus, the soda water domain coincides with the frontal zone of intracontinental collision of the Greater Caucasus (Philipp et al., 1989; *Bol'shoi Kavkaz ...*, 2007).

In contrast, waters of the CI type are characteristic of synclinal structures, where the sedimentary cover is less affected by tectonic activity. All of them are localized in the Kura and Caspian depressions along with their marginal parts adjacent to the Greater Caucasus and are partly overlain by tectonic thrusts (Aliev and Bairamov, 2007).

It is known (Kolodii, 1971) that the mud volcanic counterparts of formation waters are more enriched with Mg ion and, correspondingly, characterized by higher Mg/Ca values. The maximum Mg/Ca values are characteristic of mud volcanic waters of the She-makha–Gobustan region. At first glance, this reflects specific conditions of their formation in intense tectonic zones. It is assumed (Kissin, 1967) that tectonic strains and intense deformations of clayey sequences represent one of the factors responsible for the development of zones with abnormally high formation pressures (AHFP). As follows from the experimental data on interstitial waters squeezed out from clays under high pressures (Kryukov et al., 1962), the resulting solution can be enriched with Mg. Nevertheless, it should be noted that the maximum Mg/Ca values are characteristic of soda waters. Therefore, the growth of this coefficient can be explained by the stronger limiting influence of the carbonate equilibrium on  $[\text{Ca}^{2+}]$

than on  $[\text{Mg}^{2+}]$ . The reversed relationships of  $[\text{Ca}^{2+}]$ ,  $[\text{Mg}^{2+}]$ , and  $[\text{Sr}^{2+}]$  with the  $\text{HCO}_3^-$  concentrations support this conclusion.

One of the most remarkable features of mud volcanic waters is the presence of dissolved forms of carbon dioxide in them with high  $\delta^{13}\text{C}$  values (up to +35‰). It is known (Valyaev et al., 1985) that the isotopically heavy  $\text{CO}_2$  is generally characteristic of gases from mud volcanoes of the Caucasus region. Its genesis remains debatable and is usually attributed to deep (magmatogenic) degassing of the Earth (Lagunova, 1974; Gemp and Lagunova, 1978; Gemp et al., 1979; Valyaev et al., 1985). However, the admixture of mantle helium with high  $^3\text{He}/^4\text{He}$  values ( $20\text{--}220 \times 10^{-8}$ ) is very rare (Yakubov et al., 1980; Lavrushin et al., 1996, 2009). In addition, this inference is sharply inconsistent with recent views on the isotopic composition of mantle carbon. The high-temperature carbon-bearing mantle products, such as diamonds from kimberlite pipes, carbonatites, volcanic gases, and vapor inclusions in basalts, are mostly characterized by the  $\delta^{13}\text{C}$  value of  $-6 \pm 2\text{‰}$  usually accepted as indicator of the mantle source, as is evident from review in (Deines et al., 1992; Pokrovsky, 2000). Some mantle rocks contain reduced forms of carbon with lower  $\delta^{13}\text{C}$  values (approximately  $-25\text{‰}$ ), which are thought to be related to mantle degassing (Pineau and Javoy, 1983, 1994; Taylor, 1986) or mantle heterogeneity (Deines, 2002). As far as we know, the  $\delta^{13}\text{C}$  values exceeding zero have never been recorded in mantle rocks and high-temperature gases.

This fact unambiguously refutes the possibility of the universal participation of magmatogenic fluids in the feeding of mud volcanic systems and is consistent with an assumption on the near-surface genesis of the isotopically heavy  $\text{CO}_2$ . The formation of such carbon dioxide in the sedimentary cover is confirmed by investigations of well gases in the South Caspian and other petroliferous regions (Milkov, 2011). The anomalous  $\delta^{13}\text{C}(\text{CO}_2)$  values are documented exclusively in the upper part of the productive zone in deposits occurring at depths shallower than  $\sim 3\text{--}3.5$  km under formation temperatures amounting to  $70^\circ\text{C}$ . The presence of the isotopically heavy  $\text{CO}_2$  in this zone is thought to be related to the biodegradation of hydrocarbons near the upper boundary of their accumulation.

According to our data (Table 3, Fig. 4), the temperature interval of the formation of mud volcanic waters comprises the entire zone in question. Moreover, the average Mg–Li temperature in different mud volcanic domains of Azerbaijan never exceeds  $70^\circ\text{C}$ . Such a coincidence confirms indirectly (but independently) the objectivity of our estimates of formation temperatures by hydrochemical geothermometers.

At the same time, the data on mud volcanoes are only partly consistent with the model of “biodegradation” genesis of the isotopically heavy  $\text{CO}_2$  (Milkov, 2011). According to this model, the maximum enrichment of gases with carbon dioxide occurs at temperatures of  $20\text{--}40^\circ\text{C}$  (Fig. 1 in the above work). Moreover, this temperature interval is characterized by a tendency for the positive correlation between  $[\text{CO}_2]$  and  $\delta^{13}\text{C}(\text{CO}_2)$ .

According to our data, relationships of  $\text{HCO}_3^-$  concentrations and  $\delta^{13}\text{C}(\text{CO}_2)$  values with formation (Mg–Li) temperatures are different (Figs. 11, 12). The figures show that the fields of data points are approximated by statistically significant positive correlations for the entire temperature range yielded by the Mg–Li geothermometer ( $24\text{--}137^\circ\text{C}$ ). The Mg–Li value likely represents a function of depth. The following inference can be derived from such observations: the enrichment of mud volcanic waters with the isotopically heavy carbon dioxide is intensified in parallel with the growth of formation temperatures (at least within the obtained temperature interval) and, thus, becomes higher with the fluid generation depth.

Dependence of these processes from temperatures of interaction in the water–rock system and, thus, from the degree of postsedimentary transformations of water, organic matter, and mineral matter is emphasized by the correlation between  $\text{HCO}_3^-$  concentrations and oxygen isotopic composition in water (Fig. 7), as well as by the oxygen isotope shift in waters depending from fluid generation temperatures (Fig. 6).

Thus, analysis of waters from mud volcanoes suggests that the presence of waters enriched with  $\text{HCO}_3^-$

ion characterized by anomalously high  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values can be related to some temperature-dependent process. Judging from our data, this process can hardly be explained by the biodegradation of heavy hydrocarbons at the upper boundary of gas pools, as it is assumed for wells (Milkov, 2011). In such a situation, the correlation of  $\delta^{13}\text{C}$  and  $\text{HCO}_3^-$  with  $t(\text{Mg}\text{--}\text{Li})$  data (Figs. 11, 12) should be negative. It is conceivable that the data on mud volcanoes reflect the isotopic–geochemical properties of the “normal” sedimentary cycle of organic matter transformation during the early catagenesis of source rocks. It may be assumed that the upper part of the “oil window” is marked by chemical reactions with a significant release of the isotopically heavy carbon dioxide. At the same time, the dependence of hydrocarbon biodegradation from temperatures at their certain interval cannot be ruled out.

Thus, the question arises as to what are the factors responsible for differences in the interpretation of data obtained from wells and volcanoes? At first glance, the observations in wells seem to be more reliable, since they are based on direct temperature measurements and fluid sampling from the known depths. However, they underestimate the possibility of hydrocarbon migration from deep levels and mixing of gases from different temperature zones in traps. In their essence, oil and gas traps represent accumulating reservoirs, which can receive gases from different depths. This hampers the precise identification of the lower boundary (with respect to depth or temperature) for the distribution of isotopically heavy  $\text{CO}_2$ . In deep-seated pools, the release of such carbon dioxide can be masked by the intense influx (migration) of gases containing the isotopically heavy  $\text{CO}_2$  even from deeper levels.

It goes without saying that hydrocarbons accumulated in near-surface traps can be subjected to biodegradation. However, the powerful source of oxygen for oxidizing hydrocarbons into  $\text{CO}_2$  is unclear. Oil waters are characterized by low (reducing) Eh values (Table 2): locally, even free hydrogen sulfide can be present. The existence of compounds with active forms of oxygen is hardly probable in such environments.

As compared with hydrocarbon fields, mud volcanoes can be considered as open systems, i.e., systems of fluid discharge directly from source rocks. Mud volcanic fluids are likely generated at certain levels and, thus, their isotopic–geochemical properties reflect more adequately thermal conditions and depths of their formation.

Concept of the formation of water, gas, and clayey components in a single geochemically balanced reservoir is supported, in general, by the complex of mutually consistent isotopic–geochemical data on mud volcanoes of the Caucasus region (Lavrushin et al., 1996, 2003, 2005; Guliev et al., 2004). Therefore, as compared with the borehole data, the isotopic–geochemical properties of mud volcanic emanations

reflect more adequately or specify in many aspects the vertical geochemical and thermal zonalities in the distribution of gas–water fluids. The absence of direct measurements of temperatures (and depths) is compensated by the complex of mutually consistent temperature estimates and the data on peculiar features of the chemical ( $\text{HCO}_3^-$ , B/Cl, Li/Cl, K/Cl, Rb/Cl, Na/Cl, Cl/Br, and others) and isotopic ( $\delta^{13}\text{C}$ ,  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ) compositions (Figs 6, 7, 9, 11, 12).

For example, the enrichment of mud volcanic waters with B and Br, as well as decrease in Cl ion concentrations, noted against the background of the growth of fluid generation temperatures and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  values are consistent with concepts of the formation of mud volcanic waters during the early stage of catagenic smectite illitization (Seletskii, 1978; Kholodov, 1987, 2002; Lavrushin et al., 2003, 2005). The manifold decrease in the sorptive capacity of clays results in the influx of a significant part of absorbed ions (primarily, alkaline metals, J, Br, and B) and water contained in swelling smectite interlayers to interstitial waters. The release of its large volumes stimulates the decrease of  $[\text{Cl}^-]$  concentration.

Therefore, chloride waters occurring in the Kura region, as well as southern parts of the Shemakha–Gobustan and Absheron regions, are characterized by substantially lower temperatures of the fluid generation as compared with soda varieties (Figs. 4, 12). This is also evident from the less significant changes in their oxygen isotopic composition (Fig. 8). As compared with soda waters, they are less enriched with alkaline metals, B, and Br (relative to the Cl ion). Chloride waters also exhibit minimum  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values (Fig. 9).

Thus, if we assume the regional distribution of these two types of water, the zone of slightly mineralized soda-type fluids is located in the geological section at considerably deeper levels, as compared with brines of the Cl–Na type.

Indeed, the productive Paleocene–Miocene formations recovered by boreholes in the Kura depression almost always contain coeval waters of brine mineralization (Kerimov and Rachinskii, 2011). Waters of the  $\text{HCO}_3^-$ –Na type are rare in rocks of this age. They are recorded in some wells drilled within fields located in the Absheron Peninsula area. The last authors also assume that soda waters were injected into the upper part of the section from deeper levels, for example, from Mesozoic rocks.

Thus, elucidation of the genesis of  $\text{HCO}_3^-$ –Na waters concerns the long debated problem of hydrocarbon potential in deep zones of the South Caspian basin and, in particular, the problem of hydrocarbon potential in Mesozoic strata.

It goes without saying that the study of mud volcanic waters cannot solve unambiguously this problem. However, we assume that  $\text{HCO}_3^-$ –Na waters are not confined to particular stratigraphic level such as, for example, Mesozoic formations. They are most likely

local formations associated with zones of intense tectonic processes: stress loads, development of thrust structures, and folding. Combined with the dehydration of clay minerals and intense methane generation, such settings can stimulate the formation of local AHFP zones. According to (Popkov et al., 2010), pre-Jurassic rocks in petroliferous areas of the Ciscaucasian region contain desalinated waters of the  $\text{HCO}_3^-$ –Na type in some places. Moreover, mineralization of waters demonstrates inverse relationship with AHFP. At deeper levels, they can theoretically be characterized by regional distribution marking a stratigraphically obscure temperature zone of intense dehydration of mineral matter. Such zones can be correlated with the fluid-saturated complexes documented by seismic methods at depths of 7–13 km (Guliev et al., 1988).

Investigation of geothermal formation conditions of the mud volcanic reservoir in Azerbaijan using the hydrochemical geothermometers yields similar estimates of formation temperatures (with respect to  $t_{\text{av}}(\text{Mg–Li})$  variation range and values) for mud volcanic systems of both Taman Peninsula and eastern Georgia (Lavrushin et al., 2003). Probably, this fact indicates the unity of thermodynamic environments for the formation of mud volcanic systems of the region. The  $t(\text{Mg–Li})$  values demonstrate a tendency for their increase toward the Greater Caucasus orogen. Owing to the large area of mud volcanic activity, this tendency is best evident for volcanoes of Azerbaijan, although it is also notable in the Taman Peninsula (Russia) and Kakhetia (Georgia) (Lavrushin et al., 2003), suggesting the regional pattern of such thermal zonation.

Indeed, the map of heat flow in Azerbaijan (Aliiev, 1985) demonstrates that its values are substantially higher (50–90  $\text{mW}/\text{m}^2$ ) in the Shemakha–Gobustan and Absheron regions than in the Kura region (20–30  $\text{mW}/\text{m}^2$ ). Therefore, the observable growth of fluid generation temperatures toward the orogen can reflect more strained thermal conditions in the formation of fluid systems. At the same time, the possibility that the defined tendency in changes of fluid generation temperatures results from more intense tectonization in piedmont areas, which stimulates the exhumation of deeper waters, cannot be ruled out.

When analyzing geochemical properties of mud volcanic waters based on the data of hydrochemical geothermometers, we should also consider alternative possibilities of their interpretation. Theoretically, all the defined geochemical correlations (Figs. 3, 6, 7–12) can reflect both thermal evolution of fluid systems and mixing of waters of different types, such as Cl–Na and  $\text{HCO}_3^-$ –Na varieties. Influence of this process can also affect estimates of the formation temperatures, since they were derived from the analysis of the chemical composition of waters. It should also be noted that the term “mixing” in the situation under consideration unites two principally different geological processes. The first of them is the mixing of waters from

different aquifer complexes, reservoirs, or thermal zones. In its essence, this process reflects a simple mechanical mixing of waters from different levels.

The second process (elision) consists in the transformation of water composition in a single reservoir. It proceeds within a conditionally closed system against the background of transformation of mineral and organic matter. During this process, primarily sedimentary (sea) waters become mixed with water, which is released from the dehydrated clay minerals, for example, illitized smectite. Thermodynamic conditions required for the activation of this process correspond, in general, to the initial stage and main phase of oil generation. Therefore, the slightly mineralized water released from smectites become enriched with the dissolved forms of  $\text{CO}_2$ , which represent a byproduct of organic matter transformation. Carbonic acid is neutralized by the alkaline metal ions absorbed by clays, which results in the formation of soda waters.

It should be admitted that the available data provide no grounds for strict discrimination between these two mixing types. For example, in some situations, relationships between  $[\text{HCO}_3^-]-\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}(\text{HCO}_3^-)-\delta^{18}\text{O}$ , and  $[\text{HCO}_3^-]-t(\text{Mg}-\text{Li})$  (Figs. 7, 10, 12) can be explained by the "mechanical" mixing (calculated data are shown by a dashed line). In these figures, the lines are located near the correlation trend or are visually perceived as such. However, mixing lines in other diagrams (Figs. 3, 8, 9, 11) are poorly consistent with the observed trends:  $[\text{HCO}_3^-]-[\text{Cl}^-]$ ,  $[\text{Cl}^-]-\delta^{18}\text{O}(\text{H}_2\text{O})$ ,  $[\text{HCO}_3^-]-\delta^{13}\text{C}(\text{HCO}_3^-)$ , and  $t(\text{Mg}-\text{Li})-\delta^{13}\text{C}(\text{HCO}_3^-)$ . Such inconsistencies in configurations of the statistically substantiated trends and mixing lines imply more complex mechanisms responsible for the formation of mud volcanic waters, which cannot be described by the model of simple (mechanical) two-component mixing. This can be related to nonuniform processes of the  $\text{CO}_2$  release to interstitial waters. These processes depend on the temperatures and  $C_{\text{org}}$  concentrations in sediments or the mixing of waters from more than two aquifer complexes.

As a whole, it is possible to unambiguously state that regardless of mechanisms responsible for the formation of mud volcanic waters in Azerbaijan, at least two extreme members can be defined among them. The first (high-temperature) member is represented by soda waters with abnormally high  $\delta^{13}\text{C}(\text{HCO}_3^-)$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  values. The second (relatively low-temperature) member is characterized by waters of the chloride type with low  $[\text{HCO}_3^-]$  concentrations and lowered  $\delta^{13}\text{C}(\text{HCO}_3^-)$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  values. The simple mechanical mixing of these waters provides no universal explanation for geochemical properties of waters of

the intermediate composition. Therefore, we assume that the formation of mud volcanic waters is mostly determined by processes against the background of sedimentary cycle with the transformation of mineral and organic matter in a partly or completely closed (elision) system. In our opinion, precisely this process reflects the temperature-dependent evolution of the chemical and isotopic composition of formation waters at the early catagenesis stage.

## CONCLUSIONS

The presented data on mud volcanic waters of Azerbaijan allow the following inferences.

(1) Two main water types are definable in the mud volcanic systems of Azerbaijan:  $\text{HCO}_3^-$ -Na waters with mineralization of 8–15 mg/L and Cl-Na waters with mineralization up to ~80 mg/L. Waters of the second type are largely developed in the Kura region and adjacent areas of the Shemakha-Gobstan and Absheron regions.

(2) According to Mg-Li geothermometer data, the formation of mud volcanic waters in Azerbaijan proceeds at temperatures ranging from ~20 to ~140°C. These estimates are practically identical to fluid generation temperatures obtained for other mud volcanic regions of the Caucasus domain (Taman and eastern Georgia). Such a similarity implies the unity of thermodynamic environments of mud volcanism development.

(3) Distribution of fluid generation temperatures demonstrates a spatially regular pattern: they increase toward the Greater Caucasus orogen. For example, average fluid generation temperatures estimated for mud volcanoes of the Kura region ( $t_{\text{av}}(\text{Mg}-\text{Li}) = \sim 40^\circ\text{C}$ ) are notably lower than the values obtained for the Shemakha-Gobustan (68°C) and Absheron (63°C) regions. Therefore, it can be assumed that such zonality is characteristic of the entire domain under consideration.

(4) Proceeding from average values of thermal gradients in different areas of Azerbaijan, depths of the water formation are estimated to be ranging from ~1 to 6.0–7.5 km. Inasmuch as thermal gradients in the Kura region are characterized by lowered values, differences in the location of volcanic "roots" in the latter region, relative to other regions of Azerbaijan, appear to be less contrasting than their fluid generation temperatures.

(5) New data on the isotopic composition of mud volcanic waters ( $\delta\text{D} = -32$  to  $-32 \dots -12\text{‰}$ ,  $\delta^{18}\text{O} = -0.6$  to  $+10.4\text{‰}$ ) show that "soda" waters are generally characterized by higher  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values as compared with chloride waters. It has been established that the  $\Delta\delta^{18}\text{O}$  value ("oxygen" shift) depends on the fluid generation temperature, which allows this parameter to correlate with water interaction in the water-rock system.

(6) Investigation of the carbon isotope composition in the dissolved forms of CO<sub>2</sub> revealed that the  $\delta^{13}\text{C}(\text{HCO}_3^-)$  values vary from  $-12.9$  to  $+37.3\text{‰}$  ( $\delta^{13}\text{C}_{\text{av}} = +20.1\text{‰}$ ,  $n = 41$ ) increasing with the growth of HCO<sub>3</sub><sup>-</sup> concentrations, (B, Li, Na, K, Rb, Br/Cl values,  $\delta^{18}\text{O}$  values, and formation temperatures estimated by the hydrochemical geothermometers. All these data suggest that genesis of the isotopically heavy CO<sub>2</sub> is related to the transformation of organic and mineral matter, which proceeds at early stages of the main oil generation phase and depend on the thermal conditions of fluid generation.

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