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**GEOCHEMISTRY**

# Paroxysmal Eruption of the Karabetov Mud Volcano, Taman Mud-Volcanic Province (May 6, 2001)

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The paroxysmal stage of the Karabetov mud volcano eruption began May 6, 2001 at 21:00 LT (GMT + 03:00). According to the evidence from the nearest Anapa seismic station located 50 km away from Mount Karabetov, the event was accompanied by weak seismic activity in the region (energy class up to 4.9). The geological examination of consequences of the eruption started immediately after the outburst. As follows from the eyewitness description [1], strong rumbling, bursts of flame, and columns of smoke and dust (up to 100 m high) accompanied the paroxysm. The interpretation of large-scale aerial photographs allowed us to outline the ring structures of the crater field in the explosion center and the lineaments that intersect slopes and summit of the volcano. The eruption center is related to the ~1700-m-long lineament that extends in the northwestern direction. The next center of the volcanic outburst and the mud eruption forming a light breccia field is situated about 500 m away from the first center. The poorly cemented breccia occupies an area of approximately $4 \cdot 10^3$ $m^3$.

As a result of the eruption, the surface of the volcanic source zone was severely deformed and crosscut by a dense network of fissures that served as conducts of dry gases. A rounded mud breccia massif, up to 500 $m^2$ in area and about 800 $m^3$ in volume, was formed in the outburst center. Burning of the mud-volcanic gas at a temperature no lower than 1000–1200°C transformed the clayey rocks into brick-red scoria. Clayey volcanic bombs and lithified volcanic breccia were scattered by the outburst over an area of more than 24 000 $m^2$.

In September 2002, we sampled the dry mud-volcanic gases from the Karabetov mud volcano for the study of their chemical composition and carbon isotopes.

The chemical composition of gases ($CH_4$ and its homologues $N_2$, $CO_2$, $H_2$, and He) were analyzed on a Tsvet-500 chromatograph equipped with gas detectors based on measurements of the thermal conduction and ionization in the hydrogen flame. Low hydrocarbon concentrations were analyzed with ionization detectors in hydrogen flame. Uncertainty of the chromatographic analysis was ±2% of the measured value and increased to ±30% when the concentration of methane homologues dropped to $10^{-6}$%. The uncertainty of chromatographic analysis of nonhydrocarbon gases and high $CH_4$ contents was ±3% of the measured value (Table 1).

The carbon isotopic composition of $CO_2$ and $CH_4$ was determined on an MI-1201 mass spectrometer with an accuracy better than ±0.2‰. Analytical results (Table 2) are given in parts per thousand of $\delta^{13}C$ values referred to the PDB international standard.

As is known [2–4], some mud volcanoes of the Taman mud-volcanic province reveal a close correlation between instabilities of chemical and carbon isotopic compositions of mud gryphon gases and the number of seismic events with magnitudes above 4.5–5.0 in the northwestern sector of the Caucasus region. It is also known that hypocenters of the majority of seismic events within this and other mud-volcanic regions are localized at a depth of 15–20 km. For example, the roots of the largest mud volcanoes in southwestern Turkmenistan, Azerbaijan, and Taman probably reside in Mesozoic sedimentary rocks [5, 6]. It should be mentioned that these roots are localized within or near deep-seated fault zones. For example, the Kipyashchii Bugor mud volcano in the southwestern Turkmenistan is an element of the mud volcanic chain confined to the Gorandag–Okarem zone of deep faults extending toward territory of Iran [7]. In turn, the Dashgil mud volcano in the Shemakha–Kobystan mud-volcanic province of Azerbaijan is situated at the axis of the western pericline of the eponymous fold. This fold is a part of the Alyat Range complicated by steep longitudinal faults [8].

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**Table 1.** Chemical composition of hydrocarbons in dry gases from gryphons of the Karabetov mud volcano (September 5, 2002)

| Sample no. | Concentration, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_3H_8$ | $C_3H_6$ | $i$-$C_4H_{10}$ | $h$-$C_4H_{10}$ | $C_4H_8$ | $i$-$C_5H_{12}$ | $h$-$C_5H_{12}$ |
| 3 | 57.78 | Not analyzed | | | | | | | | |
| 4 | 64.35 | 0.53 | n.d. | 0.2037 | n.d. | 0.0502 | 0.0461 | 0.0024 | 0.0594 | 0.0278 |
| 5 | 70.20 | 0.61 | n.d. | 0.2333 | n.d. | 0.0614 | 0.0708 | 0.0021 | 0.0584 | 0.0282 |
| 6 | 74.17 | Not analyzed | | | | | | | | |

**Table 2.** Chemical composition of hydrocarbons and carbon isotopic composition in dry gases from gryphons of the Karabetov mud volcano (September 5, 2002)

| Sample no. | Concentration, % | | | | | $\delta^{13}C$, ‰ PDB | | |
|---|---|---|---|---|---|---|---|---|
| | $CO_2$ | $CH_4$ | He | $H_2$ | $N_2$ | $CH_4$ | $C_2 + C_3$ | $CO_2$ |
| 3 | 14.16 | 38.45 | 0.005 | n.d. | 28.06 | –31.7 | | n.a. |
| 4 | 14.21 | 48.55 | 0.004 | n.d. | 21.43 | –31.5 | –30.5 | ″ |
| 5 | 14.87 | 66.9 | 0.007 | 0.002 | 14.92 | –31.6 | | ″ |
| 6 | 17.39 | 69.28 | 0.003 | n.d. | 8.45 | –31.7 | | –20.7 |

Occurrences of mud volcanism are spatially and genetically related to the areas with diapiric phenomena in sedimentary sequences. The phenomenon of mud volcanism is attributed to discharge of deep-seated fluids under anomalously high formational pressure [15], dilatation, or compaction [14]. Gases in sedimentary rocks, which serve as the source of mud-volcanic breccia, also play an important role in mud-volcanic activity. Alternation of vigorous eruptions and relative quiescence (free outflow) periods is determined in many respects by specific features of gas generation in the Earth's interior.

In this work, the outburst of the Karabetov mud volcano is used to specify the yield of carbon-bearing gases on the day surface at the paroxysmal stage of volcanic eruption. It should be noted that the estimates mainly based on mud volcanoes in Azerbaijan in different periods differ by two orders of magnitude or even more [8–11].

The average quantity of gas ($\bar{q}$) consumed for the discharge of unit breccia volume is determined as [8]

$$\bar{q} = \int_{d_{\min}}^{d_{\max}} q f(x) dx, \qquad (1)$$

where $d_{\min}$ and $d_{\max}$ are minimum and maximum diameters of fragments and $f(x)$ is the differential function of fragment size distribution. It is assumed that the fragment dimensions are uniformly distributed within a range from 0.001 to 0.1 m.

According to [8], the total quantity of gas ($\bar{Q}$) released during the eruption of the given breccia volume ($W$ = 800 m$^3$) can be estimated as $\bar{Q} = \overline{qW}$,

$$\bar{q} = \frac{3\rho_G \cdot H}{d_{\max} - d_{\min}} \left[\ln\frac{d_{\max}}{d_{\min}} + \frac{2}{v_0}\sqrt{\frac{4(g+a)(\rho_s - \rho_G)}{3\lambda\rho_G}}\left(\sqrt{d_{\max}} - \sqrt{d_{\min}}\right)\right], \qquad (2)$$

where $\rho_G$ is the density of gas at its outlet on the surface; $\lambda = 0.5$; $a = v_0^2/2H$; $\rho_s$ is the density of fragments; $g$ is the acceleration of gravity; and $v_0$ is the initial velocity of fragment scattering (~10 m/s). If $v_0$ = 10 m/s and $H$ = 5 km, $\bar{q} \approx 5 \cdot 10^6 \ \frac{m^3 \text{ gas}}{m^3 \text{ breccia}}$, and $\bar{Q} \approx 4 \cdot 10^9 m^3$.

Let $q_0$ and $q$ be initial and current gas discharges, $Q_0$ be the initial gas reserve, and $Q$ be the quantity of escaped gas. Then, according to [8],

$$q = q_0\left(1 + \frac{k-1}{2}\frac{q_0}{Q_0}t\right)^{-\frac{k+1}{k-1}},$$

$$Q = Q_0\left(1 - \left(1 + \frac{k-1}{2}\frac{q_0}{Q_0}T\right)^{-\frac{2}{k-1}}\right), \qquad (3)$$

where $k$ = 1.3 is the adiabatic exponent, $t$ is the current time, and $T$ is the eruption period in the free outflow regime [8]. The initial discharge $q_0 = v_G\rho_G s$, where $s$ is the total section of all conduits (~1% of the total area of

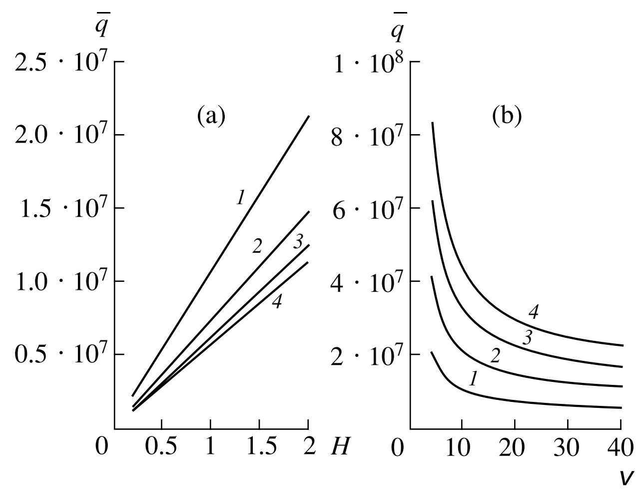


**Fig. 1.** Average quantity of gas consumed for breccia exhumation depending on (a) source depth (*H*) and (b) outflow velocity (*V*). *V* values (m/s): (*1*) 10, (*2*) 20, (*3*) 30, (*4*) 40. *H* values (km): (*1*) 10, (*2*) 20, (*3*) 30, (*4*) 40.

mud occurrence equal to $2.4 \cdot 10^4$ m$^2$). If $v_G \approx 400$ m/s and $\rho_G = 3$ kg/m$^3$, then $q_0 \approx 1 \cdot 10^6$ m$^3$/s. Taking into account that the eruption lasted about 50 min, $Q_0 \approx 3 \cdot 10^9$ m$^3$ (Fig. 1).

The chemically dry gases of the Karabetov mud volcano are mixtures of hydrocarbons of the methane series, homologues (isopentanes, normal pentanes, and hexanes), nitrogen, carbon dioxide, helium, and occasional molecular hydrogen. The helium content corresponds to natural mixtures genetically related to the metasedimentary or granitic basement rocks. The gases remain chemically unstable during a year or more after the mud volcanic outburst; i.e., processes of permanent generation and ascent of oil-series gases from their source to the surface troposphere are accompanied by appreciable changes of their chemical composition (Table 1). Methane and nitrogen contents are variable within the range of 10*n* vol%. Concentrations of methane homologues are more stable.

The carbon isotopic composition of methane is also rather uniform (Table 2) and varies only within analytical uncertainties (0.1‰ of $\delta^{13}$C PDB). This testifies either to the limited dimensions or the uniqueness of methane source with $\delta^{13}$C 10% higher than the average carbon isotopic composition of methane from the catagenesis zone of organic matter in sedimentary rocks [12]. As an alternative, it may be assumed that the source of methane beneath the Karabetov mud volcano resides in Paleozoic rocks. Gas and fragments of high-grade metamorphic rocks are exhumed to the surface during the paroxysmal eruption. Similar fragments were repeatedly found in the mud-volcanic breccia from the Taman province [6]. The mantle source of methane together with rocks characterized by a homogeneous carbon isotopic composition also cannot be ruled out [13].

The generation of hydrocarbon gases of the oil series released from the Karabetov mud volcano was accompanied by enrichment of ethane and propane in heavy carbon isotope in comparison with methane from the same samples (Table 2). This effect is likely related to isotope fractionation in the source at high temperatures and pressures. According to the seismic data [15], sources of the oil-series gases and tectonic earthquake hypocenters are conjugated in space and time.

Thus, one can draw the following conclusions.

The scale of paroxysmal eruption of the Karabetov mud volcano was governed by the spatial position of Mount Karabetov in the system of tectonically active lineaments in the northwestern Taman mud-volcanic province characterized by high subsurface seismoacoustic activity.

Dry gases supplied from gryphons into the subaerial troposphere are mixtures of methane-series hydrocarbons, nitrogen, carbon dioxide, helium, and hydrogen, i.e., gases that are compositionally closest to the gases from the provisional basement of geological structures of the northern Cis-Caucasus region.

The carbon isotopic composition of hydrocarbons from gryphon gases from the Karabetov mud volcano also fits the counterpart from the provisional basement and overlying rocks of the northern Cis-Caucasus region.


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