

# Isotopic Composition of Oxygen and Hydrogen in Mud-Volcanic Waters from Taman (Russia) and Kakhetia (Eastern Georgia)

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**Abstract**—The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in mud-volcanic waters of the Taman Peninsula and Kakhetia vary from +0.7 to +10.0‰ and from –37 to –13‰, respectively. These values increase as the Greater Caucasus is approached. The increase in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  also positively correlates with fluid generation temperatures based on hydrochemical geothermometers. This is accompanied by changes in the chemical composition of waters, in which contents of alkali metals,  $\text{HCO}_3^-$  ion, and boron increase, while the content of halogen ions (Cl, Br, J) decreases. Changes in the isotopic composition of water are also accompanied by the increase of  $\delta^{13}\text{C}$  in methane and decrease of  $\delta^{11}\text{B}$  in clays. Analysis of formal models of the evolution of isotopic composition of mud-volcanic waters showed that mud volcanoes are recharged by freshened water from the Maikop paleobasin with an inferred isotopic composition of  $\delta\text{D} \approx -40\text{‰}$  and  $\delta^{18}\text{O} \approx -6\text{‰}$ . Based on this assumption, the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values observed in mud-volcanic waters can be explained not only by processes of distillation and condensation in a closed system, but also by combined processes of isotopic reequilibration in the water–illite–methane system.

The aim of this work is to study the origination and source of water in mud volcanoes of the Kerch–Taman region using oxygen and hydrogen isotopic geochemistry. Such investigations are of great importance because of ambiguity in the existing concepts of the origin of mud volcanism. Isotopic–geochemical data ( $^3\text{He}/^4\text{He}$ ,  $^{40}\text{Ar}/^{36}\text{Ar}$ ,  $\delta^{13}\text{C}$  ( $\text{CH}_4$  and  $\text{CO}_2$ ), and  $\delta^{11}\text{B}$ ) on gas and mineral products of mud volcanism are available for this region (Lavrushin *et al.*, 1996, 1998, 2003). Nevertheless, some genetic problems still remain unclear. For example, there is still no agreement on the origination of diluted clay at depths of 1–2 km or more, as well as the formation of rootless diapir folds and zones with anomalously high formation pressure (AHFP) that are typical of mud-volcanic areas.

The currently existing main viewpoints on the origination of mud volcanoes are as follows (Kholodov, 2002; Kopf, 2002).

(1) Mud volcanoes are genetically related to the present-day magma chambers. Their channels serve as conduits for the discharge of the deep-seated juvenile matter (Kovalevskii, 1940; Valyaev *et al.*, 1985).

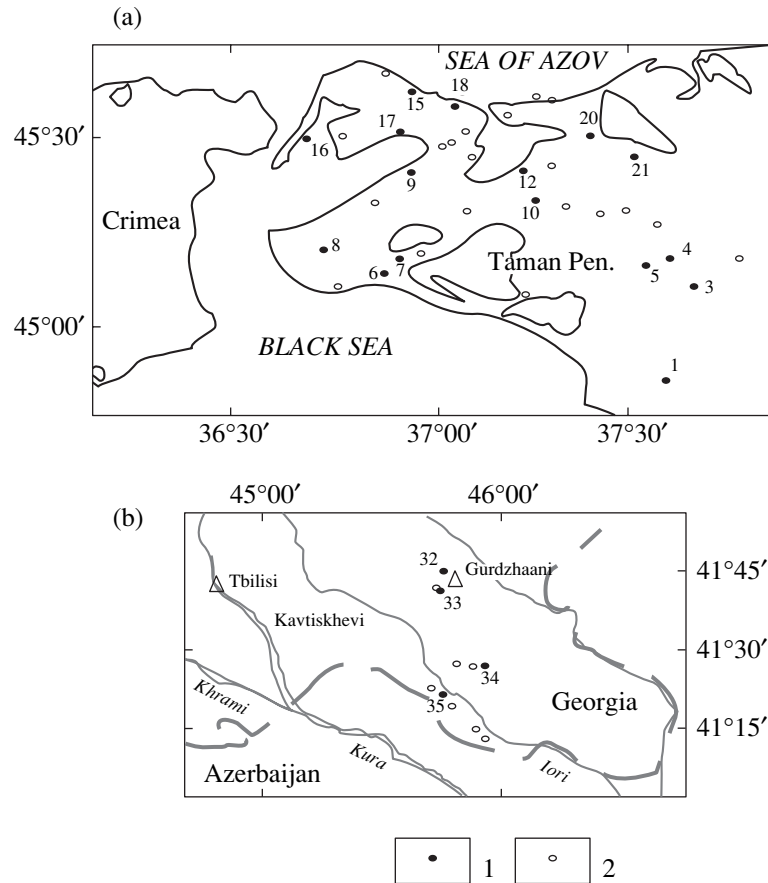
(2) Mud volcanism develops in accretionary structures under the collisional setting. Intense release of gas–water fluids from the kilometer-scale sedimentary

sequence under such conditions provokes mud volcanism. Mud volcanoes of the Barbados and Mediterranean accretionary prisms are the most prominent examples (Kopf, 2002).

(3) Mud volcanism is genetically related to the synthesis and migration of hydrocarbons (methane and oils) in the sedimentary cover of young basins (Gubkin and Fedorov, 1938). The breakdown of caps and outflow of methane along the faults fosters the emanation of liquid and solid products from upper portions of the section (gaseous volcanism).

(4) Mud volcanism and the associated formation of diapir folds and AHFP zones are initiated by elision during postsedimentary transformations (Kholodov, 2002). Of great importance are the recrystallization of smectite into hydromica and the consequent unconsolidation of clayey rocks. Under lithostatic pressure, the rocks are subsequently consolidated and pressure is partially transferred to interstitial waters, resulting in the development of AHFP zones. This mechanism explains the formation of rootless diapir folds.

(5) Since mud volcanism is typical of the Alpine molasse basins with high sedimentation rates (Braunstein and O’Brien, 1968), we assume a high possibility of the burial of unconsolidated fine-dispersed clayey



**Fig. 1.** Location scheme of (1) sampled and (2) unsampled mud volcanoes on the (a) Taman Peninsula and (b) eastern Georgia. Sample numbers are as in the first column of the table.

mass with a high content of pore water. The increase in lithostatic pressure and recrystallization of clay minerals in the cores of such structures can foster the formation of AHFP zones and rootless diapir folds and the emanation of water and clay to the surface.

The He isotopic composition in gases suggests that mud volcanoes occur not only in regions with the manifestation of mantle activity (Yakubov *et al.*, 1980; Lavrushin *et al.*, 1996). Therefore, the genetic relation between magmatism and mud volcanism is debatable. Other hypotheses are reduced to different mechanisms of water redistribution during lithogenesis. It is evident that geological processes (recrystallization and/or dehydration of clay minerals, synthesis of hydrocarbons, release of water during rock compaction, and others) used as the basis for most hypotheses can differently affect the chemical and isotopic ( $\delta D$  and  $\delta^{18}O$ ) compositions of pore solutions. In addition, the isotopic composition in mud-volcanic systems should also be affected by evaporation and condensation.

We attempted to decipher the formation mechanisms of mud volcanism using isotopic parameters of waters from mud volcanoes of Taman and Kakheta. Isotopic parameters of the major elements (oxygen and

hydrogen), which compose the aqueous phase of mud-volcanic products, may yield important information, since the water phase plays a key role in all the hypotheses listed above.

## MATERIALS AND METHODS

Systematic isotopic investigations of mud-volcanic waters of the Taman Peninsula and Kakheta have not been performed so far. The fragmentary data available for these regions are given for comparison with our results in the table.

The present communication is based on samples taken from mud volcanoes of the Taman Peninsula in 1994, 1997, and 2001. The isotopic composition of water was studied for 16 volcanoes of the Taman Peninsula in Russia and 4 mud volcanoes of Kakheta in Georgia (Fig. 1, table). The samples were stored in hermetic plastic containers before the performance of isotopic and chemical investigations. Thus, oxygen and hydrogen isotopic compositions were analyzed in the same samples that were previously used for studying hydrochemistry and isotopy of associated gas and solid phases (Lavrushin *et al.*, 2003).

Isotopic composition of mud-volcanic waters of the Taman Peninsula and Kakhelia

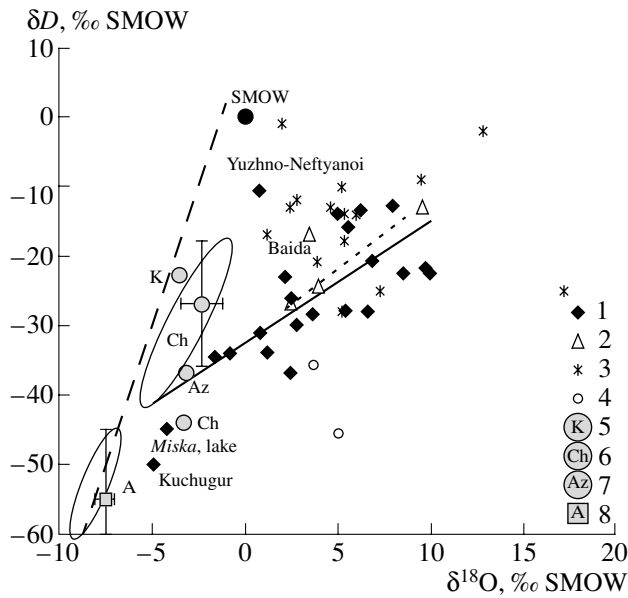
Number in Fig. 1	Sample no.	Mud volcanoes	Sampling year	Coordinates		Altitude, m	$\delta^{18}\text{O}$ , ‰	$\delta\text{D}$ , ‰
				Latitude	Longitude			
Taman Peninsula, Russia								
1	47/01	Semigorskii	2001	44°54'04.0	37°35'52.2	71	+9.7	-21.9
3	–	Gladkovskii*	2000	45°00'20.2	37°43'25.4	131	+8.0	-13.0
3	48/01	Gladkovskii	2001	45°00'20.2	37°43'25.4	131	+6.2	-13.5
4	–	Shugo***	–	–	–	~130	+3.7	-45.0
4	49/01	Shugo	2001	45°04'14.1	37°36'37.5	148	+10.0	-22.5
5	50/01	Vostok	2001	45°01'42.1	37°35'08.2	172	+6.8	-20.8
6	51/01	Bugaz	2001	45°07'07.2	36°53'51.9	13	+8.5	-22.6
7	52/01	Polivadina	2001	45°07'47.2	36°55'16.3	47	+2.8	-29.9
8	53/01	Karabet	2001	45°11'42.8	36°46'08.3	104	+6.6	-28.0
9	54/01	Shapur	2001	45°16'09.3	36°57'45.2	54	+2.2	-23.2
10	55/01	Yuzhno-Neftyanoi	2001	45°11'21.8	37°11'00.7	64	+0.7	-10.8
12	20/94	Severo-Neftyanoi	1994	–	–	~60	+2.5	-26.4
15	57/01	Kuchugur	2001	45°25'56.3	36°55'21.1	10	-4.9	-50.1
15	01/94	Kuchugur	1994	45°25'56.2	36°55'21.1	15	+5.4	-27.9
16	58/01	Chushka	2001	45°21'14.9	36°42'49.7	4	+3.7	-28.4
17	59/01	Fontalovskii	2001	45°20'53.2	36°54'18.3	29	+0.8	-30.9
18	–	Golubitskii (Sinyaya Balka)*	2000	45°21'25.8	37°05'57.1	12	-0.8	-34.0
18	60/01	Sinyaya Balka	2001	45°21'25.8	37°05'57.1	12	-1.6	-34.5
20	62/01	Miska	2001	45°16'41.1	37°23'14.8	72	+1.2	-34.0
21	63/01	Gnilaya	2001	45°15'06.5	37°26'21.0	32	+2.4	-36.8
21	–	Gnilaya*	2000	–	–	~30	+5.0	-14.0
–	–	Shapsug*	2000	–	–	–	+5.6	-16.0
Eastern Georgia								
32	09/97	Akhtala	1997	–	–	–	+9.6	-12.9
33	02/97	Phoveli	1997	–	–	–	+3.9	-24.4
34	03/97	Kila-Kupra	1997	–	–	–	+2.5	-27.0
34	–	Kila-Kupra**	1985?	–	–	–	+2.0	-1.0
35	07/97	Baida	1997	–	–	–	+3.5	-16.9

Note: (\*) Data after (Nevinsky *et al.*, 2001); (\*\*) adopted from (Seletskii, 1991); (\*\*\*) adopted from (Polyakov *et al.*, 1973).

Hydrogen and oxygen isotopic compositions were measured on a DELTA<sup>plus</sup> Thermo Quest (Finnigan) mass spectrometer at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry. The  $\delta\text{D}$  value was determined using H/Device attachment by direct water decomposition on a hot (800°C) chromium powder. Reproducibility of replicate determinations was  $\pm 0.3\text{‰}$ . The  $\delta^{18}\text{O}$  value was determined by the express method of isotopic equilibration of water samples with  $\text{CO}_2$  at 25°C (Avdeenko and Dubinina, 2001). Reproducibility of replicate determinations of  $\delta^{18}\text{O}$  was  $\pm 0.2\text{‰}$ . Measurements were controlled by MAGATE standards OH-1, OH-2, OH-3, and OH-4.

The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values in the table are given relative to the SMOW.

According to previous investigations (Lavrushin *et al.*, 2003), the majority of studied water samples are ascribed to the hydrocarbonate–chloride sodium type. Volcanoes in Taman are depleted in the TDS content as compared to volcanoes in Kakhelia (10–22 and 20–32 g/l, respectively), indicating primary differences in the seawater composition of the Indol–Kuban and Kura basins. Mud-volcanic waters are significantly enriched in alkalis, alkali-earth metals, B, I, and Br, contents of which positively correlate with the hydrocarbonate ion in most cases.



**Fig. 2.** Variations of  $\delta D$  and  $\delta^{18}O$  in mud-volcanic waters of (1) Taman (our data and Nevinsky *et al.*, 2001), (2) Georgia, (3) Azerbaijan (Esikov *et al.*, 1979; Seletskii *et al.*, 1991), (4) Turkmenistan (Seletskii *et al.*, 1973; Vetshtein, 1982), (5) Caspian Sea (Nikanorov *et al.*, 1981), (6) Black Sea, (7) Sea of Azov, and (8) atmospheric precipitation in the Black Sea–Azov region (Nikanorov *et al.*, 1981; Vetshtein, 1982; Nevinsky *et al.*, 2001). Solid line shows the general variation trend of isotopic characteristics of the Taman waters; dashed line, characteristics of Georgian mud volcanoes.

Mud-volcanic waters from the northern Taman Peninsula have a low Cl/Br coefficient ( $\sim 70$ ), which is typical of the residual brines of evaporite sequences. In southern parts of the peninsula, this coefficient increases to 140–270, approximating the value in seawater ( $\sim 300$ ). Despite significant variations in the Cl/Br coefficient, no sharp changes are observed in water salinity. Taking the biophile character of Br and I into consideration, one can suggest that mud-volcanic waters are enriched in these elements during oil-and-gas generation when Br is released from organic remnants in the sediments and transferred to the water-soluble form (Krasintseva, 1968).

On the whole, mud-volcanic and formation waters from the Tertiary molasse in the Indol–Kuban and Middle Kura sedimentary basins are similar with respect to the majority of hydrochemical characteristics. However, unlike the formation water, volcanic waters have a higher Mg/Ca coefficient (0.5–1.5) (Kollodii, 1971). This is presumably related to the formation of mud-volcanic waters in the AHFP zones, where pore waters are intensely expelled from clays. In particular, the Mg enrichment of water released from overpressured clays was repeatedly noted in experiment (Kryukov and Zhuchkova, 1962).

## RESULTS

The table and Figure 2 show that volcanic waters of the Taman Peninsula are characterized by a wide range of  $\delta D$  and  $\delta^{18}O$  values. For example, the  $\delta^{18}O$  value varies from +0.7 to +10.0‰, whereas the  $\delta D$  value ranges from  $-36.8$  to  $-10.8$ ‰. Hence, they are enriched in  $^{18}O$  and depleted in deuterium relative to the average oceanic water composition designated in Fig. 2 by “SMOW” with coordinates (0; 0).

However, some samples have anomalous isotopic parameters. For example, sample taken in 2001 from the lateral salse of the Kuchugur Volcano has the lowest  $\delta^{18}O$  ( $-4.9$ ‰) and  $\delta D$  ( $-50.1$ ‰) values. This sample also shows extremely high sulfate ion content (8080 mg/l), which is atypical of mud-volcanic waters (generally, less than 200 mg/l). Presumably, this water has subsurface origin and contains a significant admixture of groundwater. Water sampled in 1994 from the central salse of the same volcano has a significantly heavier oxygen isotopic composition ( $\delta^{18}O = +5.4$ ;  $\delta D = -27.9$ ‰). This water compositionally fits the majority of studied samples, but it has a significantly lower  $SO_4^{2-}$  content (156 mg/l). Thus, the chemical and isotopic compositions of water sample taken in 2001 from the lateral salse of the Kuchugur Volcano are atypical of volcanoes of the Taman region. In addition, the obtained isotopic parameters of the water from Sinyaya Balka Volcano ( $\delta^{18}O = -1.6$ ;  $\delta D = -34.5$ ‰) should be treated with caution, since fresh water was delivered to the mud lake coast of this volcano in 2001. This could cause the decrease in D and  $^{18}O$  contents in the studied sample.

The  $\delta^{18}O$ – $\delta D$  diagram (Fig. 2) also demonstrates that data points of the Yuzhno-Neftyanoi Volcano (Taman) and Baida Volcano (Kakhetia) are plotted slightly above the main data points. These waters have the lowest TDS content (0.3–0.6 and 5.4 g/l, respectively), which is considerably lower than the average TDS content in mud-volcanic waters of Taman ( $\sim 16$  g/l) and Georgia ( $\sim 28$  g/l). This indicates the contribution of condensation waters, which formed from vapor during the adiabatic expansion of gas (e.g., methane). The discovery of such waters may indicate the existence of two-phase gas–water system, i.e., methane pool, at a depth. Data point of the Gladkovskii Volcano (Taman) is also located above the main group in Fig. 2. However, unlike samples from the Yuzhno-Neftyanoi and Baida volcanoes, this water has a high TDS content ( $\sim 20$  g/l) and different chemical composition. Samples from the Gladkovskii Volcano represent a unique case of the emanation of chloride–sodium–calcium waters strongly enriched in Li, K, Rb, Cs, and Sr from the Taman mud volcanoes. The origin of these waters is possibly related to the contribution of chloride–calcium brines from the Jurassic–Cretaceous aquifers.

As compared to other regions with abundant mud-volcanic activity (Azerbaijan and Turkmenistan),

waters from the Taman volcanoes show the least scatter of data points in the  $\delta^{18}\text{O}$ – $\delta\text{D}$  diagram (Fig. 2). They are distinguished from the Azerbaijan volcanoes by lower  $\delta\text{D}$  values. Relative to mud-volcanic waters from western Turkmenia, data points of the Taman water are shifted to the higher  $\delta\text{D}$  and  $\delta^{18}\text{O}$  regions. It is interesting that isotopic compositions of the majority of samples from Georgian mud volcanoes are identical to those of Taman volcanoes. Sample from the Kila-Kupra Volcano strongly differs in  $\delta\text{D}$  from other volcanoes ( $\delta\text{D} = -1.0\text{‰}$ ;  $\delta^{18}\text{O} = +2.0\text{‰}$ ) (Seletskii, 1991). However, our data on this volcano show significantly lower  $\delta\text{D}$  values and an approximately similar oxygen isotopic composition (table). Like in the Kuchugur Volcano, such isotopic variations of waters taken in different years indicate that heterogeneous data may be obtained during the study of some volcanoes on the Taman Peninsula (e.g., Gniloi and Shugo). This conclusion is based on the previously noted differences in the chemical composition of waters (Shnyukov *et al.*, 1986) taken from different salses of these volcanoes.

## DISCUSSION

Isotopic composition of the Taman mud-volcanic waters exhibits spatial variations. The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values increase near the Greater Caucasus. For example, waters from volcanoes located near the Azov Sea coast (Gnilaya, Miska, Chushka, Sinyaya Balka, Kuchugur) have lower  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values than those from volcanoes of the Caucasian foothills (Shugo, Semigorskii, Gladkovskii, Vostok, and Bugaz) (table). A similar trend is observed in Kakhetia, where  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values range from  $-27$  to  $-13$  and from  $+2.5$  to  $+9.6\text{‰}$ , respectively. Like in Taman, the isotopic composition of these waters becomes heavier near the Greater Caucasus. The general trend is disturbed only by the Baida Volcano sample. The low TDS content ( $5.4\text{ g/l}$ ) indicates that this water is probably related to condensation (Lavrushin *et al.*, 2003).

The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values demonstrate a similar correlation in waters of the Taman and Georgian mud volcanoes (Fig. 2). This may indicate a common formation mechanism. However, some waters in Kakhetia have a higher TDS content (up to  $32\text{ g/l}$ ) than those in Taman. Together with data on  $\delta^{11}\text{B}$  in water (Lavrushin *et al.*, 2003), the fact mentioned above suggests that Georgian mud volcanoes were supplied with saline waters from closed basins. In addition, products of Georgian mud volcanoes differ in phase and chemical compositions of clay fractions. They formed under the influence of tectonic stress and high mantle activity. This is recorded by the  $^3\text{He}/^4\text{He}$  value (up to  $220 \times 10^{-8}$ ) in spontaneous gases (Yakubov *et al.*, 1980; Lavrushin *et al.*, 1996, 1998). However, despite the differences mentioned above, waters from both regions show a similar variation trend of  $\delta\text{D}$  and  $\delta^{18}\text{O}$ . Isotopic composition of waters from mud volcanoes in Taman and Georgia is

presumably governed by a single process and does not depend on regional conditions of their formation.

### *Relations between Chemical and Isotopic Compositions of Waters*

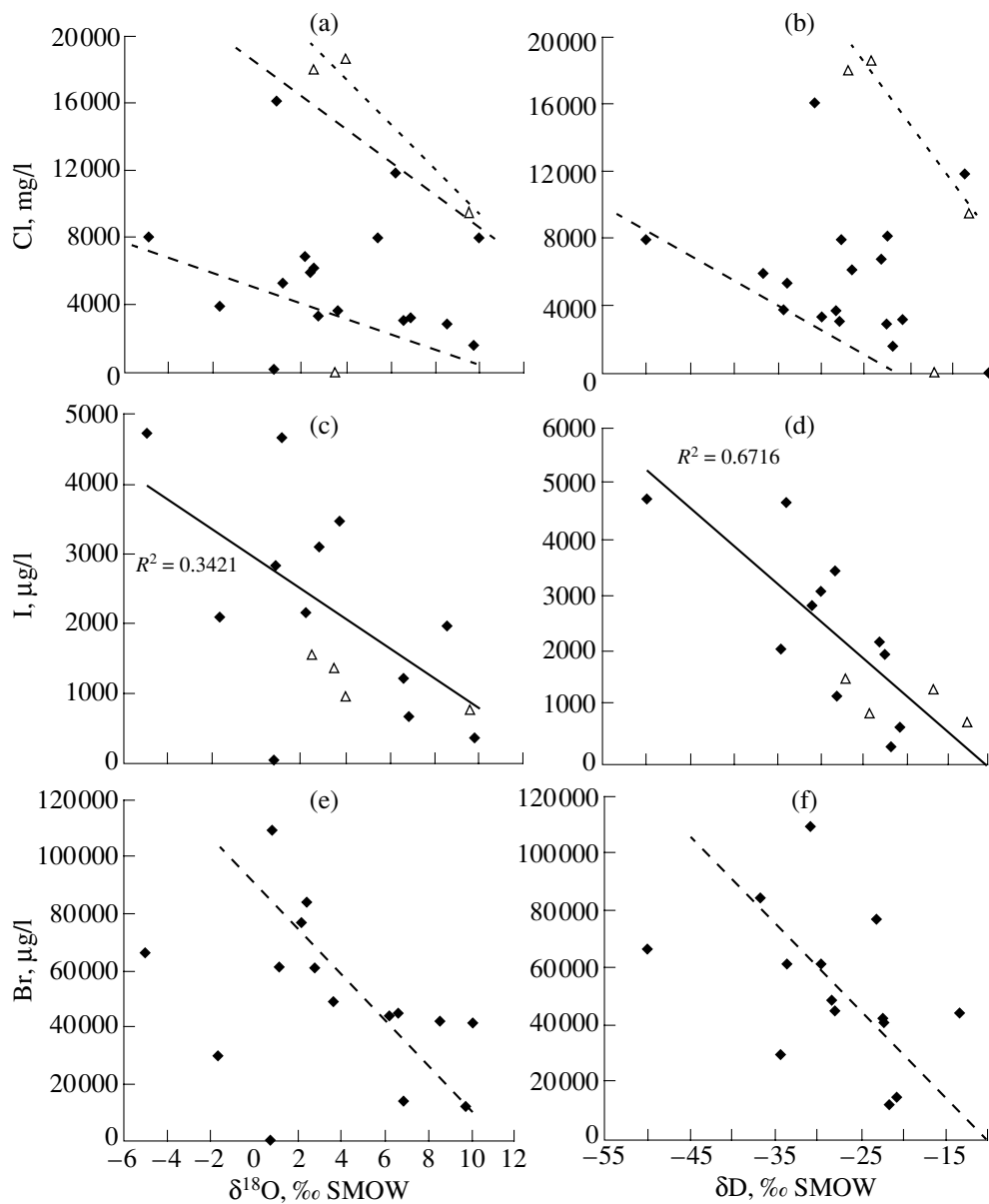
Comparison of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values with the chemical composition of waters determined in the same samples (Lavrushin *et al.*, 2003) shows that  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values inversely correlate with the contents of Cl, Br, and I ions (Fig. 3). In contrast, the contents of hydrocarbonate ion and boron positively correlate with the isotopic composition (Fig. 4). As a result, changes in the water composition from the sodium chloride to sodium hydrocarbonate–chloride type is accompanied by enrichment of water in deuterium and  $^{18}\text{O}$ . Against the background of increase in the dissolved  $\text{HCO}_3^-$  content, mud-volcanic systems show decrease in the contents of Cl, Br, and I ions, which are most stable in the solution, indicating the dilution of sodium chloride waters by the isotopically heavy waters of sodium ( $\text{HCO}_3^-$ –Na) type.

Therefore, it is also reasonable to examine the correlation of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  with ion contents normalized to Cl and Na ions. This allows the direct correlation of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  with normalized contents of most alkali and alkali-earth metals.

The normalized contents of some metals (Li/Na, K/Na, and Mg/Na) correlate with temperature conditions of interaction between groundwaters and rock-forming minerals. Therefore, they are used as geothermometers for the reconstruction of stratal temperatures of groundwater formation (Fournier and Truesdell, 1974; Fournier and Potter, 1979; Fouillac and Michard, 1981; Kharaka and Mariner, 1989). For isotopic analysis, we used the same samples as for temperature calculation (Lavrushin *et al.*, 2003). Comparison of calculated temperatures with  $\delta^{18}\text{O}$  and  $\delta\text{D}$  (Fig. 5) shows that the isotopic composition of water correlates with temperature. The obtained temperature interval ( $45$ – $170^\circ\text{C}$ ) corresponds to a depth of  $1$ – $4.5\text{ km}$ , while the change in isotopic composition, presumably, reflects the evolution of water–gas fluids at different stages of postsedimentary transformations. Similar increase in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  with depth is noted for formation waters of Northern Caucasus (Fedorov, 1989).

### *Isotopic Composition and Behavior of Isotopic Characteristics of Gaseous and Solid Phases*

Many isotopic–geochemical parameters of mud-volcanic systems correlate with each other and calculated temperatures. For example, correlation between carbon isotopic composition in gases and  $\delta^{11}\text{B}$  in clayey pulp was found for volcanoes in Taman and Georgia (Lavrushin *et al.*, 2003). The distribution of these parameters also demonstrates spatial zoning, suggesting that the isotopic composition of water (prima-



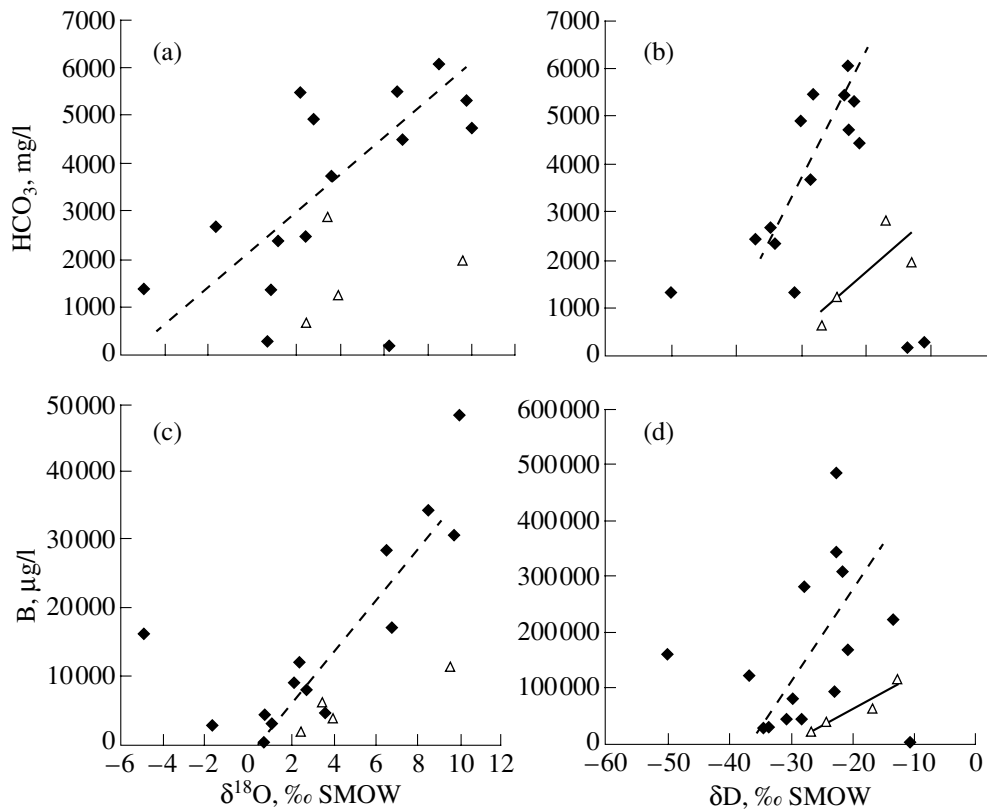
**Fig. 3.** Variations of  $\delta D$  and  $\delta^{18}O$  vs. contents of (a, b) Cl, (c, d) I, and (e, f) Br ions in waters of the Taman and Georgian mud volcanoes. Symbols are as in Fig. 2. Solid lines show proved trends; dashed lines, inferred trends.

rily,  $\delta^{18}O$ ) correlates with temperature-dependent characteristics of mud-volcanic emanations (including  $\delta^{13}C$  in gases and  $\delta^{11}B$  in clay).

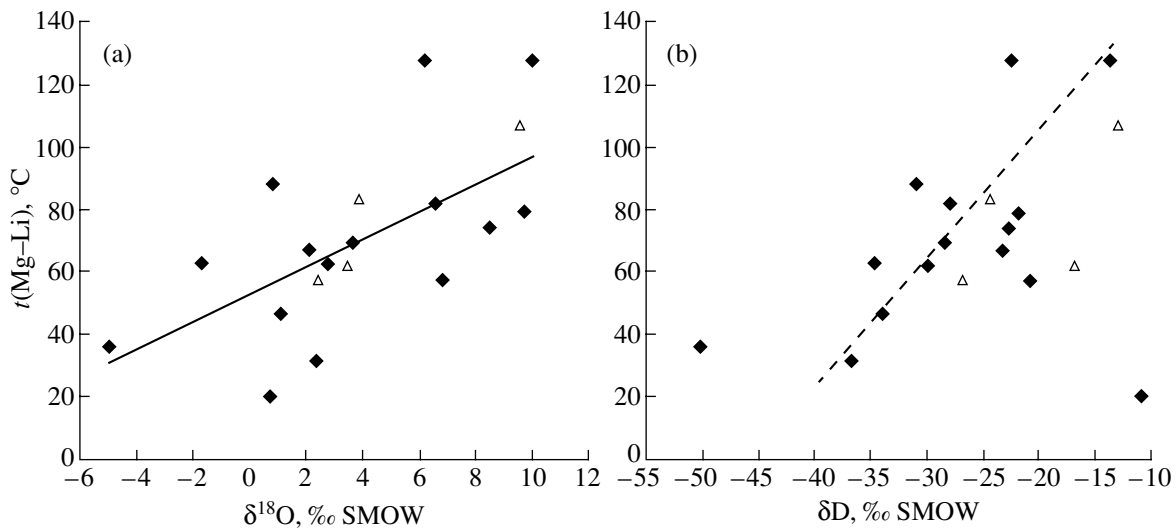
Our investigations of the isotopic composition of water supported this hypothesis. Negative correlation between  $\delta^{11}B$  and isotopic composition of water (Figs. 6a, 6b) indicates that the concentration of boron in pore waters (Fig. 4c, 4d) and their simultaneous depletion in  $\delta^{11}B$  correlate with the increase in  $\delta D$  and  $\delta^{18}O$ . Such geochemical features of boron in lithogenesis are typically related to changes in temperature conditions of the water–rock interaction and illitization of smectite (Williams *et al.*, 2001; Kopf, 2002).

The  $\delta^{13}C$  ( $CH_4$  and  $CO_2$ ) value in gases significantly varies with time and space. The variation is observed even in samples simultaneously taken from the adjacent salses (Gemp *et al.*, 1970; Valyaev *et al.*, 1985; Voitov, 2001). Therefore, we used the average  $\delta^{13}C$  value for each volcano in comparisons with the isotopic composition of water. The results show that  $\delta D$  and  $\delta^{18}O$  correlate only with  $\delta^{13}C$  ( $CH_4$ ) (Figs. 6c, 6d). This relationship evidently corresponds to the positive correlation of the heavy carbon isotope in methane with the temperature (and depth) of fluid generation (Galimov, 1968; Prasolov, 1990).

Thus, correlation of different isotopic–geochemical parameters of mud-volcanic (solid, liquid, and gaseous)



**Fig. 4.** Variations of  $\delta D$  and  $\delta^{18}O$  vs. contents of (a, b)  $HCO_3$  and (c, d) boron in waters of the Taman and Georgian mud volcanoes. Symbols are as in Fig. 2. Solid lines show proved trends; dashed lines, inferred trends.

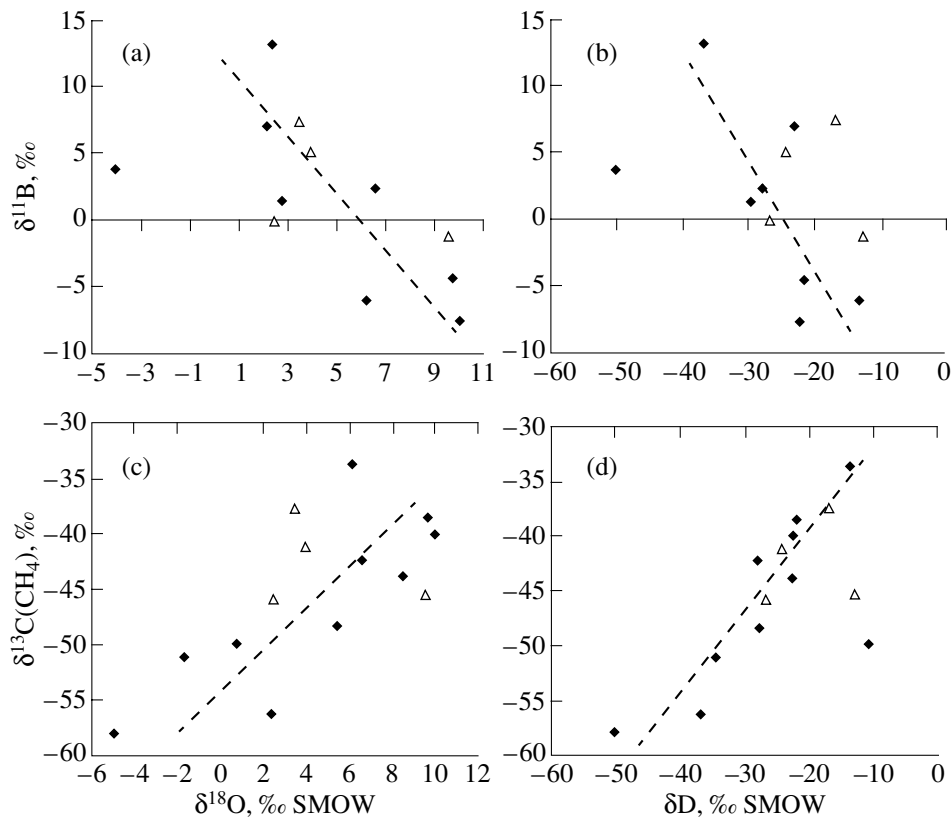


**Fig. 5.** Variations of water isotopic composition vs. temperature calculated from hydrochemical Mg–Li geothermometer for waters of the Taman and Georgian mud volcanoes (Lavrushin *et al.*, 2003). Symbols are as in Fig. 2.

emanations shows that the concentration of heavy isotopes in water is a temperature-dependent process, which presumably accompanies the transformation of organic and mineral matter at different stages of lithogenesis.

#### *Isotopic Aspect of the Formation of Mud-Volcanic Waters*

Isotopic parameters of mud-volcanic waters are governed by evolution of the primary water composi-



**Fig. 6.** Variations of water isotopic composition vs. (a, b)  $\delta^{11}\text{B}$  in clays and (c, d)  $\delta^{13}\text{C}$  in methane in mud-volcanic products of Taman and Georgia. Symbols are as in Fig. 2.

tion in the course of a wide range of phenomena that are possible in a certain geological setting. Mixing with waters of different genesis, isotopic exchange with aquiferous rocks, evaporation, and condensation are the major processes that can shift the initial isotopic composition of waters. The role of these mechanisms in the isotopic composition of mud-volcanic waters is the subject for further discussion.

The concept of primary isotopic composition of seawater, which evidently can be taken as starting point in the subsequent evolution of isotopic ratios, is very important for the subsequent reconstructions. We believe that almost all mud volcanoes of the Taman Peninsula (except the Gladkovskii Volcano) are recharged by waters from the Maikop Group rocks (Oligocene–Early Miocene molasses) located at depths ranging from 1 to ~5 km. This hypothesis is based on stratal temperature estimates obtained with the application of hydrochemical geothermometers (Lavrushin *et al.*, 2003) and is confirmed by the comparison of chemical compositions of mud-volcanic and formation waters (Yakubov *et al.*, 1980; Shnyukov *et al.*, 1986).

Although the initial isotopic composition of seawater of the Maikop paleobasin (Paratethys) is unknown, this composition can be inferred on the basis of assumptions accepted for a specific mechanism of

water formation. The trend observed on the  $\delta^{18}\text{O}$ – $\delta\text{D}$  diagram as a result of the isotopic evolution of primary waters can be induced by four mechanism models, which are described below together with comments that summarize arguments for and against.

**(1) Two-stage exchange–mixing of metamorphosed oceanic and infiltration waters.** This mechanism assumes that isotopic composition of water from the Maikop Basin corresponded to that of recent oceanic water (SMOW). In this case, the observed trend in the  $\delta^{18}\text{O}$ – $\delta\text{D}$  diagram can be explained by the postsedimentary interaction of buried waters with mineral matter (first stage) and the subsequent dilution by meteoric infiltration waters (second stage). Thus, the isotopic oxygen exchange of formation waters with the ambient silicate minerals first leads to the increase in  $\delta^{18}\text{O}$  without significant changes in  $\delta\text{D}$ . The subsequent mixing with isotopically light meteoric waters can produce  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values observed in mud-volcanic waters.

*Comment.* Judging from temperature parameters of mud-volcanic systems, illitization of smectite is the most probable process leading to increase of  $\delta^{18}\text{O}$  in water during lithogenesis. The smectite–illite transformation is accompanied by an intense (2–10 times) decrease in the ion-exchange capacity of rocks (Popov and Abdrakhmanov, 1990), resulting in the release of a



significant amount of low-salinity (interlayer and loosely bonded) water enriched in desorption-related alkali metals and boron into the pore space. Correspondingly, illitization of smectite should increase the trace component content in pore waters and decrease the content of relatively inert components of water solution (Na, Cl, and Br). These processes occur parallel to the enrichment of water in  $\delta^{18}\text{O}$ .

Indeed, mud-volcanic waters with the highest  $\delta^{18}\text{O}$  values are enriched in alkali metals and boron (Figs. 4c, 4d). However, the model of a significantly lower salinity of infiltration waters relative to sedimentation waters is refuted by the negative correlation of the isotopic composition of water with the content of dissolved halogens (Cl, Br, I) (Fig. 3). In this case, the addition of isotopically light meteoric should have decreased both salt contents and isotope ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ ) values.

Thus, the first model can be valid only if the isotopically light infiltration (meteoric) water has a higher TDS content than the isotopically heavy (formation) water. Admittedly, such a probability cannot be completely excluded. Like in other areas of the Caucasian–Caspian (southern Caspian) region, Tertiary (Neogene–Paleogene) sediments in Taman are characterized by hydrochemical inversion<sup>1</sup> (Kollodii, 1971; Shnyukov *et al.*, 1986). Therefore, infiltration waters in upper portions of the section can be significantly enriched in salts.

Such an explanation of the isotopic composition of mud-volcanic waters is based on the assumption that waters of the Maikop Basin had the SMOW-type composition. However, this hypothesis is poorly consistent with paleogeographic features of the Maikop marine basin and requires evidence. The faunal study of Maikop sediments shows that this basin occasionally contained organisms adapted to vital activity in the low-salinity waters (Zhishchenko, 1969). Recent waters of the Black and Caspian seas, which can conditionally be considered counterparts of marine basins of final stages of the Paratethys, also strongly differ from the SMOW (Fig. 2). Therefore, we have little confidence that the isotopic composition of ancient marine basin corresponded to that of recent oceanic waters.

The first model is also weakly consistent with spatial zoning in the isotopic characteristics of mud-volcanic waters mentioned above (increase in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  toward the Greater Caucasus). The Greater Caucasus serves as a regional provenance for the majority of aquifers in sedimentary basins of Cis-Caucasia. According to the first model, the contribution of infiltration waters in mud volcanoes should increase as the Greater Caucasus is approached. Therefore, it is more

reasonable to expect the opposite isotopic zoning, i.e., decrease in the content of heavy oxygen isotopes near the Greater Caucasus. Probably, the mixing with meteoric infiltration water has a subordinate or local significance as compared to other process affecting the isotopic composition of water.

Thus, the two-stage formation of the isotopic composition of mud-volcanic waters has several discrepancies with the available geological and chemical data.

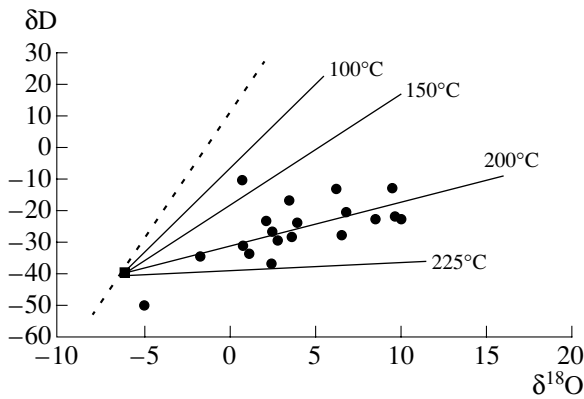
**(2) Direct mixing of seawater and isotopically heavy source.** In this model, isotopic composition of the initial seawater is significantly depleted in D and  $^{18}\text{O}$  relative to the SMOW. Hence, the trend of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  variations can be obtained by the mixing of isotopically light water of paleobasin and isotopically heavy water of a different origin, e.g., water from underlying Jurassic–Cretaceous Maikop beds.

*Comment.* As mentioned above, salinity of the Maikop paleobasin (correspondingly, isotopic composition of water) significantly changed with time. However, isotopic shifts caused by salinity change should be expressed in compositional variations along the meteoric water line in the  $\delta^{18}\text{O}$ – $\delta\text{D}$  diagram. It is assumed that the position of the ancient meteoric water line was similar to that of the recent one in the  $\delta^{18}\text{O}$ – $\delta\text{D}$  diagram (Sheppard, 1986). Therefore, extrapolation of the trend obtained to the meteoric water line may yield the required initial values of  $\delta\text{D}$  ( $\approx -40\text{‰}$ ) and  $\delta^{18}\text{O}$  ( $\approx -6\text{‰}$ ) for waters of the Maikop paleobasin. Seawater with such isotopic characteristics should be appreciably freshened.<sup>2</sup> At present, similar  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values are occasionally observed in the coastal zone of the Black Sea (Nikanorov *et al.*, 1981).

The hypothesis of mixing of mud-volcanic waters with deep brines (Kurishko *et al.*, 1968) was proposed to explain the high Mg content in mud-volcanic waters relative to that in sodium–calcium hydrocarbonate–chloride formation waters of the Maikop sediments. It was suggested that they are recharged by brines with high Na and Mg contents. However, waters of such composition are subordinate in the Cis-Caucasus. The Jurassic–Cretaceous complexes typically contain sodium–calcium chloride brines with a TDS content of  $\sim 100$ – $200$  g/l (Kurbanov, 2001). They enriched in  $\delta^{18}\text{O}$  (up to  $+9.5\text{‰}$ ) and depleted in  $\delta\text{D}$  (from  $-67$  to  $-32\text{‰}$ ). The mixing of such water with that of the Maikop paleobasin should increase the  $\delta^{18}\text{O}$  value, but the  $\delta\text{D}$  value should remain almost constant. This is not observed in reality (Fig. 2). In addition, such process should be accompanied by increase in the TDS content owing to the input of Na, Cl, and B. This is not also observed.

<sup>1</sup> Hydrochemical inversion is referred to as the unusual change in formation water salinity in the geological section. The TDS content generally increases downward the section. This rule is not observed during hydrochemical inversion and lower portions of the section can contain waters with a lower TDS content than the upper ones.

<sup>2</sup> In this case, the relatively low TDS content in mud-volcanic waters of the Taman Peninsula (14–15 g/l, on the average) and the hydrochemical inversion zone noted in aquifers of the Maikop beds (Kollodii, 1971) can be related not only to water redistribution in the water–rock or water–vapor system, but also to inheritance of the geochemical signature from the freshened paleobasin.



**Fig. 7.** Temperature evolution of isotopic parameters of water according to the Rayleigh distillation–condensation model. Dashed line shows the meteoric water line; solid line, the calculated variation curves of water isotopic composition during distillation and condensation at different temperatures.

Thus, the mixing of freshened seawaters with isotopically heavy waters from deep horizons cannot be invoked as an independent process to explain the isotopic composition of mud-volcanic waters.

**(3) Evolution of the isotopic composition of waters during evaporation and condensation.** This model is based on the assumption that mud-volcanic waters originate and migrate in the two-phase gas–water system. Under high *PT* conditions, the interphase redistribution of isotopically replaced molecules must provoke shifts in the isotopic water system. However, mechanisms of these processes can be different. Under natural conditions, both the equilibrium (distillation–condensation) process, which is mainly typical of open systems, and the Rayleigh process (distillation–condensation), which is typical of pseudoopen or completely closed systems, may be realized.

In the case of equilibrium evaporation, both vapor and condensate yield a curve with slope identical to that of meteoric water line in the  $\delta^{18}\text{O}$ – $\delta\text{D}$  diagram at temperatures up to the critical water point (Majoube, 1971; Horita and Wesolowski, 1994). However, this variant is not suitable for explaining the compositions of mud-volcanic waters of Taman and Georgia, which yield a sharply different trend relative to the slope of the meteoric water line. Therefore, it is reasonable to consider only the Rayleigh distillation–condensation model. Water compositions calculated from the corresponding evaporation–condensation equations (Hoefs, 2004; Horita and Wesolowski, 1994) form straight lines with a temperature-dependent slope (Fig. 7). In the given coordinates, data points of both residual liquid (related to distillation of the vapor phase) and condensate are plotted along the same straight line, indicating that waters subjected to distillation according to the above mechanism inherit the characteristic isotopic shifts regardless of their origin (distillate or condensate).

Figure 7 demonstrates the calculated compositional line of waters according to the Rayleigh distillation–condensation model with a slope identical to that of the compositional trend of mud-volcanic waters in Taman. The slope of this line corresponds to distillation–condensation at about 200°C in a pseudo-closed system (i.e., during distillation with vapor phase removal or condensation with condensate removal from the isotopic exchange zone). The inferred composition of waters of the Maikop paleobasin ( $\delta\text{D} \approx -40\text{‰}$  and  $\delta^{18}\text{O} \approx -6$ ) was taken as starting isotopic composition in this calculation.

*Comment.* Processes of evaporation and condensation are traditionally invoked to explain the isotopic composition of mud-volcanic waters (Esikov *et al.*, 1979; Esikov, 1995; Seletskii, 1991). Seletskii (1991) believed that the Rayleigh distillation plays a crucial role in the isotopic composition of mud volcanic waters of Azerbaijan. This conclusion was based on sharp difference of their isotopic composition from those of formation waters recovered by boreholes. However, it should be noted that such a comparison may not be correct universally, since boreholes sampled relatively shallow levels (rarely, more than 4 km), whereas roots of the Azerbaijan mud volcanoes can be located at a depth of 8 km or more (Rakhmanov, 1987; Kholodov, 2002).

Explanation of the isotopic composition of water proposed in the given model is consistent with records of volcanic activity in the form of constant (in some cases, catastrophic-scale) release of spontaneous gases. Dry gas jets and freshened (condensation) waters are often observed on volcanic hills. These observations suggest that mud-volcanic fluids originate and migrate in the two-phase (gas–water) system with the volume ratio of gaseous and liquid phases permanently varying during their movement along the mud-volcanic channel. Under such conditions, the Rayleigh distillation–condensation system can play a crucial role in the isotopic composition of water and provoke significant shifts relative to the isotopic composition of formation waters circulating under more stable conditions.

Since fluid formed at deeper levels should undergo a greater number of evaporation and condensation as it migrates to the surface, the fluid generation depth should correlate with the alteration degree of the isotopic composition of water. Multistage distillation and condensation should decrease the content of dissolved salt (primarily halogens), on the one hand, and should not prevent the water enrichment in hydrocarbonate ion, on the other hand. Kollodii (1971) invoked such an explanation for the formation of condensation waters of the sodium hydrocarbonate type that are abundant in petroleum provinces of the southern Caspian region and Taman Peninsula.

The position of data points of the Yuzhno-Neftyanoi (Taman) and Baida (Georgia) volcanoes can be explained by this model using equilibrium processes of

evaporation and condensation in the course of water transportation and emanation. In this case, isotopic shifts will be parallel to the meteoric water line. This assumption agrees with the chemical composition of samples that are characterized by anomalously low TDS content and typical features of condensation waters.

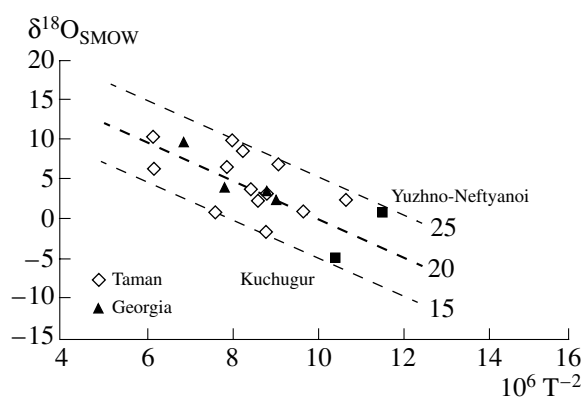
This model has some contradictions. Using the Rayleigh distillation model and varying temperature in the system, we can select a trend that best corresponds to the real relations between  $\delta D$  and  $\delta^{18}O$  values in mud-volcanic waters (Fig. 7). However, temperature (200°C) obtained for the calculated trend seems to be significantly higher than the estimate based on hydrochemical geothermometers (50–100°C). In addition, the coincidence between calculated and observed trends implies that all mud-volcanic waters in both Taman and Georgia formed at the same temperatures.

Spatial zoning well expressed in the distribution of  $\delta D$  and  $\delta^{18}O$  values on the Taman Peninsula is also poorly consistent with the formation mechanism of mud-volcanic waters discussed above. It is quite evident that accidental factors and, primarily, volume ratios of liquid and gas play a significant role in the third model. Therefore, correlation of these parameters with the distance of mud volcano from the Greater Caucasus can hardly be conceived.

Thus, the Rayleigh distillation–condensation model, which, at first glance, best describes isotopic variations in water, does not take into consideration fluid temperature variations, which are recorded from temperature-dependent components of water (Li/Na, Na/K, Mg/Li,  $\delta^{11}B$ , and others) and gas ( $\delta^{13}C(CH_4)$ ) phases of mud-volcanic emanations, and does not explain lateral zoning observed in the isotopic composition of water.

**(4) Postsedimentary transformation of freshened seawater during combined reequilibration.** This model implies the change of freshened seawater ( $\delta D \approx -40\text{‰}$  and  $\delta^{18}O \approx -6\text{‰}$ ) in a closed rock space during lithogenesis with no contribution of alien waters. Unlike the first model, this model requires the explanation of changes in both oxygen and hydrogen isotopic compositions of water. As was discussed in the first model, transformation of sediments in deep zones result in the dehydration and recrystallization of minerals. Recrystallization of smectite into illite is accompanied by the release of  $\delta^{18}O$ -rich loosely- or strongly-bonded waters associated with smectite. The enrichment of water in  $\delta^{18}O$  can also be caused by the interaction with carbonates from sedimentary rocks.

It is also known that temperature conditions of the illitization of smectite and the active phase of oil-and-gas generation (oil window) are similar. It is possible that synthesis of oil and methane from solid and water-soluble organic compounds provides favorable conditions for the enrichment of water in deuterium.



**Fig. 8.** Variations of oxygen isotopic composition vs. Mg–Li temperatures. Dashed line shows the change of  $\delta^{18}O$  in water equilibrated with illite having  $\delta^{18}O = 15, 20,$  and  $25\text{‰}$  (relative to SMOW) at different temperatures.

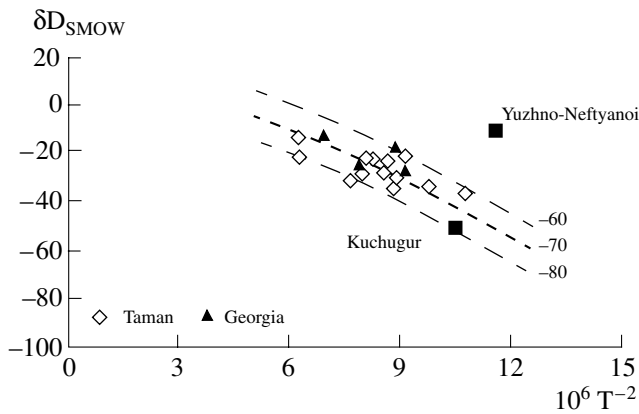
Thus, we can suggest that pore (sea) waters were involved in isotopic exchange with two main buffering components: clay minerals for the oxygen isotope system and methane for the hydrogen isotope system. The exchange with clay minerals and methane leads to increase in the oxygen isotopic composition and  $\delta D$  value, respectively.

The role of these processes can be estimated by calculations taking into consideration temperature conditions in accordance with the available data on fractionation coefficients of oxygen and hydrogen isotopes in the illite–water and methane–water systems (Bottinga, 1969; Eslinger *et al.*, 1979). Since the formation temperatures of mud-volcanic waters are not known exactly, we used estimates based on hydrochemical thermometers for the calculations (Lavrushin *et al.*, 2003).

Results of the calculation of oxygen and hydrogen isotopic compositions in formation waters equilibrated with illite and methane are shown in Figs. 8–10. The calculated values coincide with those for the Taman mud-volcanic waters if the average  $\delta^{18}O$  value varies from 15 to 25‰ in illite (Fig. 8) and  $\delta D$  varies from  $-80$  to  $-60\text{‰}$  in methane (Fig. 9). In the generalized  $\delta^{18}O$ – $\delta D$  diagram (Fig. 10), the equilibrium illite– $CH_4$ – $H_2O$  exchange curves occupy a position close to the compositional trend of mud volcanoes, but they do not exactly correspond to the trend.

This can be related to incomplete isotopic exchange under natural conditions, whereas the degree of isotopic exchange in calculations was taken to be 100%. Inaccurate correspondence to the accepted model can also result from error in the temperature estimate based on hydrochemical thermometers.

*Comment.* As was mentioned above, illitization of smectite is accompanied by two competitive processes, namely desorption of chemical elements from the exchange clay complex with the corresponding enrichment of water in trace components and decrease in



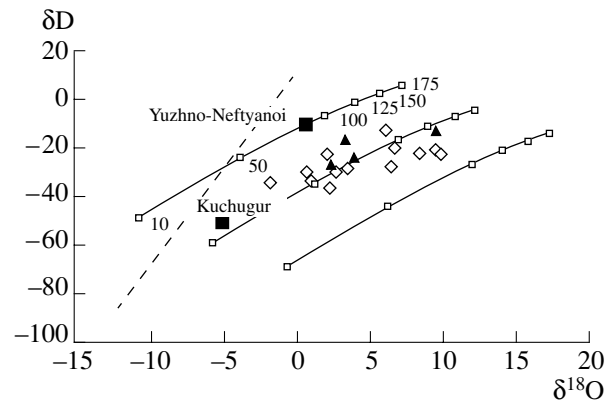
**Fig. 9.** Variations of isotopic composition vs. Mg–Li temperatures. Dashed lines show change of  $\delta D$  in water equilibrated with methane having  $\delta D = -60, -70,$  and  $-80\text{‰}$  (relative to SMOW) at different temperatures.

salinity (content of major components) of pore waters due to increase in solvent volume. From this point of view, correlations of  $\delta D$  and  $\delta^{18}O$  with halogen contents can easily be explained in the framework of the fourth model (Fig. 3).

Positive correlation of the hydrogen isotopic composition of water with the  $HCO_3$  ion content (Figs. 4a, 4b)<sup>3</sup> may indicate the existence of interrelation between the isotopic composition of water and the degree of organic matter transformation during lithogenesis, since carbon dioxide, which controls the  $HCO_3$  content, is a product of hydrocarbon synthesis. This conclusion is also consistent with the proposed model that admits the role of organic matter in the isotopic composition of water.

At first glance, the common trend for chemically different water samples from Taman and Kakhertia (Fig. 2) is poorly consistent with such a model. Processes of the formation of isotopically heavy waters considered above seem to be specific, since they depend on several local factors, such as the composition and permeability of host rocks, the presence or absence of organics, and so on. However, this contradiction is eliminated if we follow the concepts of genetic relationship between mud volcanism and hydrocarbon synthesis, which occur simultaneously with mineral transformations of thick clayey sequences (Gubkin, 1938; Kholodov, 2002). In other words, mud volcanism originates only in certain areas where the thickness of clayey rocks and intensity of oil-and-gas generation have attained the required ratio.

<sup>3</sup> The  $HCO_3$  concentration in mud-volcanic waters can be as much as 6.2 g/l. However, it should be noted that the real content of this ion can be somewhat lower, since we conditionally accepted this parameter as the alkalinity value, i.e., the sum of weak (carbonic, boric, and organic) acids normally expressed in mg-equiv/l but recalculated for the  $HCO_3$  concentration.



**Fig. 10.** Temperature evolution of the isotopic composition of water equilibrated with illite and methane. Dashed line shows the trend of meteoric waters. Numbers denote the temperature of isotopic reequilibration. For calculations, we used the following three variants of isotopic parameters of  $\delta D_{\text{methane}}$  and  $\delta^{18}O_{\text{illite}}$ :  $(-60 \text{ and } +15), (-70 \text{ and } +20),$  and  $(-80 \text{ and } +25)\text{‰}$  (relative to SMOW).

Unlike the Rayleigh distillation–condensation model, the combined isotopic reequilibration model is based on real temperature parameters of water formation. This explains the general geographic zonation of the isotopic composition of water and other temperature-dependent components of mud-volcanic emanations (e.g.,  $\delta^{13}C(CH_4)$  and  $\delta^{11}B$  of clays) (Fig. 6). This zonation can reflect increase in both fluid generation depth and heat flow as the Greater Caucasus is approached. Thus, the chemical and isotopic compositions of mud-volcanic waters do not contradict the concept of the combined influence of the illitization of smectite and synthesis of hydrocarbons at different temperatures.

It should also be noted that real isotopic characteristics of  $\delta D$  (methane) and  $\delta^{18}O$  (illite) values in the Taman volcanoes are unknown. The  $\delta^{18}O$  interval accepted in the calculations is typical of illite, whereas the  $\delta D$  interval (from  $-80$  to  $-60\text{‰}$ ) can be strongly overestimated. Such an assumption is based on  $\delta D$  values (from  $-236$  to  $-159\text{‰}$ ) obtained for methane from mud volcanoes in Turkmenistan and Azerbaijan (Erokhin and Titkov, 1982; Valyaev *et al.*, 1985). However, such a discrepancy is not critical for the given model, since isotopic exchange in the methane–water system can be incomplete in mud-volcanic reservoirs, whereas the theoretical trend is based on the assumption of isotopic equilibrium of gas and mineral phase with water.

## CONCLUSIONS

Models considered in the present communication for the explanation of isotopic compositions of mud-volcanic waters of Taman and Georgia are based on the formalization of natural variations in accordance with

topology of the  $\delta^{18}\text{O}$ – $\delta\text{D}$  diagram. Therefore, none of them can satisfactorily explain all available geochemical and geological characteristics of mud-volcanic activity. One can only suggest that the third and fourth models of isotopic evolution of the water phase of mud-volcanic emanations are closest to real observations. It is evident that these processes are not isolated in nature and they can be superimposed on each other. Their reasonable combination can presumably exclude contradictions mentioned above between the calculated and some measured geochemical data.

Presumably, formation mechanisms of mud-volcanic waters considered in this communication are far short of being the single models. For example, migration of gas–water fluids in the pore media can be accompanied by membrane effects. However, it is rather difficult to take into account their influence on the isotopic composition of water.

Summarizing the discussion of results and calculations, one can draw the following conclusions.

(1) Mud-volcanic waters of the Taman Peninsula and Georgia are characterized by  $\delta^{18}\text{O}$  variation from +0.7 to +10.0‰ and  $\delta\text{D}$  variation from –37 to –13‰. Both Taman and Kakheta waters show a general spatial trend: the oxygen and hydrogen isotopic compositions become heavier as the Greater Caucasus is approached. They evolve from the sodium chloride–carbonate type to the sodium hydrocarbonate variety in the same direction.

(2) The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values correlate with fluid generation temperatures calculated from hydrochemical geothermometers. It is evident that the concentration of heavy hydrogen and oxygen isotopes in mud-volcanic waters depends on temperature.

(3) The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values demonstrate positive correlation with alkalies, alkali-earth metals, boron, and  $\text{HCO}_3$  and negative correlation with dissolved halogens (Cl, Br, and I). Hence, the isotopic composition of water is strongly affected by the illitization of smectite and the consequent release of loosely bonded water and desorption of trace components from the exchange smectite complex. Dependence of isotopic parameters on the  $\text{HCO}_3$  content in the solution also indicates a possible relation with transformations of organic matter during lithogenesis. The negative correlation of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  with the isotopic composition of boron ( $\delta^{11}\text{B}$ ) incorporated in the exchange clay complex confirms the inferred influence of smectite–illite transformation on the isotopic composition of water.

(4) Formation mechanisms of mud-volcanic waters discussed above make it possible to reconstruct their isotopic composition in the ancient marine basin (Paratethys) that served as provenance for mud-volcanic systems of Taman and Georgia. The basin was probably filled with freshened water characterized by  $\delta\text{D} \approx -40\text{‰}$  and  $\delta^{18}\text{O} \approx -6\text{‰}$ .

(5) Water of mud-volcanic systems actively participated in the postsedimentary transformation of mineral and organic matter, resulting in changes in its isotopic and chemical compositions. Thus, assumption of the inertness of water based on the formal hypothesis of mud volcano formation as a result of tectonic collision or compaction of thick molasse sequences is incorrect.

(6) The data presented in this communication are consistent with hypotheses of the gaseous or elisional origin of mud-volcanic systems. Model calculations show that the influence of isotopic reequilibration in the illite–methane–water system is no less significant than the impact of the Rayleigh distillation–condensation system. Combination of these processes can explain nearly all isotopic–geochemical features of mud-volcanic emanations.

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