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Isotopic–Geochemical Peculiarities of Gases in Mud Volcanoes of Eastern Georgia

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Abstract—Isotopic-geochemical study revealed the presence of mantle He ($^3He/^4He$ up to 223×10^{-8}) in gases from mud volcanoes of eastern Georgia. This fact confirms that the Middle Kura basin fill encloses an intrusive body previously distinguished from geophysical data. Wide variations in the carbon isotopic composition of CH_4 and CO_2 and the chemical composition of gas and water at a temporally constant $^3He/^4He$ ratio indicate their relation with crustal processes. Unusual direct correlations of the $^3He/^4He$ ratio with the contents of He and CH_4 and the $^{40}Ar/^{36}Ar$ ratio can be explained by the generation of gas in the Cenozoic sequence of the Middle Kura basin.

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INTRODUCTION

Mud volcanism has been the focus of attention over a long time. However, its causes and mechanisms remain controversial. Based on morphological similarity, this phenomenon was initially attributed to magmatic activity (Kovalevskii, 1940, and others). This concept was later replaced by the notion that mud volcanic activity is related to oil and gas generation (Gubkin and Fedorov, 1938) and elision processes operating in a sedimentary sequence (Kholodov, 2002). However, attempts are continuing to demonstrate the endogenic (magmatogenic) origin of mud volcanic fluid (Kovalevskii, 1940; Valyaev et al., 1985; Gemp and Lagunova, 1978; Lagunova, 1974, 1975). However, no indisputable evidence are available for the mantle origin of mud volcanic hydrocarbons (Lavrushin et al., 1996).

Mud volcanism as geological phenomenon is typical of sedimentary basins of fold mountain belts and, therefore, can be an indicator of high geodynamic activity. It is recently interpreted as the result of evolution of accretionary complexes, in which the hydrocarbon-generating sedimentary cover was subjected to intense dynamic tectonic loadings. This process promoted a high vertical permeability of rocks, resulting in the transportation and surface discharge of gas-saturated pulp.

In the territory of the Former Soviet Union (FSU), manifestations of mud volcanism are known in the Kerch–Taman province, eastern Georgia (Kakhety), Azerbaijan, Turkmenistan, and Sakhalin. Spatial relation with modern magmatic activity is noted only for mud volcanoes in Sakhalin and Georgia. This raises the question as to whether magmatism affected the composition of mud volcanic fluids.

To shed light on this question, we considered volcanoes of Kakhety, which are located in the western part of the Kura trough in the Kura and Iori river valleys. Mud volcanic fluids in this area are characterized by the highest $^3He/^4He$ (up to 2×10^{-6}) values in the Caucasus (Matveeva et al., 1978; Yakubov et al., 1980). They significantly exceed not only the canonical radiogenic crustal value ($\sim 2 \times 10^{-8}$), but also the modern atmospheric ratio (1.4×10^{-6}). Even if ignore correction for isotopic contamination, such a value distinctly indicates the input of mantle-derived He having $^3He/^4He \sim n \times 10^{-5}$ (Mamyrin and Tolstikhin, 1981). Hence, the presence of other mantle derivatives cannot be excluded. In this paper, we attempted to solve this problem by geochemical studies of mud volcanoes in eastern Georgia.

METHODS

Mud volcanoes of eastern Georgia were sampled on September, 1997. These works continue the study of He isotopic composition in mud volcanic fluids of Caucasus (Matveeva et al., 1978; Yakubov et al., 1980; Buachidze and Mkheidze, 1989; Polyak et al., 1996; Lavrushin et al., 1996, 1998). We studied four volca-

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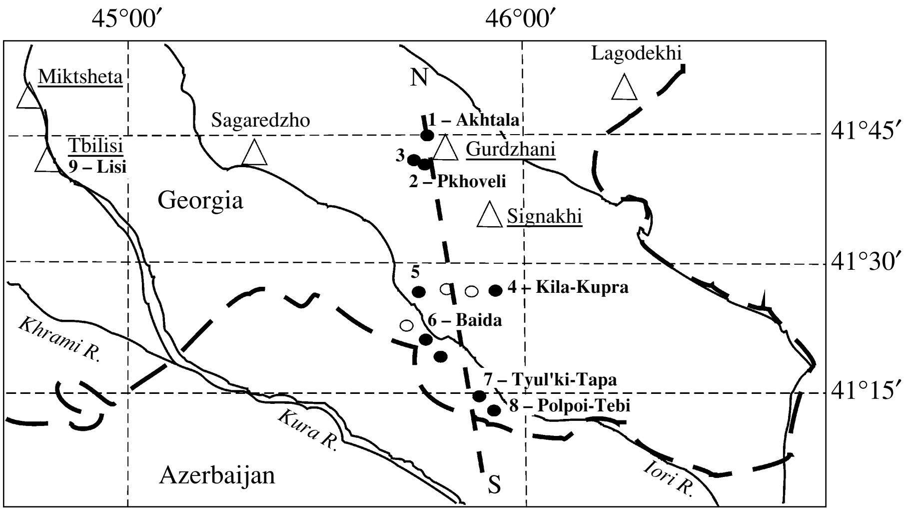

Fig. 1. Location scheme of sampled objects in eastern Georgia

noes, including Pkhoveli Volcano sampled for the first time, as well as the Mzhave mineral spring, and the Zemo-Machkhaani borehole with a weak oil production (Fig. 1). All these objects demonstrate uninterrupted release of gas phase. Pkhoveli Volcano was distinguished by the lowest activity during sampling: gas emanations from its central mud salse were sporadic. This and most other volcanoes presumably operated in a pulsed mode, when periods of relative quiescence were replaced by intense activity. This interpretation is supported by the exposure of dried mud flows on the cone slopes.

Gases were sampled in 220–320 cm^3 glass containers using a water replacement technique, plugged with rubber stopper under water seal, and preserved in upturned form. Concentrations of He, Ne and Ar, as well as $^3He/^4He$, $^{40}Ar/^{36}Ar$, and $^4He/^{20}Ne$ ratios, were analyzed on a MI 1201IG mass spectrometer at the Geological institute of Kola Scientific Centre using method described in (Kamenskii et al., 1990 and others). The chemical composition of gas was analyzed at the Geological Institute of the Russian Academy of Sciences in Moscow. At the same institute, carbon isotopic composition of CH_4 and CO_2 was analyzed on a MI 1201B mass spectrometer.

For isotopic studies, gases were separated, and CH_4 was oxidized on CuO at 1000°C. The measurement accuracy of $\delta^{13}C$ was ~0.25‰. In order to eliminate the influence of atmospheric contamination during sampling or laboratory measurements, measured $^3He/^4He$ ratio was corrected using He/Ne ratio (taking the whole neon to be of atmospheric origin) or, which is more reliable, $^4He/^{20}Ne$ (Prasolov, 1990). The results of calculations are shown in table.

GEOLOGICAL STRUCTURE OF STUDY AREA

Tectonic Setting of the Kura Trough

The Kura trough is conditionally divided into three basins: Upper Kura, Middle Kura, and Lower Kura. Mud volcanoes are noted in the Middle and Lower Kura basins. The largest number of modern and ancient volcanoes (~220) is located in the Lower Kura basin in the Azerbaijan territory (Rakhmanov, 1987). Only 15 mud volcanic edifices are known in the Middle Kura basin in the territory of eastern Georgia and western Azerbaijan.

According to recent concepts, the fold mountain belt of the Greater and Lesser Caucasus and intermontane troughs were formed owing to tectonic compression caused by northward movement of the Arabian microplate (Khain, 1982; Koronovskii and Belov, 1987; Gamkrelidze and Giorgobiani, 1987; Gamkrelidze, 1989; Nikishin et al., 1997; Philip et al., 1989). Some structures of the southern slope of the Greater Caucasus are interpreted as accretionary complexes (Fig. 2). The compression resulted in intense piling of the complexes and wide development of tectonic nappes, with the horizontal amplitude varying from 4–5 to 25–30 km (Dotduev, 1987). According to Khain (1982), the total horizontal compression of the Caucasian structure was no less than 200 km.

It is believed that formation of the Caucasus mountain system in the present-day form began in the Late Alpian and evolved in several (up to five) main compressional phases over the last ~16.5 Ma (Nikishin et al., 1997). Each of these phases was accompanied by a rapid subsidence of molasse basins that surrounded the Greater Caucasus. Tectonic movements in the Quaternary time were differentiated in more detail. In particular, it was noted that the rate of vertical movements in Pleistocene at the eastern flank of the Greater Caucasus was almost an order of amplitude higher than that at the western one (Lukina, 1987).

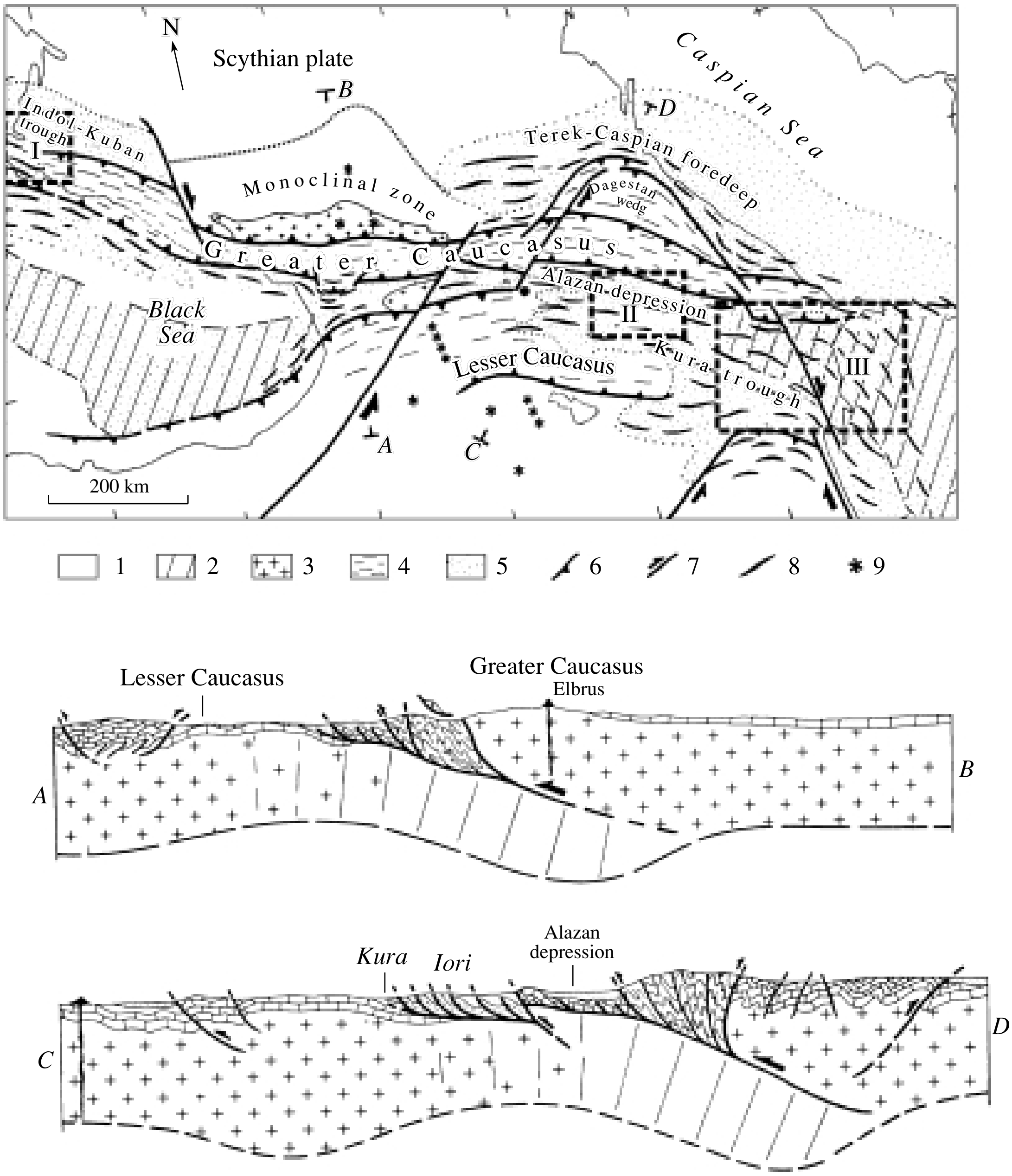

Fig. 2. Tectonic scheme of the Caucasus region. Based on (Philipp et al., 1989). (I–III) Areas of mud volcanism: (I) Kerch–Taman, (II) eastern Georgia, (III) South Caspian (Azerbaijan). (1) Continental crust; (2) oceanic or transitional crust; (3) basement exposures; (4) folded Mesozoic and Paleogene deposits; (5) young sedimentary basins; (6) main thrusts; (7) main strike-slips; (8) folds in the young sedimentary basins; (9) Neogene–Quaternary volcanic centers.

Structural Features of the Middle Kura Basin

In the Middle Kura basin, the consolidated crust is subsided deeper than anywhere else in Georgia. Therefore, geological structure of the basin was studied mainly by geophysical methods (Krasnopevtseva et al., 1977; Ioseliani and Diasamidze, 1983; Chelidze, 1983; Adamiya, 1985). It was established that the thickness of sedimentary cover in the basin is as high as 13–14 km, including 4–6 km of the Mesozoic complex. The latter is overlain by Paleogene, Neogene, and Quaternary molasse complexes, the thickest of which are the sediments of the Maikop marine (5–6 km) and Shirak freshwater-continental (2–2.5 km) (Meotian–Pontian) formations (Radzhabov et al., 1985). Note that significant thicknesses of molasse filling of the Middle Kura basin could result from the tectonic repetition of the same measures in geological sequences and the development of tectonic nappes (Adamiya et al., 1989).

With thickening of the sedimentary cover, the total thickness of crust decreases from 50–52 km beneath the

Isotopic–geochemical features of spontaneous gases of mud volcanoes in Georgia

No. in Fig. 11	Sampling locality	Sampling no.	Sampling date	CO_2	CH_4	N_2	O_2 + Ar	$\delta^{13}C$ ‰ PDB		He	Ne	Ar	$^3He/^4He_{meas}$ ($\times 10^{-8}$)	$^3He/^4He_{corr}$ ($\times 10^{-8}$)	$^4He/^{20}Ne$	$^{40}Ar/^{36}Ar$	Reference
				vol %				CH_4	CO_2	ppm							
1	Akhtala m.v.	9709	1997	1.02	96.16	2.77	0.05	–46.2	–	67.6	0.14	196	130	130	516	333.0	1
1	Akhtala m.v., field 1	GIB1	–	–	–	–	–	–	–	71	0.097	162	135	135	800	355.6	1
1	Akhtala m.v., field 2	GIB2	–	–	–	–	–	–	–	70	0.122	169	139	139	626	352.6	1
1	Akhtala m.v., field 1	–	1977	8.18	89.9	1.75	n.d.	–43.0	–9.8	–	–	–	–	–	–	–	2
1	Akhtala m.v., field 3	–	1977	5.88	90.82	2.13	n.d.	–46.0	–15.8	50	–	–	120	–	–	–	2, 3, 4
1	Akhtala m.v.	–	–	–	–	–	–	–	–	50	–	–	122	–	–	–	3
1	Akhtala m.v., field 4	–	1977	3.03	85.34	11.62	n.d.	–46.4	–8.1	–	–	–	–	–	–	–	2
1	Akhtala spr.	–	–	–	–	–	–	–	–	–	–	–	9.7	–	–	–	4
3	Mzhave (Pkhoveli) spr.	9701	1997	2.48	84.55	12.66	0.31	–47.5	–32.3	7.5	0.69	1510	50.2	47.9	11.9	299.3	1
3	Mzhave (Pkhoveli) spr.	–	–	–	–	–	–	–	–	–	–	–	80	–	–	–	4
2	Pkhoveli m.v.	9702	1997	4.14	76.52	19.15	0.186	–25.7	–	5.2	0.18	201	25	23.9	31.9	302.4	1
2	Pkhoveli m.v.	–	1977	5.39	81.37	13.22	n.d.	–56.7	–15.7	–	–	–	–	–	–	–	2
4	Kila-Kupra m.v.	9703	1997	3.2	93.01	3.62	0.16	–31.1	–11.4	18.5	0.14	133	216	216	145	310.7	1
4	Kila-Kupra m.v.	9704	1997	3.2	93.01	3.62	0.16	–57.7	–	40.6	0.12	116	222	222	369	316.8	1
4	Kila-Kupra m.v.	9704	1997	–	–	–	–	–56.5	–	–	–	–	–	–	–	–	1
4	Kila-Kupra m.v.	9705	1997	–	–	–	–	–45.5	+6.2	26.5	0.14	157	223	223	209	310.8	1
4	East Kila-Kupra m.v.		1977	1.45	97.81	0.33	n.d.	–48.9	–3.0	20	–	–	200	–	–	–	2, 3, 4
5	Zemo-Machkhaani bh.	9706	1997	–	–	–	–	–	–	6.4	0.12	215	116	116	61.2	302.9	1
6	Baida m.v.	9707	1997	8.79	90.42	0.72	0.07	–35.5	–19.2	15.7	0.091	87.8	50.5	50.4	190	300.7	1
6	Baida m.v.	9708	1997	3.04	94.5	2.4	0.06	–23.4	–12.4	15.8	0.16	189	57.3	57.1	110	295.2	1
6	Baida (Aldazhigi) m.v.	–	–	8.08	78.25	n.d.	n.d.	–46.1	+11.7	10	–	–	30	–	–	300.7	4
6	Baida m.v.	–	–	8.28	91.65	n.d.	n.d.	–42.3	+11.3	–	–	–	10	–	–	–	4
6	Baida m.v.	–	1977	–	–	–	–	–	–	10	–	–	51	–	–	–	3
7	Tyul'ki-Tapa m.v., southern gryphon 2	–	–	10.86	89.03	n.d.	n.d.	–	–	10	–	–	55	–	–	–	3, 4
7	Tyul'ki-Tapa m.v., northern gryphon 11	–	–	–	–	–	–	–53.1	+5.9	10	–	–	49	–	–	–	3, 4
8	Polpoi-Tebi m.v.	–	–	–	–	–	–	–	–	20	–	220	53	–	–	–	3, 4
	Lakbe m.v.	–	1977	8.96	72.58	8.52	n.d.	–44.4	+12.9	–	–	–	–	–	–	–	2
9	bh. Lisi-1, 1926–2500 m	–	–	–	–	–	–	–	–	–	–	–	56	–	–	–	

Note: Abbreviations: (m.v.) mud volcano, (spr.) spring, (bh.) borehole; (n.d.) not detected; (–) data absent. Data source: (1) this work; (2) (Valyaev et al., 1985); (3) (Yakubov et al., 1980); (4) (Buachidze and Mkheidze, 1989).

Greater Caucasus to 40–42 km in Southern Kakhety (Shengelaya, 1978; Philip et al., 1989). This phenomenon is attributed to isostatic subsidence of crust owing to sedimentary load and eclogitization of its lower horizons (Krasnopevtseva et al., 1977). The roof of basement in intermontane troughs is traced by geophysical data and exposed at the surface in the Dzirul Massif (Krasnopevtseva et al., 1977). In this area, the basement is made up of Riphean metamorphosed rocks penetrated by Paleozoic volcanic rocks. Crystalline basement of the Transcaucasus, like of the entire Caucasus, was formed during the Baikalian folding.

Noteworthy is that the basement of the Middle Kura basin contains an extended geological body with almost mantle P_v velocities (7.5–7.8 km/s) at a depth range of 20–40 km (Chelidze, 1983). This body is interpreted as mafic–ultramafic intrusion of unknown age.

Manifestations of the Youngest Magmatism

Although the youngest volcanism in the Caucasus segment of the Alpian belt is related to collision setting, the composition of Caucasian volcanics is mainly determined by subduction, which caused heterogeneity in the upper mantle and crust (Koronovskii and Demina, 1996). The youngest magmatism of the Greater Caucasus was thought to be of crustal origin (Milanovskii and Koronovskii, 1973; Koronovskii and Belov, 1987). However, Sr, Nd, and O isotope data showed that magmatic complexes of the Greater Caucasus were derived from mantle source and contaminated with crustal substance to different degrees in the intermediate chambers and volcanic conduits (Bubnov et al., 1995; Bubnov, 2003; Chernyshov et al., 2002).

Many volcanic centers of the Greater Caucasus and Transcaucasus are confined to the sublongitudinal and northeastern pull-apart and strike-slip-thrust structures; i.e., they are related to evolution of the left-lateral Agrakhan–Tbilisi–Levantiya strike-slip zone, which developed in response to spreading of the Red Sea in the Miocene (Koronovskii, 1994). The study area is located to the east of the fault zone, but it can be affected by subsidiary an auxiliary fault zone.

Structural Control of Mud Volcanism

Detailed geological structure of the Kura and Alazan interfluve is discussed in (Khain and Shardanov, 1952; Mamedov, 1968; Yakubov et al., 1980). The Middle Kura basin contains several structures of the lower orders (Fig. 3). The tectonic scheme shows that almost all groups of mud volcanoes are confined to walls of the Alazan and Mirzaan depressions, i.e., to slopes of the Alazan–Agrichai (Kakhety) and Chatminskii anticlinoriums. The exception is the Kila-Kupra volcanic edifice, which is located in the central part of the Mirzaan depression. However, mud volcanic edifices in this area are confined to the local zone of anticlinial folds. Similar trends are observed in other areas of the Caucasian region (Shnyukov et al., 1971; Yakubov et al., 1980).

In the Quaternary, the highest tectonic activity was observed in the northern part of the considered area. For instance, the thickness of Quaternary sediments in the Alazan depression reaches 800 m (Philip et al., 1989). This depression was formed due to local extension accompanying strike-slip deformations (Kopp, 1989). It is separated from the Mirzaan depression by the Kakhety anticlinorium, with the Akhtala (Gurdzhaani) mud volcano on its northern slope and Pkhoveli Volcano on the southern slope (Figs. 1, 3). The Alazan depression and Kakhety anticlinorium are separated by a deep-seated fault representing the continuation of the sublatitudinal Ildokan fracture zone. The Kakhety anticlinorium is the eastern continuation of the Argun–Zhivan zone of the southern slope of the Greater Caucasus. This structure was also developed due to tectonic compression, as indicated by isoclinal imbricated folding. Like in the entire region, folds here are often thrusted and overturned to the south (Yakubov et al., 1980).

The Chatminskii anticlinorium (Priiorskii Rise) with Geokchai anticlinorium (Azerbaijan) as its eastern continuation bounds the southern margin of the Mirzaan depression. En-echelon thrusts separate this rise system from the Lesser Caucasus anticlinorium. Most mud volcanoes of Southern Kakhety, including Baida (Alachyg) group volcanoes, Tyul'ki-Tapa and Polpoi-Tebi volcanoes, are located on the northern slope of the Chatminskii anticlinorium.

CHEMICAL COMPOSITION OF THE GAS PHASE

Major Components

The gas phase of mud volcanic fluids consists of CH_4 with the subordinate N_2 and CO_2 (table). In addition to gas, water, and pulp, the ejecta often contain oil and concentrations of methane homologues in the gas phase can reach a few percents (Buachidze and Mkheidze, 1989).

Proportions of major components in the studied gases significantly vary with time and space (table). In particular, the methane content in Pkhoveli Volcano varies from 99.1 vol % (Lagunova and Gemp, 1978) to 81.4 vol % (Valyaev et al., 1985), accounting for 76.5 vol % during our sampling in 1997. Correspondingly, the contents of other components also varied in such a way that the N_2 content during our sampling reached 19.2 vol %. It is interesting that the simultaneously sampled Mzhave (or Pkhoveli) Spring located near Pkhoveli Volcano contains less nitrogen but more methane than volcanic gases (table), indicating lateral variations in the gas composition.

Variation in the major element composition of gas phase is also characteristic of other volcanoes. For instance, according to (Buachidze and Mkheidze, 1989), the CO_2 content varies from 0.2 to 11.6 vol % at

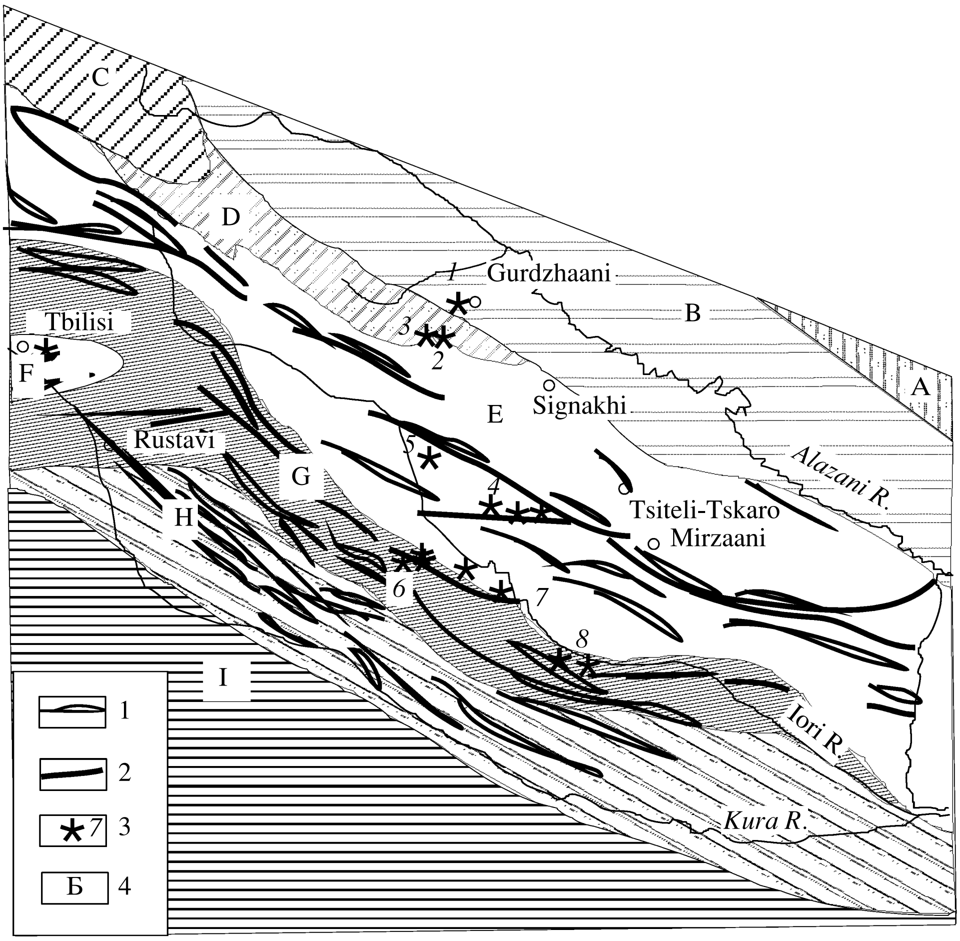

Fig. 3. Distribution of mud volcanoes relative to the main structural elements of the Middle Kura basin.
Note: (1) Structures; (2) faults; (3) mud volcanoes; (4) tectonic zones: (A) Greater Caucausus, (B) Alazan–Agrichai synclinorium (Alazan depression); (C) Argun–Zhivan fold zone; (D) Kakhety anticlinorium, (E) Mirzaan–Aresh synclinorium (Middle Kura or Mirzaan depression), (F) Adzhar–Trialet fold zone, (G) Chatmin anticlinorium, (H) Dzheiranchel synclinorium, (I) Lesser Caucasus.

Kila-Kupra Volcano and from 3 to 11.5 vol % at Baida Volcano. The N_2 content in these volcanoes increases by even two orders of magnitude: from 0.33 to 31 and from 0.72 to 70 vol %, respectively. The CO_2 and N_2 contents at Akhtala Volcano vary within 10 vol % (Valyaev et al., 1985).

Similar variations found in other mud volcanic areas of the Caucasian region, for instance, in the Taman Peninsula (Voitov, 2001), are traditionally regarded as the result of its high tectonic and seismic activity. Variations in gas composition can be caused to some extent by disequilibrium in the gas–water system. However, volcanic gases of the Middle Kura basin are discharged by pulses, when relatively "quiet" stages of methane accumulation in the feeding reservoir (with growth of CO_2 and N_2 fractions in the salse gases) are alternated with periods of its intense discharge.

Inert Gases

Data on contents of He, Ne, and Ar in the studied gases are shown in table. With the single exception of Pkhoveli Volcano (sample 9702), the He content in these gases is higher than 5.24 ppm (i.e., more than air contents). The highest He content (up to 70 ppm) was noted in the gases of Akhtala Volcano.

The Ne content in mud volcanic gases varies from 0.097 to 0.18 ppm. Gas bubbles in borehole with low oil yield (sample 9706) have an intermediate Ne content of 0.12 ppm, which sharply increases up to 0.69 ppm in gases from the Mzhave Spring (sample 9701) located in the vicinity of Pkhoveli Volcano. The same gas is characterized by the maximal Ar content (1510 ppm), whereas other samples contain 88–220 ppm Ar (averaging about 170 ppm), which is almost ten times lower than that in the spring. In general, the Ne and Ar contents are less variable than the He content. Omitting sample from the Mzhave Spring, their variations are no more than two times, the range being significantly narrower than the scatter of N_2 and CO_2 contents.

Correlation between Ne and Ar indicates their atmospheric origin. The He content shows positive correlation with the excess (relative to air) radiogenic ^{40}Ar in sample Ar, i.e., with increase in $^{40}Ar/^{36}Ar$ (Fig. 4).

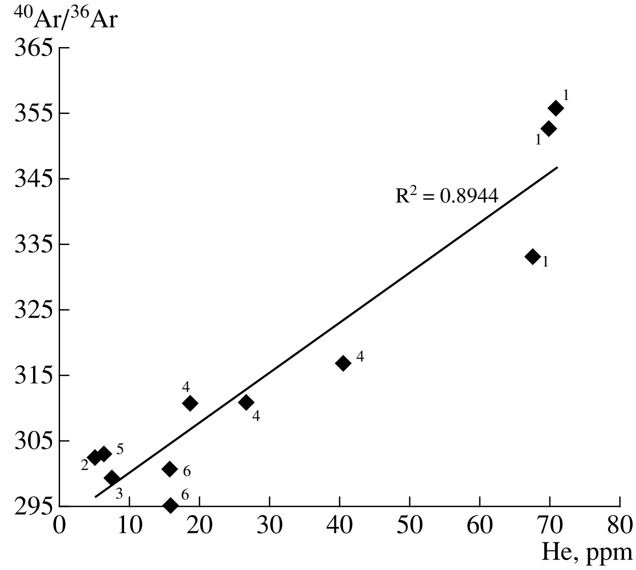

Fig. 4. Variations of the He content vs. the $^{40}Ar/^{36}Ar$ ratio in gases of mud volcanoes in Georgia (numbers correspond to sampling sites, see table and Fig. 1).

HELIUM ISOTOPIC COMPOSITION (R)

Variations in R with Time

In order to recognize systematic spatial variations in the He isotopic composition, it is necessary to estimate the temporal stability of the $^3He/^4He$ ratio in the sampling site after correction for air contamination. In dynamic systems, such as underground fluids, this ratio can be variable like the contents of many gases. Therefore, regional variations can be erroneous.

However, study of the same objects at different times in various regions, for instance over the last 25 years of the 20th century in the Baikal–Mongol region (Polyak et al., 2000), Kamchatka, North Caucasus, Iceland, Italy, New Zealand, Mexico, and other regions, yielded practically identical results, thus demonstrating the temporal stability of He composition in the underground fluids and the absence of interlaboratory deviations. This stability provides ground to compare the results obtained in various sites and at different times in order to recognize the spatial difference in the He isotopic composition of underground fluids.

The same pattern is observed in the study area (table). Sampling of different salses of Kila-Kupra Volcano confirms the previously established high $^3He/^4He$ ~ 2×10^{-6} values in its gases (Matveeva et al., 1978; Yakubov et al., 1980). Well agreement with previous results was also recorded for Akhtala Volcano. At Baida Volcano, $^3He/^4He$ values in our samples from different salses are similar to those obtained in the late 1970s (Yakubov et al., 1980), but they differ from other published values (Buachidze and Mkheidze, 1987; Matveeva et al., 1978). Although, the latter values can be derived from other cones of the complex Baida volcanic edifice (among the three structures studied), the $^3He/^4He$ values (~5×10^{-7}) obtained for Baida Volcano are similar to those for other volcanoes of the same Priorskii rise (Chatminskii anticlinorium).

Distribution of $^3He/^4He$ in the Middle Kura Basin

According to the obtained data, the $^3He/^4He$ ratio in the mud volcanic gases of southern Kakhety varies within an order of magnitude: from 2.5×10^{-7} in sample 9702 (Pkhoveli Volcano) to 2.2×10^{-6} in salses of Kila-Kupra Volcano. It is obvious that the He isotopic composition of underground fluids changes systematically across the Middle Kura basin (Fig. 5). Gases of Akhtala Volcano on the southern wall of the Alazan depression has nearly atmospheric He isotopic composition ($^3He/^4He = (1.30–1.39) \times 10^{-6}$). However, the $^4He/^{20}Ne$ ratio in these gases is thousands of times higher than atmospheric values (table). Based on isotope data (Fig. 6), excess He in these gases is a mixture of crustal He with the canonical radiogenic $^3He/^4He$ (~2×10^{-8}) and mantle He having a MORB $^3He/^4He$ ratio of ~1.2×10^{-5} (Mamyrin and Tolstikhin, 1981). Such isotopic signatures indicate that the contribution of mantle He accounts for about 10%. Southward, on the northern slope of the Mirzaan basin (Mzhave Spring and Pkhoveli Volcano), the $^3He/^4He$ ratio in fluids decreases, indicating a decrease in the mantle He contribution (≤4%). The same contribution is observed in the gases from volcanoes on the southern wall of the Mirzaan depression: Baida, Tyul'ki-Tapa, and Polpoi-Tebi. However, the central part of the depression is characterized by the highest ratios: gases of Kila-Kupra are characterized by $^3He/^4He = (2.0–2.2) \times 10^{-6}$, which significantly exceeds the atmospheric value and corresponds to almost 20% of the contribution of mantle component (Fig. 5). This fact distinctly indicates a discharge of mantle flow in the considered part of the Kura trough. Consequently, the Earth's interiors was characterized by extension setting, which provides their permeability for vertical flows in spite of the great thickness of sedimentary cover (up to 14 km). Similar $^3He/^4He$ $(1.0–3.8) \times 10^{-6}$ ratios were noted in the mud volcanoes of Sakhalin (Lavrushin et al., 1996) and Alaska (Motyka et al., 1989). However, these areas contain manifestations of the youngest magmatism in geological sections or on the surface. Such He composition is rare in sedimentary basins. Exceptions are Sacramento and San Joaquin depressions (Jenden et al., 1988), and the Pannonian basin (Cornides et al., 19986; Deak, 1988; Ballentine

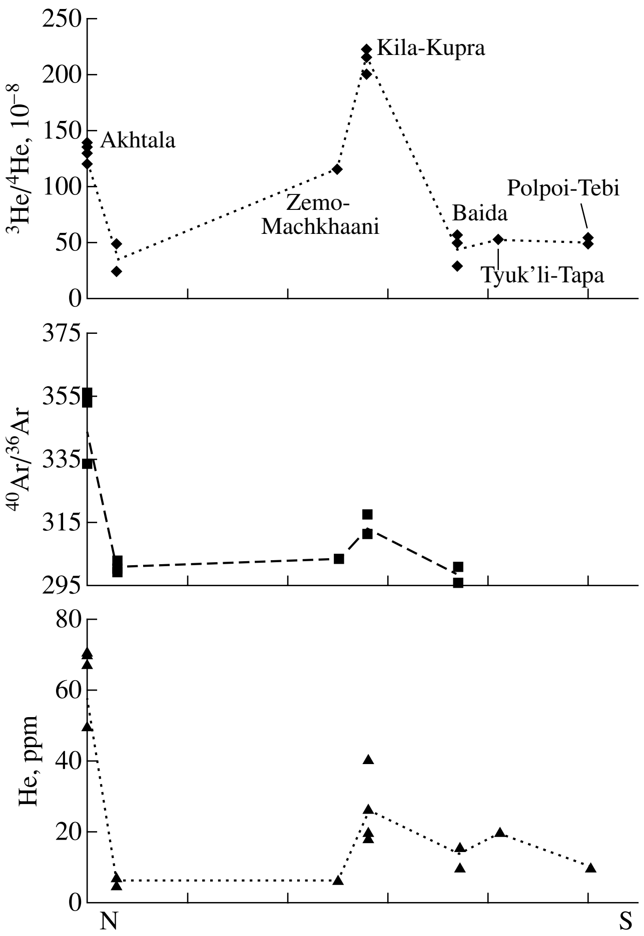

Fig. 5. Isotopic–geochemical features of mud volcanoes in Georgia (profile I–I in Fig. 1 across the strike of the Middle Kura basin).

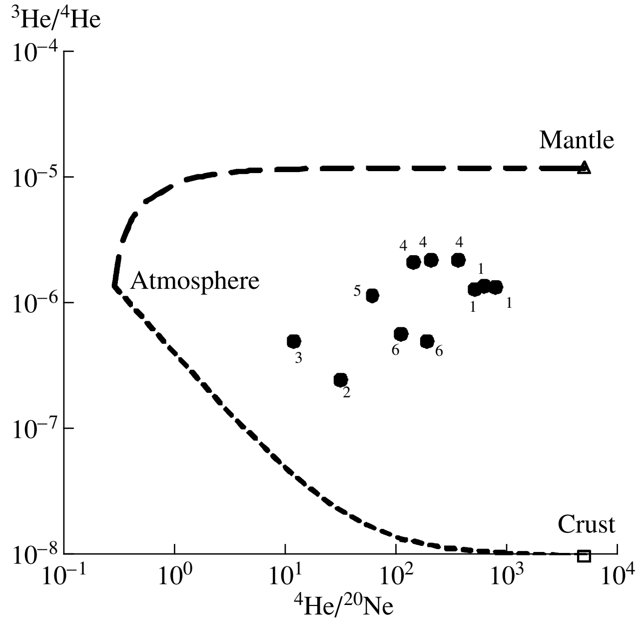

Fig. 6. Variations of $^3He/^4He$ vs. $^4He/^{290}Ne$ in spontaneous gases of mud volcanoes in Georgia (numbers correspond to sampling sites, see table and Figs. 1). Two dotted lines show the mixing curves with air of mantle and crustal gases.

and O'Nions, 1992, 1994). The latter is termed extensional basin produced by crustal extension in response to the ascent of mantle diapir, in contrast to the concurrent pre-Alpian (Molasse) trough and intermontane trough of the Po River (Paduan), which are considered loading basins.

Helium isotopic signs of extension on the Alazan depression wall support previous concepts of its formation (Kopp, 1989). These signs are even more prominent in the central part of the Mirzaan depression and they must be taken into account in reconstructing its tectonic evolution. The helium isotopic composition presumably marks the presence of a deep-seated magmatic body inferred from deep geophysical data. However, the anomaly of Kila-Kupra Volcano may be of local significance. This assumption follows from the decrease of $^3He/^4He$ to 1.1×10^{-6} in gas from the Zemo-Machkhaani borehole located approximately 5–7 km west of the volcano. However, this value is much higher than that measured in mud volcanic gases on the northern (Pkhoveli) and southern (Baida, Tyul'ki-Tapa, and Polpoi-Tebi) walls of the Mirzaan depression.

Helium Isotopic Specifics of Mud Volcanic Fluids from Southern Kakhety

Thus, the results obtained confirm and supplement the published data (Matveeva et al., 1978; Yakubov et al., 1980; Buachidze and Mkheidze, 1989), indicating a significant contribution of mantle He in the studied fluids. This is a distinctive feature of the mud volcanoes of southern Kakhety relative to analogous objects in other regions, for instance in the Indol–Kuban foredeep, where mantle He is practically absent (Lavrushin et al., 1996). Gases sampled from several mud volcanoes in the Lower Kura basin 200–250 km southeast of the study area have a low $^3He/^4He$ ratio. The ratio differs from the canonical radiogenic values, possibly, because they were not corrected for atmospheric He. However, the thickness of sedimentary cover decreases west of Kila-Kupra and the $^3He/^4He$ ratio also decreases to $(5–7) \times 10^{-7}$ in underground fluids of the Georgian Block or Dzirula Massif (Buachidze and Mkheidze, 1989), including thermal waters discharged from the Lisi borehole (table). Thus, decrease in the He isotope ratio along the strike of the Kura trough in both directions from found southern Kakhety maximums recorded in our work constrains the extensional zone.

The helium isotopic composition shows no significant systematic variations in the "anti-Caucasian" strike from the study area. Fold mountain systems of the Lesser Caucasus and Talysh massif, which surround the Kura trough in the south and contain numerous manifestations of young magmatism, are characterized by a distinct contribution of the mantle component in underground fluids, reaching 50% in some places (Matveeva et al., 1978). The fluid manifestation closest to the studied mud volcanoes in the north is the Khzan Or Spring, which is located on the northern slope of the Main Caucasus Ridge about 70 km away from Akhtala Volcano. The spring yields nitrogen–methane gases (62 vol % N_2, 34 vol % CH_4) with $^3He/^4He = 5.3 \times 10^{-8}$, which is close to the canonical radiogenic value (Gazaliev and Prasolov, 1988). The same He isotopic composition was determined in the adjacent springs with a similar gas composition in Mountainous Dagestan (Polyak et al., 1998; Polyak et al., 2000). These gases are interpreted believed to be generating in the molasse sequence of the Terek–Caspian foredeep, which is partly overthrusted by the Dagestan wedge from the southwest. However, the admixture of mantle He appears again in the spontaneous gases of mineral waters further west along the strike of the Greater Caucasus (northwest of the study area). It is especially prominent in the central segment of the Greater Caucasus near the youngest Kazbek and Elbrus volcanic centers, where the highest $^3He/^4He$ ratio approaches MORB values (0.84×10^{-6}) (Polyak et al., 2000). Previous researchers believed that this isotopic He maximum together with the Lesser Caucasus maximum marks *the zone of elevated fluid permeability* (Matveeva et al., 1978, p. 315). However, the same reasons were proposed by these authors to explain the anomaly of southern Kakhety, which was additionally studied by us and is located beyond this zone (Fig. 1 in this work). This fact indicates a more intricate distribution (complex alternation) of extension–compression zones in the collisional setting and confirms the recent concept of tectonic evolution of the Caucasus segment of the Alpian belt (Philip et al., 1989; Koronovskii, 1994, and others).

Extensional settings provide favorable conditions for the intrusion of mantle melts into the crust. In this context, data on the He isotopic composition in the mud volcanic gases of Kakhety independently confirm that the sequence of the Middle Kura basin contains intrusive body, which was distinguished earlier only from geophysical data (Chelidze, 1983). Based on high $^3He/^4He$ ratio, this object can be ascribed to the last (collisional) stage of the magmatic evolution of the Caucasus region.

GAS ORIGIN IN THE LIGHT OF ISOTOPE DATA

Argon

The Ar isotopic composition typically shows some admixture of deep-seated component—excess (relative to atmosphere) radiogenic $^{40}Ar_{rad}$. Its contribution is maximum in the Akhtala gases, where $^{40}Ar/^{36}Ar$ = (333–356). However, its fraction does not exceed 20% of the atmospheric Ar even in this case.

As was noted above and shown in Fig. 4, the fraction of excess $^{40}Ar_{rad}$ in Ar (for 95% confidence probability) correlates positively with the total He content. This is reasonable if ^{40}Ar and ^4He, the predominant He isotope, are of radiogenic origin. At the same time, the obtained data with a lower confidence probability (90%) show signs of positive correlation between $^{40}Ar/^{36}Ar$ and $^3He/^4He$ ratios, i.e., correlation of excess $^{40}Ar_{rad}$ with the contribution of mantle He in fluid (Fig. 5). At first glance, such a correlation could be caused by the influx of radiogenic Ar together with the light ^3He from upper mantle (Ozima and Podosek, 1987; Prasolov, 1990, and others). However, although both these isotope ratios ($^{40}Ar/^{36}Ar$ and $^3He/^4He$) are elevated in the same sites in the southern part of the Alazan depression (Akhtala Volcano) and central part of the Mirzaan depression (Kula-Kupra Volcano), their peak heights show an opposite correlation (Fig. 5), thus indicating the ambiguity of this correlation. It should be noted in this context that the He isotope ratios close to the canonical crustal $^3He/^4He = \sim 10^{-8}$ typically associate with the high $^{40}Ar/^{36}Ar$ ratio in other studied areas, including the Caucasus (Lavrushin, 2002). Therefore, specific combination of He and Ar isotopic signatures in the mud volcanic fluids of eastern Georgia is presumably related to high geodynamic activity of the region. This activity caused the formation of diverse fault zones, which penetrate both sedimentary cover and the basement of the Kura trough and serve as pathways for fluid migration from different sources (crust and mantle), which are marked by different isotopic signatures and mixed in the feeding reservoirs of mud volcanoes.

It is noteworthy that the $^4He/^{40}Ar_{rad}$ ratio in the studied gases varies from 1.2 to 10.6. This value is an indicator of *PT* conditions of the escape of radiogenic gases from the parental rock, because the escape rate of He during heating is higher than that of Ar. Therefore, this ratio in "cold" gases of hydrocarbon reservoirs approaches 20 with decreasing depth (temperature), whereas fluid inclusions in magmatic rocks are characterized by $^4He/^{40}Ar \leq 5$ (Prasolov et al., 1986; Prasolov, 1990). Tectonic brecciation of rocks favors the simultaneous release of radiogenic gases (as at high temperatures).

Simple mixing of mantle and crustal gases should result in opposite relation between $^4He/^{40}Ar_{rad}$ and $^3He/^4He$ ratios. The mud volcanic fluids sampled show no relations between these parameters (Fig. 7). Upon omitting sample 9707 (Baida Volcano) from these data, the reduced sampling with confidence probability of 95% shows a significant positive correlation instead of negative one. Such correlation could arise from the heating of crustal rocks by the intruding mantle melt. The stronger this pulse, the more intense its thermal effect on the host rocks. Consequently, the larger greater amount of released radiogenic gases will be incorporated in the freely circulating intracrustal fluids

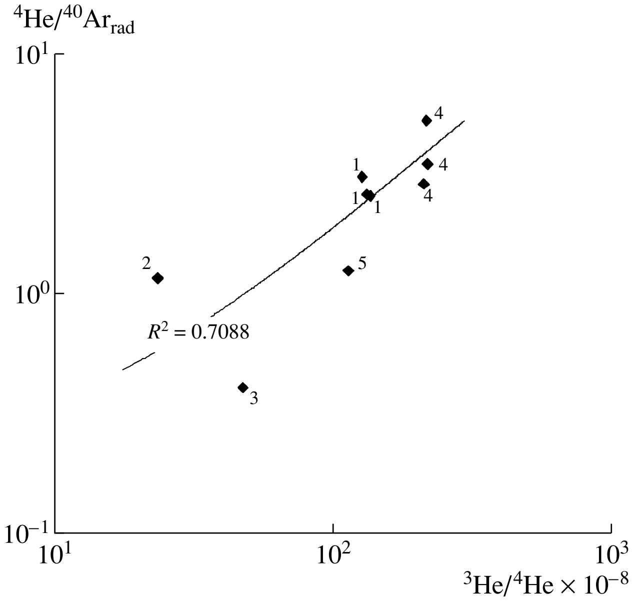

Fig. 7. Variations of $^3He/^4He$ and $^4He/^{40}Ar_{rad}$ in spontaneous gases of mud volcanoes in Georgia (numbers correspond to sampling sites, see table and Fig. 1).

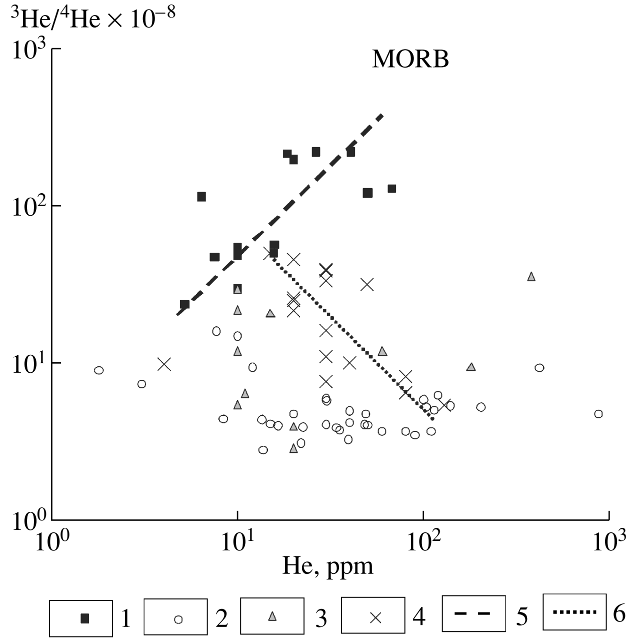

Fig. 8. Variations of $^3He/^4He$ vs. the He content in spontaneous gases of mud volcanoes. (1) Georgia (table); (2) Kerch–Taman area (Lavrushin et al., 1996); (3) Azerbaijan (Yakubov et al., 1980); (4) Turkmenistan (Yakubov et al., 1980; Lavrushin et al., 1996). Lines show inferred trends for gases: (5) Kakhety; (6) Turkmenistan.

(in addition to mantle derivatives released immediately from the melt). Owing to such influx of crustal ^4He, the $^3He/^4He$ ratio in the newly forming fluid decreased steadily relative to those in the intruding melt, as is observed in the mud volcanic gases of eastern Georgia.

The same processes are presumably responsible for the unique specifics of gases of Kakhety volcanoes: positive (Fig. 8) instead of the typical negative correlation of $^3He/^4He$ with the total He content (Polyak et al., 2000). Mud volcanoes having the highest He contents and $^3He/^4He$ ratios (Kila-Kupra and Akhtala) are confined to large tectonic brecciation zones. These zones presumably drain not only fluids forming in the young molasse sequence, but also serve as discharge channels for the deep-seated derivatives (including the mantle-derived ones). The formation of such dependence is presumably related to a very unusual geological setting, when the He content in crustal gases seems to be significantly lower than that in the mantle-derived gases.

This situation can occur in the sedimentary cover of young depressions and/or in rocks of the basement subjected to the youngest tectonomagmatic reworking. In the first case, the young sediments had not enough time to accumulate significant amounts of radiogenic He in gases (more than in mantle derivatives, ~100 ppm). In the latter other case, the high He contents were not preserved. Tectonic brecciation of the basement rocks and intrusion of silicate melt lead to a significant increase in the rate of vertical mass transfer, thus preventing the accumulation of radiogenic He in crustal gases.

In general, these considerations are consistent with geological conditions of the formation of the Kura trough. Its sedimentary cover is mainly represented by young molasse, whereas the underlying and Paleozoic rocks were subjected for a long time to tectonic stresses caused by the intracontinental collision setting.

Carbon-Bearing Gases

The studied gases are characterized by diverse carbon isotopic composition: $\delta^{13}C_{CO_2}$ varies from –19 to +12.9‰ and $\delta^{13}C_{CH_4}$ varies from –57.7 to –23.4‰ (averaging –43.1 ± 4.5‰). The adjacent hydrocarbon reservoirs of eastern Georgia have $\delta^{13}C_{CH_4}$ from –40 to –29‰ (Buachidze and Mkheidze, 1989), while mud volcanoes of Azerbaijan show $\delta^{13}C_{CH_4}$ from –61.2 to –36.6‰ and $\delta^{13}C_{CO_2}$ from –36.9 to + 23.4‰ (Valyaev et al., 1985). Thus, mud volcanoes from southern Kakhety and Azerbaijan have a similar carbon isotopic composition of CH_4, but mud volcanoes of Azerbaijan have the higher $\delta^{13}C_{CO_2}$.

The $\delta^{13}C$ values in the carbon-bearing mud volcanic gases strongly vary both in samples taken simultaneously from different salses and in samples taken at

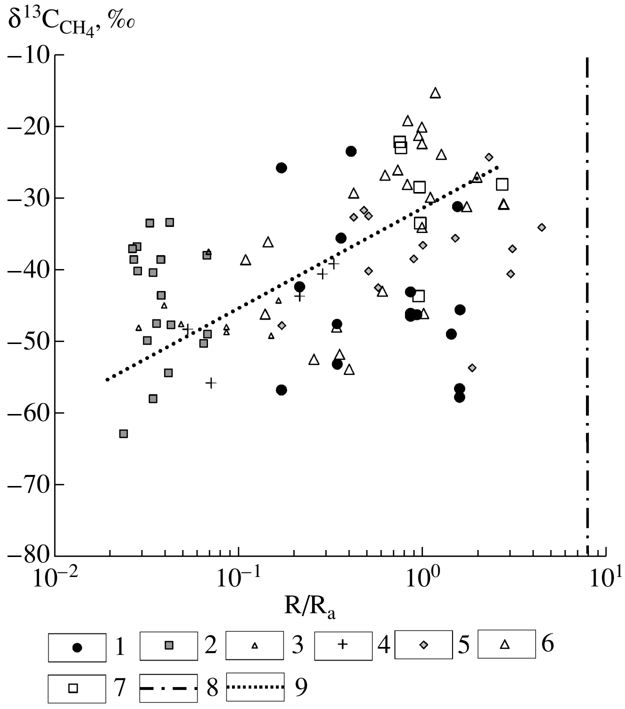

Fig. 9. Correlation of the isotopic composition of helium and methane carbon in mud volcanoes. (1) Georgia; (2) Kerch–Taman area; (3) Azerbaijan; (4) Turkmenistan; (5) Sakhalin (based on table and (Gemp et al., 1970; Valyaev et al., 1985; Yakubov et al., 1980; Lavrushin et al., 1996)); (6) California (Jenden et al., 1988); (7) Alaska (Motyka et al., 1989); (8) curve of mantle end member for island-arc systems; (9) correlation trends.

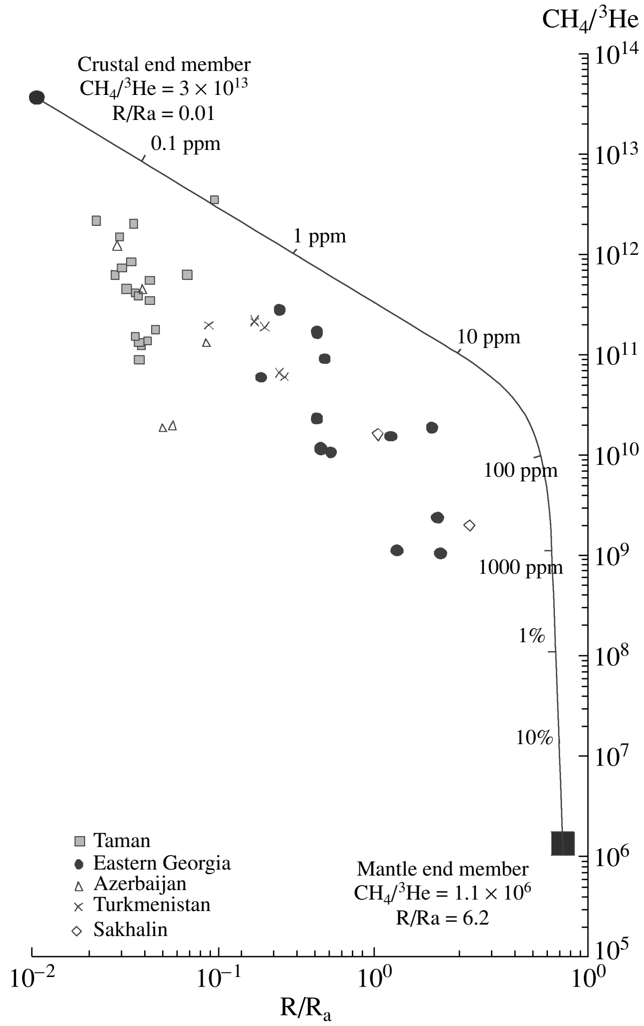

Fig. 10. Correlation of $CH_4/^3He$ vs. R/R_a in the gases of mud volcanoes of the FSU. Line denotes the mixing curve of end members: "crustal" ($CH_4/^3He = 3 \times 10^{13}$ and 0.01 R_a) and "mantle" ($CH_4/^3He = 3 \times 10^6$ and 6.2 R_a) (Jenden et al., 1993).

different years (table). The causes of these variations, especially differences in the composition of synchronous samples from the adjacent salses, are unclear. This phenomenon can be related to the partitioning of carbon isotopes between CO_2 and CH_4 in the gas–solution system. Similar variations of $\delta^{13}C$ were noted in volcanoes of the Taman Peninsula (Voitov, 2001). Hence, application of $\delta^{13}C$ in the mud volcanic gases for estimating their generation temperatures, as was proposed for hydrocarbon fields (Prasolov and Lobkov, 1977; Prasolov, 1990), is doubted.

The $\delta^{13}C$ value in CH_4 and CO_2 shows significant spatiotemporal variations against the background of constant $^3He/^4He$. Therefore, variations in the carbon isotopic composition, like those in the proportions of gas components, were not caused by processes in the sedimentary cover of the Middle Kura basin rather than changes in the mantle flow. The data obtained (Fig. 9) agree with the previously established trend (Lavrushin et al., 1996) of methane enrichment in the isotopically heavy carbon with increasing the He isotope ratio. It is noteworthy that positive correlation between ^{13}C in methane and $^3He/^4He$ ratio is observed not only in mud volcanic gases, but also in methane from stratal reservoirs and mineral springs of California and Alaska (Jenden et al., 1988; Motyka et al., 1989). This trend is possibly a general phenomenon, reflecting the simultaneous increase of "thermogenic" methane and mantle He with increasing temperature in the areas of magmatic activity. However, the fraction of mantle methane (Fig. 10) remains insignificant (no more than 0.1% of the total gas volume) even against such relatively high background He isotope ratios (Lavrushin et al., 1996).

Thus, the data obtained point to a pure crustal origin of mud volcanic gases. However, helium isotope systematics does not provide insight into the mechanism of their generation in crust, because we cannot estimate the contribution of "biogenic" and "abiogenic" sources in the formation of hydrocarbon reservoirs.

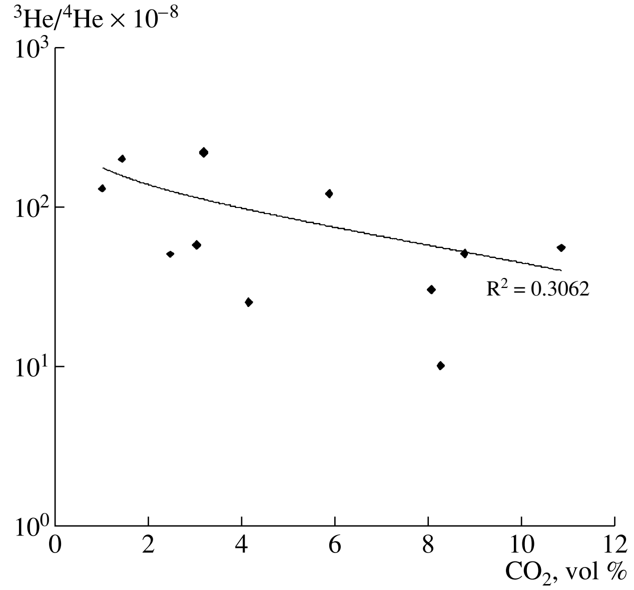

Fig. 11. Variations of R vs. the CO_2 content in spontaneous gases of mud volcanoes in Georgia.

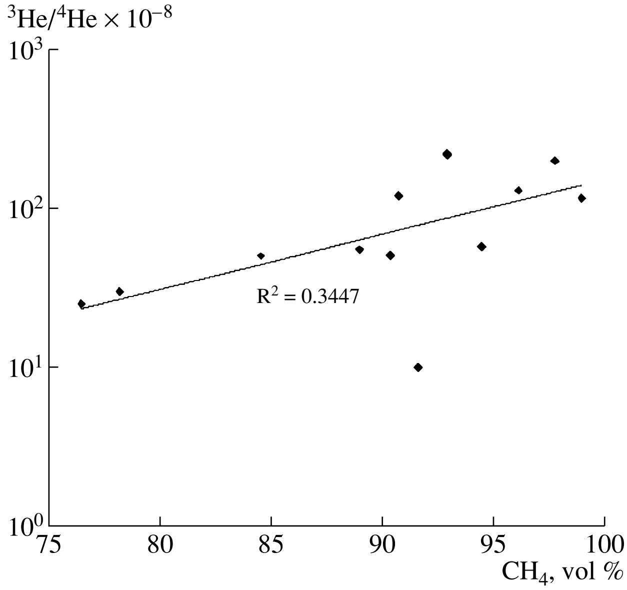

Fig. 12. Variations of R vs. the methane content in spontaneous gases of mud volcanoes in Georgia.

Genetic Features of Gases

Gases of mud volcanoes in Georgia show atypical trend of decreasing CO_2 content (at the expense of CH_4 increase) with increase of the $^3He/^4He$ ratio (Figs. 11, 12). This feature is inconsistent with the generally accepted concepts of gas evolution of groundwaters depending on the effect of magmatic processes (Disler, 1971; Ivanov, 1977; Kononov, 1983, and others). According to these concepts, the tectonomagmatic rejuvenation of ancient fragments of the Earth's crust is accompanied by changes in the chemical composition of underground gases. Contents of methane and nitrogen, which predominate in the gas phase of fluids of ancient continental blocks, sharply decrease with increasing volcanic activity, being present only as admixture against the background of high CO_2 content. This regularity is also valid for the Caucasus, where practically all CO_2-rich gases contain mantle He, whereas N_2- and N_2-CH_4-rich gases are characterized by low (crustal) $^3He/^4He$ ratios (Polyak et al., 2000).

Unusual relations between $^3He/^4He$ and contents of carbon-bearing gases in Kakhety volcanoes can be caused by tectonic setting in the Middle Kura basin. The higher R values are typical of the central part of the basin having the thickest sedimentary cover and, correspondingly, the greatest reserves of sedimentary organic matter, which provides more intense processes of methane generation. In contrast, walls of the basin are characterized by a lower thickness of cover and, correspondingly, more intense napping and faulting. Under these conditions, the carbonate-bearing minerals are probably decomposed to form metamorphogenic CO_2.

CONCLUSIONS

Sampling of mud volcanoes of Kakhety showed that the youngest tectonic processes related to elevated mantle activity were responsible for the specific chemical and isotopic features of volcanic gases.

1. Unlike other mud volcanic areas of the Caucasus, counterparts in the Middle Kura basin contain He with high $^3He/^4He$ (up to 2.23×10^{-6}), which is the product of mantle magma degassing.

2. The highest $^3He/^4He$ ratios were found in volcanoes from the central part of the basin, whereas its walls are characterized by the lower values. This fact presumably reflects the tectonic nature of positive and negative structures of the Middle Kura basin: depressions were formed in the zones of local extension, while anticlines were restricted to the zones of compression.

3. Unlike other strongly varying isotopic-geochemical characteristics of mud volcanic fluids ($\delta^{13}C_{(CO_2,\ CH_4)}$), and general composition of gases and water), the $^3He/^4He$ ratio remains unchanged with time. Therefore, changes in isotopic characteristics and proportions of carbon-bearing gases were caused only by intracrustal processes.

4. Gases of Kakhety demonstrate an unusual direct correlation of $^3He/^4He$ ratio with contents of He, CH_4, and $^{40/36}Ar$ ratio, i.e., with crustal components. This is presumably related to a specific geological structure of the Middle Kura basin, where gases are generated in a thick sedimentary cover owing to high magmatic and geodynamic activity (stress loadings, tectonic napping, thrusting, faulting, and others).

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