Doklady Earth Sciences, Vol. 394, No. 1, 2004, pp. 42–45. Translated from Doklady Akademii Nauk, Vol. 394, No. 1, 2004, pp. 85–88.

GEOCHEMISTRY

Exhalative and Carbon Isotope Instabilities in Gryphon Gases from the Bugaz Mud Volcano and Conjugated Tectonic Structures (Taman Mud Volcanic Province)

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Presented by Academician V.N. Strakhov July 9, 2003

Received July 15, 2003

According to modern concepts, the roots of mud volcanoes in the Taman mud volcanic province are not older than Oligocene [1] and rocks containing the hydrocarbon component of gases are not older than Cretaceous [2]. However, according to petrographic data [3], mud volcanic breccia in the Taman province contain quartz porphyries, glassy obsidians, trachytoids, and igneous rock fragments of Late Jurassic or even older age. Gaseous exhalations from mud volcanoes of the West Kuban longitudinal and Kerch–Taman transverse troughs (particularly, the Bugaz and other mud volcanoes) contain CO_2 with the mantle carbon signature (Table 1) [14].

Gas samples were taken from gryphons of the Bugaz mud volcano in 1995 and 1996. Samples were also taken from gaseous exhalations in deep fracture zones controlling the Bugaz Volcano. Analytical results showed that, in addition to CH_4 and its homologues, CO_2 with mantle signature is also present in these samples (Table 2). At the same time, individual hydrocarbons display a significantly wide range of methane-series components (Table 1).

Gas samples taken in 1995 from exhalations in deep fracture zones, which control the Bugaz mud volcano, contain H, He, CH_4, CO_2, N, and a wide range of methane homologues including pentane (Table 2).

Similar gaseous exhalations are recorded in metasedimentary rocks of the northern and northeastern areas of the Ciscaucasus. Their hydrocarbons have a light composition with methane accounting for 99.99 vol % (Table 1). The content of methane homologues does not exceed 0.00*n* vol %. The majority of samples contain hexane and other methane-series components. They include both normal and isomer forms of butanes and pentanes, as well as unsaturated compounds (olefins), although the olefin content does not exceed the detection limit of hydrogen flame ionization method ($<10^{-5}$%) (Table 2).

It is worth mentioning that the application of hydrogen sensors with a sensitivity of 10^{-6} vol % made it possible to discover a linear zone of hydrogen gas seepage in the rock massif hosting the Bugaz mud volcano [6]. The linear zone spatially coincides with the surface projection of a regional conjugation of Maikopian clays and underlying Paleozoic rocks. This zone is also outlined in the helium field, testifying to the connection of mud volcanic roots with Proterozoic volcanosedimentary rocks (Fig. 1).

Methane carbon samples taken from gryphons of the Bugaz mud volcano in 1995 are characterized by $\delta^{13}C$ values ranging from –39.5 to –46.9‰. These values are 2–3‰ higher relative to those recorded in 2002 (Fig. 2).

At the same time, methane carbon demonstrates higher isotope stability in time relative to CO_2 carbon in samples taken from natural gaseous exhalations in linear fracture zones controlling the Bugaz mud volcano.

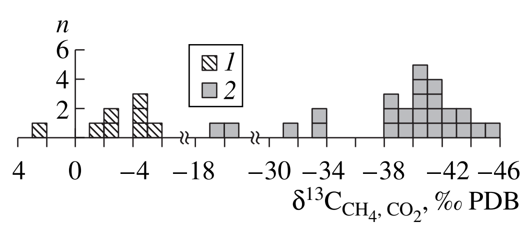

Fig. 1. Summary histogram showing the distribution of the $\delta^{13}C$ value in gases from the Bugaz mud volcano. (*1*) $\delta^{13}C_{CO_2}$; (*2*) $\delta^{13}C_{CH_4}$.

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Table 1. Chemical and isotopic compositions of gases from mud volcanic gryphons of the Bugaz Volcano, Taman mud volcanic province

Ord. no.	Sampling time	Chemical composition, vol %					Isotopic composition, $\delta^{13}C$, ‰ PDB	
		He	N_2	CH_4	Total solid HC	CO_2	CH_4	CO_2
Sept. 9, 1995 (based on data of V.P. Rudakov *et al.*)								
1	10:00	0.0022	0.00	95.03	0.0025	4.97	–32.8	n.d.
2	11:00	0.0037	3.27	88.26	0.0060	4.77	–42.9	n.d.
Sept. 11, 1995 (based on data of V.P. Rudakov *et al.*)								
3	11:00	0.0020	8.99	87.94	0.0038	3.08	–41.7	n.d.
4	11:15	0.0031	0.00	91.14	0.0037	8.62	–42.8	n.d.
5	11:20	0.0031	0.97	90.24	0.0052	8.78	–41.2	n.d.
6	11:45	0.0032	0.00	88.62	0.0026	11.37	–40.1	n.d.
7	12:00	0.0041	1.99	89.45	0.0027	8.55	–41.7	n.d.
8	12:15	0.0032	0.24	93.42	0.0011	6.33	–40.0	n.d.
9	12:30	0.0031	0.00	90.00	0.0094	9.99	–41.0	n.d.
Oct.31, 1996 (based on data of V.A. Alekseev, N.G. Alekseeva, and G.I. Voitov)								
10	08:12	0.000	5.20	73.98	0.280	21.25	–31.1	–1.9
11	08:45	0.0034	2.68	81.00	0.190	19.03	–43.9	–0.8
12	09:00	0.0034	3.80	81.54	0.170	16.42	–39.2	–4.0
13	09:15	0.0000	3.38	78.84	0.170	18.11	–33.1	n.d.
14	09:30	0.0034	9.00	74.52	0.260	19.56	–18.9	–4.6
15	10:00	0.0034	2.02	80.06	0.920	16.15	–45.4	–4.0
16	10:30	0.0085	2.86	78.840	1.340	16.60	–19.7	n.d.
17	11:00	0.0086	2.70	76.68	0.640	18.35	–41.4	n.d.
18	12:00	0.0051	2.90	77.22	1.190	17.87	–38.7	–1.5
19	May 18, 1997	0.0040	1.05	89.40	0.000	9.63	–40.1	+1.5
Sept. 9, 2002 (based on data of G.I. Voitov)								
20		0.003	0.00	85.80	268.34	9.50	–39.5	n.d.
21		0.003	0.00	85.51	210.56	8.21	–38.1	n.d.
Sept. 12, 2002 (based on data of G.I. Voitov)								
22		0.002	18.20	72.09		8.29	–37.6	–4.1
23		0.002	11.44	77.68		8.29	–40.9	n.d.
24		0.002	8.84	82.38		7.00	–38.4	n.d.
25		0.002	21.84	65.69		8.21	–39.6	n.d.

Note: (n.d.) Not determined.

Let us note that the $\delta^{13}C$ value in CO_2 carbon ranges from +7.8 to –8.3‰ PDB, indicating the juvenile or metamorphic origin of hydrocarbon gases in mud volcanoes of the Taman province [4].

Gas samples taken in September 2002 from deep fracture zones are characterized by $\delta^{13}C$ variation from –40.9 to –53.6‰ in methane carbon. The $\delta^{13}C$ value ranges from –18.0 to –46.0‰ in methane carbon from gryphons of the Bugaz mud volcano (Fig. 1).

The chemical and carbon isotopic signatures of gaseous gryphons of the Bugaz mud volcano and gaseous (He- and H_2-rich) exhalations from deep-seated linear fracture zones oriented along the sea coast suggest that the complex gas systems were formed in rocks older

Table 2. Chemical and isotopic compositions of gases from seeps in the fracture zone controlling the Bugaz mud volcano, Taman mud volcanic province

Ord. no.	Sampling time	Chemical composition, vol %					Isotopic composition, $\delta^{13}C$, ‰ PDB	
		He	N_2	CH_4	Total solid HC	CO_2	CH_4	CO_2
Sept. 9, 1995 (based on data of V.P. Rudakov *et al.*)								
1	11:40	0.0036	2.50	59.51		37.89	−42.7	+7.0
2	11:50	0.0053	22.62	55.32		22.06	−40.2	−3.0
3	12:00	0.0041	0.00	89.52		10.77	−42.7	+0.0
4	12:10	0.0013	3.17	87.72		9.09	−42.3	+7.0
5	12:20	0.354	57.75	9.43		32.76	n.d.	−8.0
6	12:30	0.0036	4.99	58.16		36.84	−42.7	+4.0
7	13:30	0.0045	0.00	88.25		11.74	−46.9	+2.0
8	14:00	0.0059	38.16	36.85		24.99	−39.5	−7.0
Sept. 12, 2002 (based on data of G.I. Voitov)								
9		0.002	22.64	61.30		13.39	−53.6	n.d.
10		0.002	23.40	63.10		10.37	−49.3	+2.7
11		0.002	4.36	80.08		13.65	−40.9	n.d.

Note: (n.d.) Not determined.

than Mesozoic and Cenozoic (Fig. 2). Mud volcanic gryphons of the Bugaz mud volcano are indistinct on the daytime surface. On the recent orogenic map of the Taman Peninsula, the gryphons occupy a marginal position in the chain of subaerial mud volcanoes (Bugaz, Polivodin, Severnyi Kiziltash, Vyshestel'bmen, Yuzhnyi Neftyanoi, Kamyshevat, and others) of the Kizeltash anticline [6]. The Novorossisk ring structure (up to 70 km in diameter) identified by A.P. Pronin is located 3 km southeast of the Bugaz Volcano. The available data indicate that the ring structure governs locations of the majority of large seismic events within the northwestern Caucasus, including the seismic shock of November 9, 2002 ($M = 4.9$, $H = 20$ km) (Fig. 3). The ring structure also provides energy required for physico-

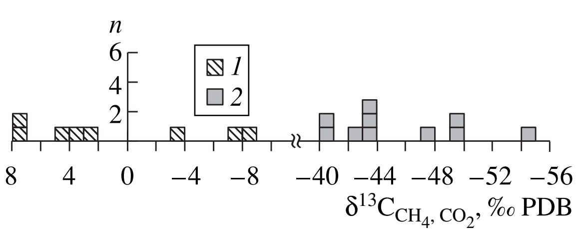

Fig. 2. Summary histogram showing the distribution of the $\delta^{13}C$ value in gases from the fracture zone controlling the Bugaz mud volcano. (*1*) $\delta^{13}C_{CO_2}$; (*2*) $\delta^{13}C_{CH_4}$.

chemical reactions during the formation of petroliferous structures and carbon isotopic fractionation in gases of the oil series. Moreover, this structure is probably responsible for isotopic instability during chain reactions and the consequent mass transfer from the gas generation zone to discharge zones in the Earth's troposphere.

The northwestern sector of the Greater Caucasus witnessed several seismic events with $M > 4.5$ in the second half of the 20th century. Comparison of these earthquakes and the intensity of organic gas generation, which is accompanied by chemical and isotopic instabilities, indicate a sufficiently explicit correlation of the preparation of tectonic earthquake centers with processes of the generation of petroliferous structures in reaction chambers.

Thus, we can make the following conclusions:

(1) The chemical and isotopic compositions of gases from the Bugaz mud volcano are characterized by temporal instability. Juxtaposition of carbonaceous gas generation centers and earthquake hypocenters testifies to the tectonic nature of these processes and the link of earthquake hypocenters with mantle depths. This conclusion is supported by the behavior of carbon isotope parameters. Their mantle signature is frequently recorded in the carboxyl component of natural gases in mud volcanic systems.

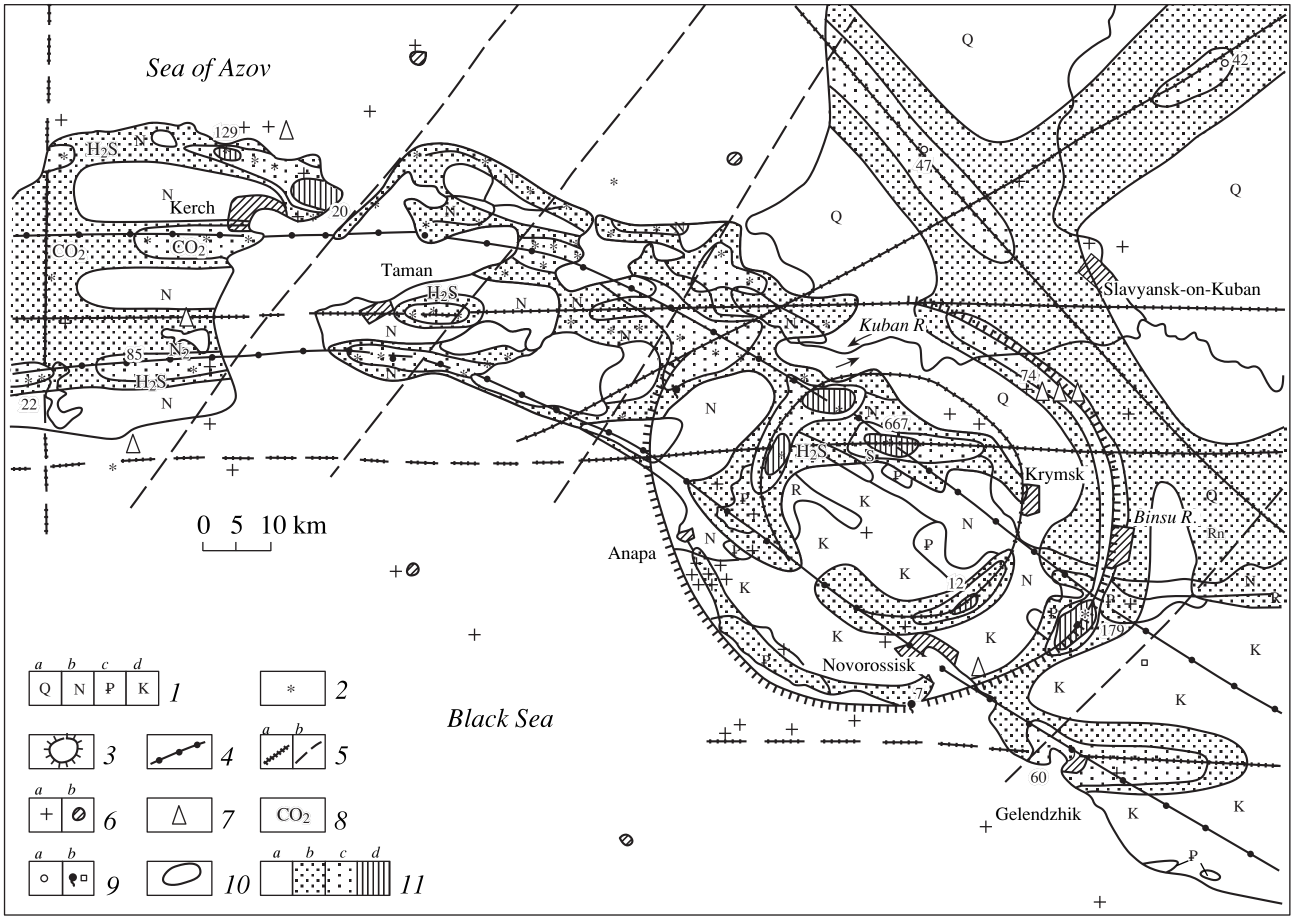

Fig. 3. Map of He field and active fractures in the northwestern Greater Caucasus. (*1*) Sedimentary rocks: (*a*) Quaternary, (*b*) Neogene, (*c*) Paleogene, (*d*) Cretaceous; (*2*) mud volcanoes; (*3*) active fractures in the Novorossisk deep-seated ring structure; (*4*) mantle-related Cenozoic fluid-conducting fractures; (*5*) active linear fractures: (*a*) transregional, (*b*) regional; (*6*) epicenters: (*a*) shallow earthquakes, (*b*) deep earthquakes (hypocenter depth >30 km); (*7*) hydrocarbon manifestations in sedimentary rocks; (*8*) anomalously high concentrations of abyssal gases in groundwaters and mud volcanic exhalations: (CO_2) carbon dioxide, (H_2S) hydrogen sulfide, (CH_4) methane and other hydrocarbons, (Rn) radon, (N_2) nitrogen, (S) native sulfur; (*9*) anomalously high He concentrations (10^{-5} ml/l): (*a*) boreholes, (*b*) springs and wells; (*10*) isolines of He concentration in groundwaters; (*11*) He concentration (10^{-5} ml/l): (*a*) <20, (*b*) 21–40, (*c*) 41–100, (*d*) >100.

(2) The abyssal origin of gryphon gases in the Bugaz mud volcano is also indicated by the following facts. Helium and molecular hydrogen concentrations in the gryphon gases are typical of Paleozoic rocks. The $\delta^{13}C$ values in CO_2 are anomalous. This was previously attributed to the juvenile origin and metamorphic character of carbon isotope in gaseous exhalations derived from mantle depths that governed the Bugaz mud volcano.

ACKNOWLEDGMENTS

This work was supported by the Presidium of the Russian Academy of Sciences (program no. 13, project no. 1.4), the Russian Foundation for Basic Research (project nos. 02-02-16100, 03-05-64020, and 03-05-96704), and the Russian Science Support Foundation.

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