# Strontium and Oxygen Isotopic Systems in Waters of Mud Volcanoes of the Taman Peninsula

**M. I. Bujakaite, V. Yu. Lavrushin, B. G. Pokrovsky, O. E. Kikvadze, and B. G. Polyak**

*Geological Institute, Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 119017 Russia*

*e-mail: bujakaite@ginras.ru*

Received February 18, 2013

**Abstract**—Ten of eleven analyzed water samples from mud volcanoes of the Taman Peninsula are characterized by $^{87}Sr/^{86}Sr$ ratio within 0.70734–0.70957, which overlaps the values typical of the Mesozoic and Cenozoic sedimentary carbonates, but sharply differs from the value in the clayey sediments of the Maikop Group ($0.7157 \pm 0.0022$). These data indicate that the strontium isotopic composition is mainly defined by carbonate reservoirs, with relatively little effect of elision solutions, input of which is noticeable only in the water of Gladkovsky Volcano ($^{87}Sr/^{86}Sr = 0.71076$). The high $\delta^{18}O$ in mud volcanic waters (up to 14.2‰) can also be attributed to ionic exchange with sedimentary carbonates at temperatures around 150°C.

**DOI:** 10.1134/S0024490213060023

## INTRODUCTION

Mechanisms of mud volcanism and sources of mud volcanic fluids have been discussed over several tens of years. According to the most widespread viewpoint, mud volcanism is closely related to the transformation of organic matter in sedimentary cover and the formation of petroleum fields (Gubkin and Fedorov, 1938; Kholodov, 2002), although no consensus has been reached so far concerning the depth of mud volcanic systems. The geological position of roots of the volcanic apparatus is constrained by the age of rock fragments and mud volcanic breccia. It was previously believed that breccia of the Taman volcanoes does not contain rocks older than the Maikop Group (Avdusin, 1948; Belousov and Yarotskii, 1936). However, later studies established that many volcanic ejections contain fragments of older rocks: Eocene, Paleocene, Cretaceous, and even Upper Jurassic (Shardarov et al., 1972). Fragments of the Lower Cretaceous rocks identified by petrographic data (without chronostratigraphic constraints) were found in breccias of the Semigorsky, Shugo, Gladkovsky, Severo-Akhtanizovsky, Kuchugursky, Karabetova Gora, Gnilaya Gora, Miski, and Sopki volcanoes. Dating of fragments of glauconite sandstones from Shugo Volcano yielded the Lower Cretaceous age of 120 Ma (Shnyukov et al., 1986). However, it should be noted that the age of breccias is not always constrained by biostratigraphic or geochronological data, while accurate stratigraphic assignment can hardly be given from lithological features alone.

In the opinion of Kholodov (2002), sources of mud volcanoes are more often localized in clay sequences, which compose the upper ~5 km of sedimentary cover, and are mainly fed by elision solutions formed during the smectite–illite transformations. At the same time, geophysical data reported in this work indicate that volcanic roots reach much greater depths. It was also assumed that mud volcanic systems (including those of the Taman Peninsula) represent the discharge channels of deep hydrocarbon fluids (Kovalevskii, 1940, Valyaev et al., 1985; Valyaev, 1994; and others), but magmatogenic components marked by mantle helium were not detected (Lavrushin et al., 1996).

The study of oxygen and hydrogen isotopic compositions in waters of mud volcanoes revealed their significant difference from atmospheric precipitates and surface waters of the region (Lavrushin et al., 2005), It was also proposed that strong $^{18}O$ concentration (up to 10‰) in waters of some volcanoes was caused by intense geochemical processes in the water–rock system, for instance, by the transformation of smectite into illite; wide variations in oxygen isotopic composition, by the mixing of elision and porous waters. Similar conclusions were obtained by researchers who studied the geochemistry of the Taiwan mud volcanoes (Cheng-Feng You et al., 2004) and the Mediterranean area (Dählmann and de Lange, 2003).

In this work, we attempted to shed light on the genesis of mud volcanic emanations on the basis of new strontium and oxygen isotopic data on water samples from 11 mud volcanoes of the Taman Peninsula (Fig. 1).

## MATERIALS AND METHODS

Water samples from 11 mud volcanoes located in different parts of the Taman Peninsula (Fig. 1) were collected in June 2009. Sample preparation and extraction of Sr for isotopic analysis were carried out by the standard method of ion-exchange chromatog-
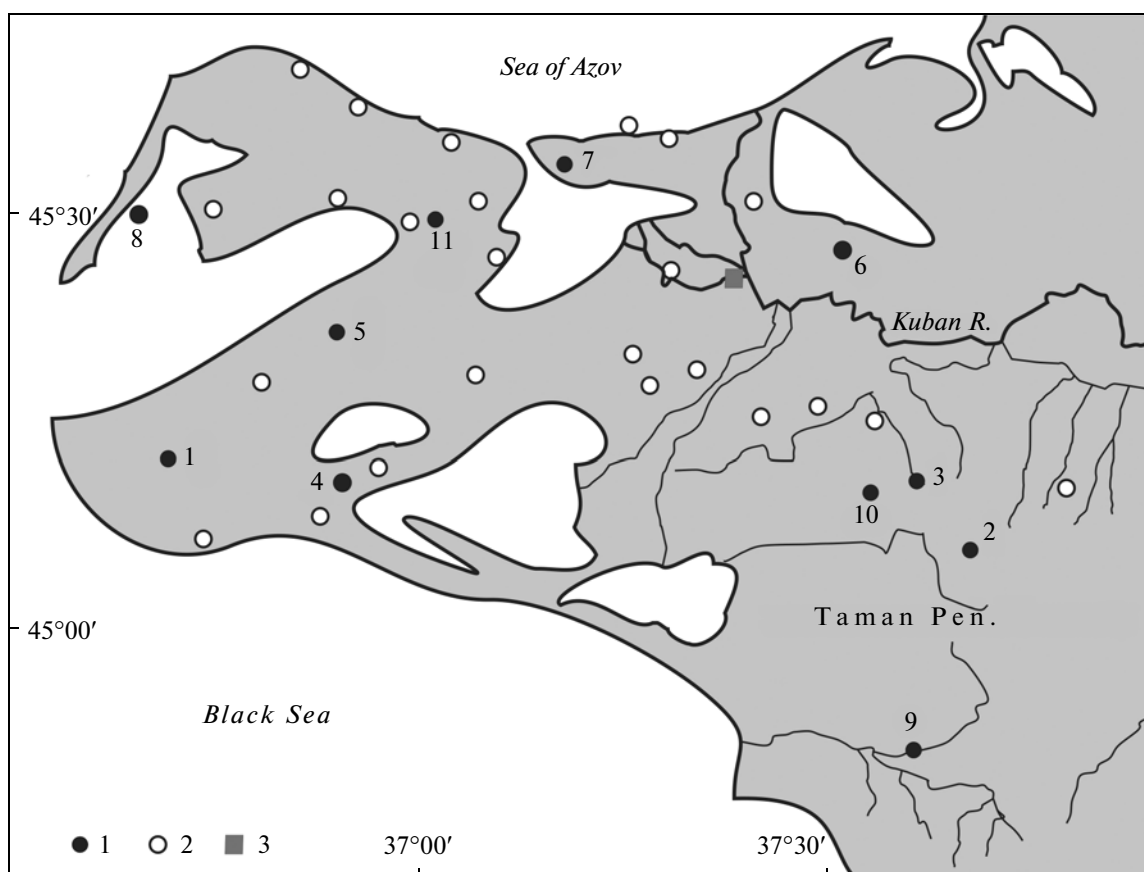
**Fig. 1.** Location scheme of the studied mud volcanoes. (1) Volcanoes with water analyzed for the strontium and oxygen isotopic composition; (2) other mud volcanoes of the Taman Peninsula; (3) water sampling localities, Kuban River. Numbers in figures denote volcanoes: (1) Karabetova Gora; (2) Gladkovsky, (3) Shugo, (4) Bugazsky, (5) Shapursky, (6) Gnilaya Gora; (7) Sopka, (8) Chushka, (9) Semigorsky, (10) Vostok, (11) Central Tsimbaly.

raphy in the Laboratory of Isotope Geochemistry and Geochronology, Geological Institute, Russian Academy of Sciences. The $^{87}Sr/^{86}Sr$ ratio in waters of mud volcanoes was analyzed in the Laboratory of Geosciences Environment Toulouse (GET, France) on a MAT-261 mass spectrometer accurate to ±0.00004. Measurements of $^{87}Sr/^{86}Sr$ in the Kuban River water and in four carbonate samples extracted from clays of mud volcanoes by leaching in 2N HCl were conducted on a MAT-260 mass spectrometer accurate to ±0.0001 at the Geological Institute, Russian Academy of Sciences.

Oxygen isotopic composition was determined using Thermoelectron complex, which includes a Delta V Advantage mass spectrometer and Gas-Bench-II device. The values of $\delta^{18}O$ are given in ‰ relative to V-SMOW standard. Accuracy (reproducibility) of $\delta^{18}O$ and $\delta^{13}C$ determinations is within ±0.2‰.

Concentrations of Sr and Rb were measured by ICP-MS on a Thermo Elemental X-7 ICP-MS (US) apparatus at the Analytical Center, Institute of Micro-

electronics Technology and High Purity Materials, Russian Academy of Sciences (Chernogolovka).

Contents of chlorine and dissolved inorganic carbon ($HCO_3$) were determined by the titration of aqueous solutions in the Laboratory of Chemico-Analytical Studies, Geological Institute, Russian Academy of Sciences (Cl determinations) and immediately after sampling during expedition ($HCO_3$).

## RESULTS

The $^{87}Sr/^{86}Sr$ ratio in the studied samples varies from 0.70734 to 0.71076 (Table 1). However, this value falls in a comparatively narrow range from 0.70838 to 0.70899 in most of samples (seven of eleven). A much lower value $^{87}Sr/^{86}Sr = 0.70734$ was recorded in the water of Semigorsky Volcano in the southern part of the Taman Peninsula (Fig. 1), while higher values (0.70935, 0.70957, and 0.71076) were obtained in waters of the Gnilaya Gora, Shugo, and Gladkovsky volcanoes located on the eastern periphery of the studied area.

**Table 1.** Strontium and oxygen isotopic compositions and some chemical data on waters from the Taman mud volcanoes

| Author's no. | Volcano | $^{87}Sr/^{86}Sr$ | d$^{18}$O, ‰ | Sr, mg/L | Rb/Sr | Cl, g/L | Ca/Cl | HCO$_3$, g/L |
|---|---|---|---|---|---|---|---|---|
| 1/09 | Karabetova Gora | 0.70899 | 14.2 | 0.379 | 0.089 | 1.45 | 0.0145 | 9.15 |
| 2/09BG | Gladkovsky | 0.71076 | 5.0 | 41.99 | 0.014 | 11.35 | 0.1374 | 0.34 |
| 3-1/09 BG | Shugo | 0.70957 | 5.2 | 12.37 | 0.0033 | 7.80 | 0.0038 | 3.93 |
| 4-1/09 | Bugaz | 0.70854 | 10.1 | 1.362 | 0.0015 | 2.62 | 0.0094 | 6.01 |
| 6-1/09 | Shapursky | 0.70834 | 3.2 | 2.449 | 0.0156 | 5.74 | 0.0025 | 7.38 |
| 9-2/09BG | Gnilaya Gora, central part | 0.70935 | 1.9 | 0.593 | 0.0023 | 5.81 | 0.0008 | 2.56 |
| 11/09 BG | Sopka | 0.70898 | −3.4 | 0.108 | 0.017 | 3.05 | 0.0032 | 1.46 |
| 12/09 | Chushka | 0.70855 | 3.0 | 2.478 | 0.0028 | 4.25 | 0.0072 | 5.40 |
| 14-1/09 | Semigorsky | 0.70734 | 10.3 | 5.088 | 0.0021 | 2.13 | 0.0064 | 5.25 |
| 15/09 | Vostok | 0.70861 | 3.3 | 0.662 | 0.0117 | 3.19 | 0.0050 | 3.72 |
| 17-1/09 | Central (east) Tsimbaly | 0.70844 | 3.8 | 1.412 | 0.0013 | 3.55 | 0.0084 | 3.63 |
| 8r/09 | Kuban River | 0.7087 | −12.1 | — | — | — | — | — |
| 1/09 | Karabetova Gora, carbonate leachate from clay | 0.7090 | 33.0 | — | — | — | — | — |
| 3/09 | Shugo, the same | 0.7086 | 30.7 | — | — | — | — | — |
| 11/09 | Sopka, the same | 0.7085 | 31.1 | — | — | — | — | — |
| 12/09 | Chushka, the same | 0.7083 | 29.9 | — | — | — | — | — |

Values of $\delta^{13}$C in carbonates: 1/09 = 0.9, 3/09 = 3.6, 11/09 = 7.9, 12/09 = −0.5‰. Dashes denote data are absent.

The Sr contents in the waters of mud volcanoes vary in extremely broad ranges from 0.1 to 50 mg/L and show no correlation with its isotopic composition (Fig. 2). Waters with low Sr contents (<1 mg/L) could most readily be contaminated by allogenic Sr, but they are characterized actually by a small scatter of $^{87}Sr/^{86}Sr$ ratio (from 0.70861 to 0.70935). An increase in the Sr content is accompanied by the increase of $^{87}Sr/^{86}Sr$ in volcanoes in the eastern part of the peninsula and decrease of $^{87}Sr/^{86}Sr$ in the southern and western parts (Table 1, Fig. 2). The values of $^{87}Sr/^{86}Sr$ show positive correlation with the Cl content and negative correlation with the content of inorganic carbon (Figs. 3a, 3b).

Mud volcanic waters have low Rb/Sr ratio (0.089–0.013). Given that these waters are of the Maikopian age (around 25 Ma), the maximal value leads to correction for the radioactive Rb decay of <0.0001 for the Sr isotopic ratio, while other values give at least an order of magnitude lower correction. Therefore, the radioactive decay during the existence of solutions can be excluded as reason for $^{87}Sr/^{86}Sr$ variations in our considerations concerning the possible age of mud volcanic waters.

The value of $\delta^{18}$O in the studied water samples varies from −3.4 to + 14.2 ‰ (Table 1). The lowest $\delta^{18}$O was noted in the water of Sopka Volcano; the highest, in Karabetova Gora Volcano. The average $\delta^{18}$O in waters of the Taman volcanoes is 5.1 ± 4.8‰, which is well consistent with the previous data (Lavrushin et al., 2005). Complex relations between oxygen and strontium isotopic compositions (Fig. 4) point to at

least three sources of the matter, and their geochemical nature will be considered in the next section. Here, we only note that the modern seawater ($^{87}Sr/^{86}Sr$ = 0.70915, Sr = 8 mg/L, $\delta^{18}$O = 0 ± 1‰, HCO$_3$ = 0.14 g/L, Cl = 19.35 g/L) does not coincide with end members in any of the diagrams presented above (Figs. 2–4)
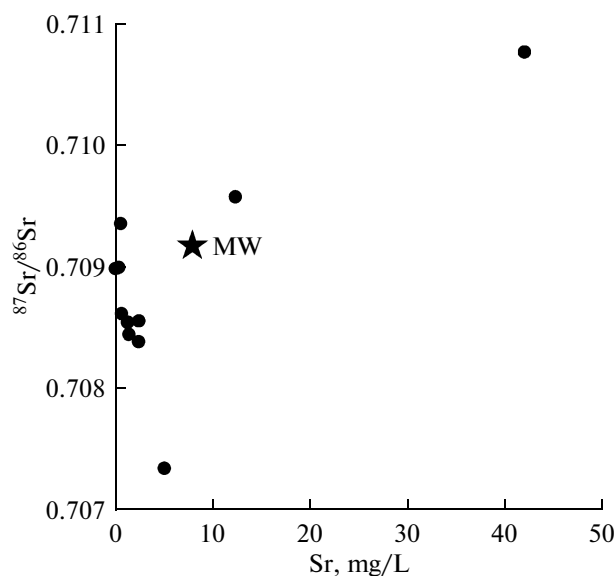


**Fig. 2.** Strontium isotopic composition vs. Sr content variations in waters of volcanoes of the Taman Peninsula. (MW) Modern seawater.
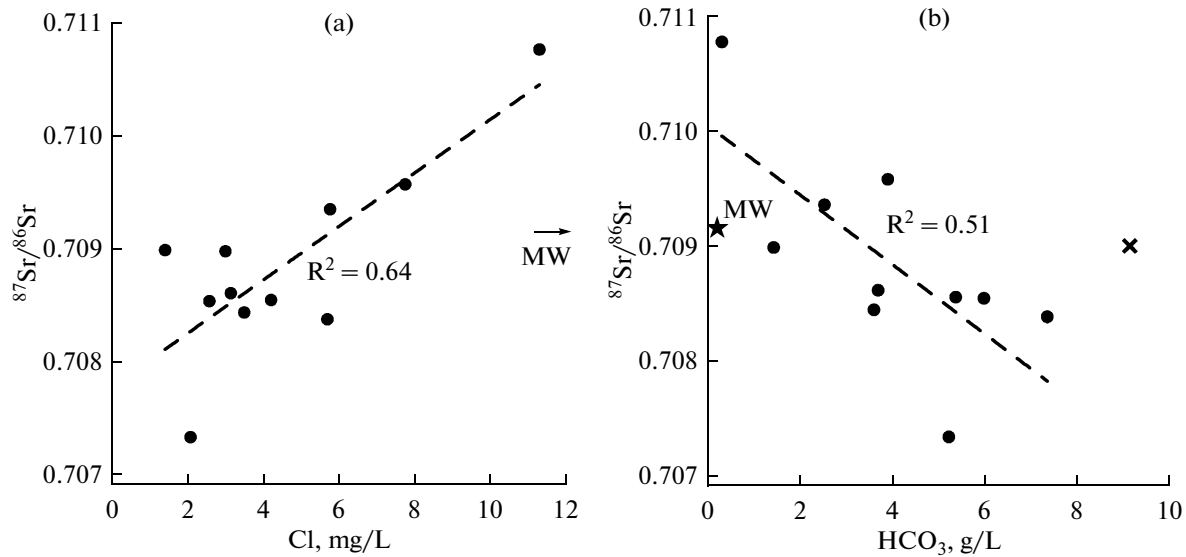
**Fig. 3.** Srontium isotopic composition vs. chlorine (a) and bicarbonate ion (b) variations in waters of mud volcanoes. (✕) water of Karabetova Gora Volcano (omitted from calculation of the correlation coefficient); (MW) modern seawater.

and, hence, cannot be considered as principal source of mud volcanic emanations.

Dispersed carbonate material occurring in small amounts (from 1 to 12%) in the cement of mud volcanic breccias is practically similar to the waters of the Karabetova Gora and Churka mud volcanoes in terms of the strontium isotopic composition. Carbonate
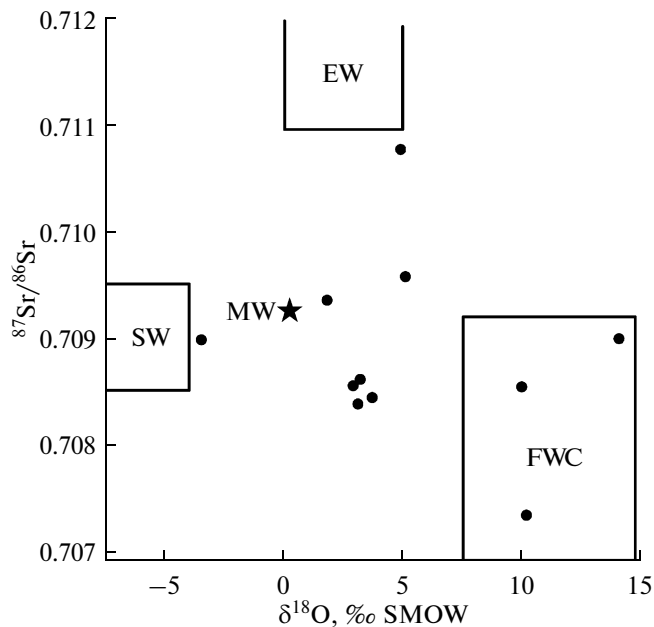


**Fig. 4.** Oxygen and strontium isotopic composition in waters of mud volcanoes and their probable sources. (SW) Surface waters of the atmospheric origin, (EW) elision waters, (FWC) formational waters in deep carbonate reservoirs, (MW) modern seawater.

material from breccias of the Shugo and Sopka volcanoes has slightly lower $^{87}Sr/^{86}Sr$ than water (Table 1).

## DISCUSSION

As demonstrated by numerous examples, the strontium isotopic composition of groundwaters is determined by the composition of reservoirs (Faure, 1986), which can be divided into three main types: (1) mantle-derived igneous rocks with $^{87}Sr/^{86}Sr = 0.704 \pm 0.002$ (Vinogradov and Vakin, 1983); (2) sedimentary carbonates inheriting the seawater strontium isotopic composition, which increased from 0.7068 to 0.70915 during the Mesozoic and Cenozoic (Veizer et al., 1999); and (3) ancient silicate rocks and their disintegration products representing terrigenous sediments with high $^{87}Sr/^{86}Sr$ (>0.712) and broad variations of the strontium isotopic composition (Faure, 1986).

Table 2 lists the strontium isotopic data on the terrigenous rocks of the Maikop Group, which are considered as the most probable sources of elision solutions that played a certain role in feeding mud volcanoes of the Taman Peninsula. They have expectedly high average $^{87}Sr/^{86}Sr$ ratio of 0.716 at a scatter from 0.711 to 0.720. The presented average value can be considered as the most probable one for elision waters formed during the smectite–illite transition.

As mentioned above, volcanogenic rocks in the sedimentary cover of the Taman Peninsula are practically absent, while gases of mud volcanoes are devoid of mantle helium. This excludes igneous rocks as a possible source of Sr in volcanic waters. The scatter of $^{87}Sr/^{86}Sr$ values obviously points to a mixing of two Sr sources: terrigenous and carbonate. The latter source clearly prevails in mud volcanoes of the Taman Penin-

**Table 2.** Strontium isotopic composition and Rb and Sr contents in clay rocks of the Maikop Group, Kuban superdeep well

| Laboratory no. | Author's no. | Depth, m | $^{87}Sr/^{86}Sr$ | Sr, mg/L | Rb, mg/L | $^{87}Rb/^{86}Sr$ |
|---|---|---|---|---|---|---|
| 4346 | 87 | 3905.4 | 0.7197 | 74.9 | 115 | 4.45 |
| 4347 | 77 | 3878 | 0.7114 | 51.7 | 18.7 | 1.05 |
| 4383 | 44* | 3772.5 | 0.7163 | 26.2 | 146.3 | 16.2 |
| 4390 | 44** | 3772.5 | 0.7167 | 379 | 134 | 1.02 |
| 4349 | 425 | 2466.0 | 0.7172 | 74.8 | 82.7 | 3.20 |
| 4384 | 425* | 2255.0 | 0.7142 | 176 | 130 | 2.15 |
| 4387 | 425** | 2255.0 | 0.7160 | 114 | 130 | 3.31 |
| 4357 | 87 | 455.0 | 0.7144 | 158 | 143 | 2.62 |
| 4354 | 70 | 372.0 | 0.7147 | 151 | 145 | 2.79 |
| 4351 | 61 | 320.3 | 0.7168 | 144 | 120 | 2.40 |

\* Fraction <0.001 mm; ** fraction 0.001−0.002; others are bulk samples.

sula (Fig. 5). The lowest $^{87}Sr/^{86}Sr = 0.70734$ established in the waters of Semigorsky Volcano practically coincides with the $^{87}Sr/^{86}Sr$ value in the Late Jurassic−Early Cretaceous seawater (Veizer et al., 1999). Hence, the Jurassic carbonates, which compose the lower part of the sedimentary cover of the Taman Peninsula, represent one of the main Sr sources. It should also be noted that most calcareous fragments were found in the breccias of Semigorsky Volcano, which is nearest to the Greater Caucasus foothills.

Terrigenous source played the most important role in waters of Gladkovsky Volcano, which are significantly enriched in the radiogenic Sr as compared to other volcanoes. The chemical (Cl−Ca−Na) composition of waters of this volcano strongly differs from that of mud volcanoes in the Taman Peninsula having mainly (HCO₃-(Cl)-Na) composition (Shnyukov et al., 1986; Lavrushin et al., 2005). Efficient leaching of Sr from terrigenous rocks in the given case is obviously related to the high content of chlorine likely derived from evaporites. At the same time, the reason for a positive correlation between $^{87}Sr/^{86}Sr$ and the Cl content remains unclear. It is much easier to explain the negative correlation between $^{87}Sr/^{86}Sr$ and the bicarbonate ion content: the higher the carbon dioxide content in the solution, the more intense its interaction with carbonate rocks.

The mixed terrigenous−carbonate source of Sr is inferred for the main group of mud volcanoes. We can suppose formally that the only Sr source in them was not the Jurassic rocks, but younger carbonates: $^{87}Sr/^{86}Sr = 0.708-0.709$ was typical of seawater and, correspondingly, carbonates within the Cretaceous to Neogene interval (Fig. 5). It should be taken into account that evolutionary $^{87}Sr/^{86}Sr$ curves are defined by the minimal values obtained for the least altered (ideally, unaltered) carbonates, while higher values indicate contamination by the terrigenous Sr.

It is highly possible that all waters of mud volcanoes contain variable proportions of "carbonate" and "ter-
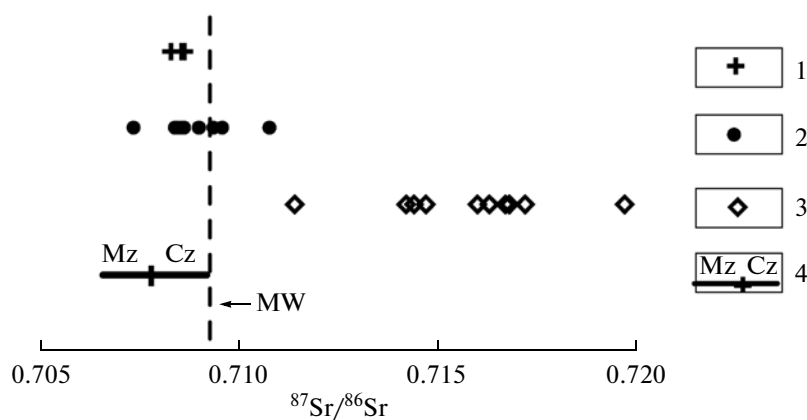


**Fig. 5.** Comparison of the strontium isotopic composition in mud volcanoes, sedimentary carbonates, and clay rocks of the Maikop Group. (1, 2) Mud volcanoes: (1) carbonates, (2) waters; (3) clays of the Maikop Group; (4) Mesozoic and Cenozoic sedimentary carbonates (Veizer et al., 1999).

rigenous" Sr, which is confirmed by the correlation between $^{87}Sr/^{86}Sr$ and total carbonate content. Assuming that the $^{87}Sr/^{86}Sr$ value in the "carbonate" Sr was close to the Jurassic values (~0.707), while the value in the "terrigenous" Sr is ~0.716, as in the Maikop Group, we may estimate that the "carbonate" and "terrigenous" Sr in the main group of the studied waters (0.70838–0.70899) accounted for approximately 80 and 20%, respectively. Since $^{87}Sr/^{86}Sr$ in natural solutions draining the Jurassic and younger carbonate sequences is more than 0.707, the presented values should be considered as minimal for the "carbonate" Sr and maximal for the "terrigenous" Sr. At any assumptions, the fraction of "carbonate" Sr in the water of Semigorsky Volcano should be estimated at no less than 90%.

The oxygen isotopic composition of groundwaters is controlled by much more factors than the strontium isotopic composition. These factors include are not only the reservoir composition, but also temperature and mass balance in the water/rock system, as well as initial $\delta^{18}O$ characterizing the origin of water.

Significant contribution of the $^{18}O$-depleted atmospheric water is identified only in salsa of Sopka Volcano ($\delta^{18}O = -3.4‰$, Table 1). Waters of other volcanoes are enriched in $^{18}O$ relative to atmospheric and sea water. Obviously, precisely these high and even ultrahigh 14.2‰ values (up to 14.2‰, Karabetova Gora Volcano) characterize the "roots" of mud volcanoes, whereas surface waters of the atmospheric origin (field IIB, Fig. 4) are involved in mud volcanism near or even at the Earth's surface.

Waters draining carbonate reservoirs at high temperatures (FWC field, Fig. 4) theoretically should have the higher $\delta^{18}O$ values than waters draining the terrigenous sequences, because sedimentary carbonates have much higher $\delta^{18}O$ values (25–30‰) than terrigenous rocks (15–20‰). This conclusion is well consistent with empirical data: $\delta^{18}O$ in the highly concentrated brines hosted in carbonate reservoirs at a depth of more than 3 km reaches 6–8‰ (Sheppard, 1986; Kharaka and Thordsen, 1992), which approximately corresponds to isotopic equilibrium with carbonates ($\delta^{18}O = 25‰$) at 100°C (O'Neil et al., 1969). The chemical and isotopic composition of these waters usually ascribed to "formational" waters was modified too much to establish their primary nature. These may be both buried marine and atmospheric waters. At higher temperatures and lower water/rock ratios, oxygen isotopic shift in the carbonate-hosted thermal waters may reach 15–20‰. An extremely high $\delta^{18}O = 14.7‰$ was determined in the Lanzarote Spring area (Canary Islands), where temperature reaches 300°C (Arana and Panichi, 1974). It is pertinent to mention that this value is very close to $\delta^{18}O = 14.2‰$ found in waters of Karabetova Gora Volcano (Table 1).

In some previous works, the high $\delta^{18}O$ values were mainly attributed to the dehydration of clay minerals. In our opinion, this conclusion should be corrected.

The oxygen isotopic composition in water released during the smectite–illite transition is hardly possibly to determine experimentally. Therefore, its value is usually estimated from isotopic equilibrium, which is 14–15‰ in the smectite–water and illite–water systems at 100°C and 9–10‰ at ~150°C (Savin and Lee, 1988; Sheppard and Gilg, 1996). Since $\delta^{18}O$ values are usually close to 20‰ in clay minerals of terrigenous rocks and 25‰ in authigenic marine rocks (Savin and Epstein, 1970a, 1970b), the oxygen isotopic composition of elision waters is estimated at ~10‰ (Lavrushin et al., 2005).

However, these authors ignored the following important points: (1) Natural clays usually contain 50–60% of clay minerals proper and 40–50% of mineral detritus mainly represented by quartz, which has close or even somewhat lower $\delta^{18}O$ than clay minerals. Fractionation of oxygen isotopes between quartz and water reaches 21–22‰ at ~100°C and 15–17‰ at ~150°C (Clayton et al., 1972; Zheng, 1993). Correspondingly, the values of $\delta^{18}O$ in water in equilibrium with quartz at 100°C should be close to 0‰, while the isotopic composition of water in equilibrium with the quartz–smectite mixture is no more than 5‰. (2) Clay minerals show inner fractionation of oxygen isotopes between the silicate component and OH group, with $\delta^{18}O$ in the latter approximately 30‰ lower than in the "whole" mineral (Hamza and Epstein, 1980; Girad and Savin, 1996). There are grounds to suggest that water released during the dehydration of hydroxyl-bearing minerals partially inherits the isotopic composition of the OH group. Either this fact or kinetic effects explain the following fact: the dehydrated water obtained in laboratory experiments is strongly $^{18}O$-depleted as compared to its equilibrium composition in the mineral–water system (Clayton and Mayeda, 2009; Dubinina et al., 2012). Regardless of temperature, water released during the dehydration of serpentine was, in particular, depleted by 27‰ in $^{18}O$ with respect to the "whole" mineral (Clayton and Mayeda, 2009).

Taking the aforementioned facts into consideration, we can accept that the $\delta^{18}O$ value in elision waters (EW field, Fig. 4) ranges from 0 to + 5‰, which is close to value in water of Gladkovsky Volcano with essentially "terrigenous" strontium isotopic composition. The higher $\delta^{18}O$ typical of waters of mud volcanoes indicate a high-temperature contact with sedimentary carbonates.

## CONCLUSIONS

In terms of strontium isotopic composition, waters of mud volcanoes of the Taman Peninsula are very close to the Mesozoic and Cenozoic carbonate sedimentary rocks from the lower part of sedimentary cover and sharply differ from terrigenous clay rocks of the Maikop Group. hence, volcanic waters were mainly derived from carbonate reservoirs, while the

calculated fraction of "terrigenous" Sr extracted by elision waters from the Maikop Group rocks in most volcanoes accounts for $10-15‰$, except for Semigorsky ($<10\%$) and Gladkovsky (up to $30\%$) volcanoes.

Oxygen isotopic data are well consistent with this conclusion. The values of $\delta^{18}O$ in the volcanic rocks reach $14.2‰$, which may be interpreted as the result of isotopic exchange with sedimentary carbonates at temperatures around $150°C$. The large scatter of $\delta^{18}O$ from $-3.4$ to $14.3‰$ can partially be related to the admixture of elision waters, but it is likely more related to the contamination by atmospheric groundwaters, which have a little effect on the isotopic composition due to the low Sr content.

Isotopic data are well consistent with the fact that mud volcanic breccias of some volcanoes contain fragments of the Mesozoic limestones from the lower part of sedimentary cover in the Taman Peninsula. It is possible that waters of mud volcanoes, which were initially contained in the carbonate reservoirs beneath the Maikop Group, penetrated the Maikop clays along tectonically weak zones. This assumption disagrees with the chemical data on groundwaters of the Mesozoic horizons, which are characterized by Cl−Na and Cl—Ca−Na brines with mineralization up to 160 g/L (Kollodii, 1971, 1983; Popkov et al., 2010). However, this inconsistency may partly be avoided by assuming that the salt load is lost during the processes of evaporation and condensation.

It was noted in (Kholodov, 2002; Yakubov et al., 1980; Popkov, 2006) that the Cenozoic sedimentary cover could contain large tectonic sheets made up of Mesozoic carbonates. Therefore, it is conceivable that the strontium isotopic composition of mud volcanic waters was formed at a depth of 3 to 4 km in contact with the allochthonous Mesozoic carbonates.

## ACKNOWLEDGMENTS

## REFERENCES

Arana, V. and Panichi, C., Isotopic composition of steam samples from Lanzarote, Canary Island, *Geothermics,* 1974, vol. 3, pp. 142−145.

Avdusin, P.P., *Gryazevye vulkany Krymsko-Kavkazskoi geologicheskoi provintsii: petrograficheskie issledovaniya* (Mud Volcanoes in the Crimean−Caucasian Geological Province: Petrographic Studies), Moscow: AN SSSR, 1948.

Belousov, V.V. and Yarotskii, A.L., *Gryazevye sopki Kerchensko-Tamanskoi oblasti, usloviya ikh vozniknoveniya i deyatel'nosti* (Mud Mounds in the Kerch−Taman Region: Conditions of Their Origin and Activity), Moscow: ONTI NKGP SSSR, 1936.

Chen-Feng, You, Gieskes, J.M., Typhoon Lee, et al., Geochemistry of mud volcano fluids in the Taiwan accretionary prism, *Appl. Geochem.,* 2004, vol. 19, pp. 695−707.

Clayton, R.N. and Mayeda, T.K., Kinetic isotope effects in oxygen in the laboratory dehydration of magnesian minerals, *J. Phys. Chem. A*, 2009, vol. 113, pp. 2212−2217.

Clayton, R.N., O'Neil, J.R., and Mayeda, T.K., Oxygen isotope exchange between quartz and water, *J. Geophys. Res.*, 1972, vol. 77, pp. 3057−3067.

Dählmann, A. and de Lange, G.J., Fluid-sediment interactions at eastern Mediterranean mud volcanoes: A stable isotope study from ODP Leg 160, *Earth Planet. Sci. Lett.*, 2003, vol. 212, pp. 377−391.

Dubinina, E.O., Perchuk, A.L., and Korepanova, O.S., Oxygen isotope effects during the dehydration of glaucophane shale: Experimental data at P−T conditions of the subduction zone, *Dokl. Earth Sci.*, 2012, vol. 444, no. 5, pp. 521−525.

Faure, G., *Principles of Isotopic Geology*, New York: Wiley, 1986. Translated under the title *Osnovy izotopnoi geologii*, Moscow: Mir, 1989.

Girard, J.P. and Savin, S.M., Intracrystalline fractionation of oxygen isotopes between hydroxyl and non-hydroxyl sites in kaolinite measured by thermal dehydratation and partial fluorination, *Geochim. Cosmochim. Acta*, 1996, vol. 60, pp. 469−487.

Gubkin, I.M. and Fedorov, S.F., *Gryazevye vulkany Sovetskogo Soyuza i ikh svyaz' s genezisom neftyanykh mestorozhdenii Krymsko-Kavkazskoi geologicheskoi provintsii* (Mud Volcanoes in the Soviet Union and Their Connection with the Genesis of Oil Fields in the Crimean−Caucasian Province), Moscow: AN SSSR, 1938.

Hamza, M.S. and Epstein, S., Oxygen isotopic fractionation between oxygen of different sites in hydroxyl-bearing silicate minerals, *Geochim. Cosmochim. Acta*, 1980, vol. 44, pp. 173−182.

Kharaka, Y.K. and Thordsen, J.J., Stable isotope geochemistry and origin of waters in sedimentary basins, in *Isotope Signatures and Sedimentary Records*, Clauer, N. and Chaudhuri, S.N.Y., Eds., 1992, vol. 43, pp. 411−466.

Kholodov, V.N., Mud volcanoes. Regularities of distribution and genesis: Communication 2. Geological-geochemical features and formation model, *Lithol. Miner. Resour.*, 2002, no. 4, pp. 325−343.

Koepnick, R.B., Denison, R.E., Burke, W.H., et al., Construction of the Triassic and Jurassic portion of the Phanerozoic curve of seawater $^{87}Sr/^{86}Sr$, *Chem. Geol.,* 1990, vol. 80, pp. 327−349.

Kollodii, V.V., Nature and formation conditions of waters in mud volcanoes, in *Proiskhozhdenie nefti i gaza i formirovanie ikh promyshlennykh zalezhei* (Origin of Oil-and-Gas and the Formation of Their Economic Pools), Kiev: Naukova Dumka, 1971, pp. 317−339.

Kollodii, V.V., *Podzemnye vody neftegazonosnykh provintsii i ikh rol' v migratsii i akkumulyatsii nefti* (Groundwaters of Petroliferous Provinces and Their Role in the Migration and Accumulation of Oil), Kiev: Naukova Dumka, 1983.

Kovalevskii, S.A., *Gryazevye vulkany Yuzhno-Kaspiiskogo regiona (Azerbaidzhan i Turkmeniya)* (Mud Volcanoes in the Southern Caspian Region: Azerbaijan and Turkmenistan), Baku: Aztoptekhizdat, 1940.

Lavrushin, V.Yu., Polyak, B.G., Prasolov, E.M., and Kamenskii, I.L., Sources of material in mud volcanic products: Evidence from isotope, hydrochemical, and geological data, *Lithol. Miner. Resour.*, 1996, no. 6, pp. 613−634.

Lavrushin, V.Yu., Dubinina, E.O., and Avdeenko, A.S., Isotopic composition of oxygen and hydrogen in waters of mud volcanoes, in Taman (Russia) and Kakhetia (eastern Georgia), *Lithol. Miner. Resour.*, 2005, no. 2, pp. 133−146.

O'Neil, J.R., Clayton, R.N., and Mayeda, T.K., Oxygen isotope fractionation in divalent metal carbonates, *J. Chem. Phys.*, 1969, vol. 51, pp. 5547−5558.

Popkov, V.I., Nappe structure of the northwestern Caucasus, *Dokl. Earth Sci.*, 2006, vol. 411, no. 2, pp. 215−218.

Popkov, V., Larichev, V., and Medvedev, S., Polycomponent and freshened waters of petroliferous basins in the Scythian−Turan plate, *Geol. Geokh³m. Goryuch. Kopalin*, 2010, no. 2 (151), pp. 78−88.

Savin, S.M. and Epstein, S., The oxygen and hydrogen isotope geochemistry of clay minerals, *Geochim. Cosmochim. Acta*, 1970a, vol. 34, no. 1, pp. 25−42.

Savin, S.M. and Epstein, S., The oxygen and hydrogen isotope geochemistry of ocean sediments and shales, *Geochim. Cosmochim. Acta*, 1970b, vol. 34, no. 1, pp. 43−63.

Savin, S.M. and Lee, M., Isotopic studies of phyllosilicates, *Rev. Mineral.*, 1988, vol. 19, pp. 189−223.

Shardarov, A.N., Malyshek, V.T., and Peklo, V.P., Roots of mud volcanoes in the Taman Peninsula, in *Geologicheskii sbornik* (Geological Collection), Moscow: Gostoptekhizdat, 1962, issue 10, pp. 53−66.

Sheppard, S.M.F., Characterization and isotope variations in natural water, *Rev. Mineral.*, 1986, vol. 16, pp. 165−183.

Sheppard, S.M.F. and Gilg, H.A., Stable isotope geochemistry of clay minerals, *Clay Miner.*, 1996, vol. 31, pp. 1−24.

Shnyukov, E.F., Sobolevskii, Yu.V., Gnatenko, G.I, et al., *Gryazevye vulkany Kerchensko-Tamanskoi oblasti (atlas)* (Mud Volcanoes of the Kerch−Taman Region: Atlas), Kiev: Naukova Dumka, 1986.

Valyaev, B.M., Hydrocarbon degasification of the Earth: Scales and role in petroleum accumulation, *Geol. Nefti Gaza*, 1994, no. 9, pp. 38−42.

Valyaev, B.M., Grinchenko, Yu.I., Erokhin, V.E., et al., Isotope signature of gases form mud volcanoes, Litol. Polezn. Iskop., 1985, no. 1, pp.72−87.

Veizer, J., Ala, D., Azmy, K., et al., $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater, *Chem. Geol.*, 1999, vol. 161, no. 1, pp. 59−88.

Vinogradov, V.I. and Vakin, E.A., Isotopic composition of Sr in thermal waters of Kamchatka, *Dokl. Akad. Nauk SSSR,* 1983, vol. 273, no. 4, pp. 965−968.

Yakubov, A.A., Grigor'yants, B.V., Aliev, A.D., et al., Gryazevoi vulkanizm Sovetskogo Soyuza i ego svyaz' s *neftegazonosnost'yu* (Mud Volcanism in the Soviet Union and Connection with Petroleum Potential), Baku: ELM, 1980.

Zheng, Y.-F., Calculation of oxygen isotope fractionation in anhydrous silicate minerals, *Geochim. Cosmochim. Acta,* 1993, vol. 57, pp. 1079−1091.

*Translated by M. Bogina*