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Uzon volcano caldera (Kamchatka): A unique natural laboratory of the present-day naphthide genesis

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Abstract

Oil shows from the thermal springs of the Uzon volcano caldera have been studied by gas chromatography–mass spectrometry methods. Based on the composition and distribution of biomarker molecules, their genetic identity with the organic matter of Pliocene–Quaternary deposits has been established. It has been shown that the Uzon caldera is a unique natural laboratory of the present-day oil formation from the organic matter of Pliocene–Quaternary sediments. It has been stated that attempts to consider the compounds forming these oil shows as a product of hydrothermal abiogenic synthesis are absolutely unfounded.

Keywords: Uzon caldera; oil; biomarker hydrocarbons

Introduction

In recent years, in the research literature (particularly in Russia), publications regularly have sprung up, in which conceptions of abiogenic synthesis of oil, lacking the system analysis of the whole set of geological and biochemical facts, are developed. As the most forcible arguments used as an evidence of genetic relation of oil to magmatic chambers, the examples of hydrocarbon (HC) identification in the products of activity of modern volcanoes are generally given. The findings in the Uzon volcano caldera (Kamchatka) are frequently mentioned as an example of these naphthide shows (Beskrovnyi and Lebedev, 1971; Beskrovnyi et al., 1970, 1971).

Brief characterization of the Uzon volcano caldera

In 1969, when examining the Central area of the thermal field, the authors of the works (N.S. Beskrovnyi, S.F. Glavatskikh, B.A. Lebedev, and S.I. Naboko) found oil shows in test pits near the mud pots (Beskrovnyi and Lebedev, 1971; Beskrovnyi et al., 1970, 1971). The oily green, in some cases, colorless, oil spots, odorless or with strong kerosene odour, came to the surface of hot water filling the test pit. To reveal the nature of these naphthides, in 2007–2008, the workers of the IPGG SB RAS and IVS FEB RAS collected and examined the oil shows in this caldera at the up-to-date analytical level (Fig. 1). The results of these investigations are reported in this paper.

The Uzon–Geyser volcano-tectonic depression is located in the central part of the Eastern volcanic belt of Kamchatka and represents an oval-shaped kettle of 15 × 7.5 km in size, almost up to the top filled (in the southeastern sector) with the young extrusive domes. The caldera basement, occupying the western sector of the depression, is underlain by a complex of Pliocene volcano-sedimentary deposits. The present-day appearance of caldera has formed about 40 kyr years ago after a phase of intense eruptions. Gas jets with a temperature of 97–99 °C, mud pots, thermal springs, and warm lakes occur in fumarole fields. According to estimates, the temperature could reach 200–250 °C at a depth of 500 m (Karpov, 1988).

The lakes, forming at the bottom of calderas and in zones of active water-, and gas exchange, are inhabited with specific microorganisms: mesophylls growing at temperatures below 40 °C, thermophylls growing at temperatures from 40 to 70 °C,

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Fig. 1. Uzon volcano caldera.

and extreme thermophylls that grow at temperatures above 70 °C (Zavarzin et al., 1989).

The lacustrine sediments of the postcaldera complex, which are composed of a relatively thick (to some hundreds of meters) sequence of ash-pumice, psammitic and psephitic acid tuffs, penetrated by extrusive domes and products of eruptive volcanism, contain spores, pollen of plants, and remains of diatomic algae of the Middle–Late Pleistocene age (Beskrovnyi et al., 1970). The organic carbon content in sediments varies from 0.2 to 1.4%.

Geochemistry of oil from the Uzon caldera

The hydrocarbon type content of oil shows from the Uzon caldera is dominated by hydrocarbons (90–93%). Among them, the saturated HC by weight are twice as much as the aromatic ones. The concentration of heterocyclic compounds accounts for 7–10%. The content of asphaltenes in the examined samples is very low, no more than 0.3%.

C_{10}–C_{37} *n*-alkanes, aliphatic isoprenanes (C_{13}–C_{25}), steranes (C_{21}–C_{22} and C_{27}–C_{30}), and terpanes (C_{19}–C_{35}) have been identified in the fraction of saturated hydrocarbons. The distribution of normal alkanes in oil is unimodal, with the peak (10–16% of the total *n*-alkanes) at C_{18}–C_{20} hydrocarbons (Fig. 2). The ratio of C_{27}/C_{17} *n*-alkane concentrations in oil is <0.2. The CPI is equal to 0.9–1.0.

Monomethylalkanes and isoprenanes have been identified in isoalkanes. The aliphatic isoprenanes are dominated by phytane and pristine (to 53% of the total isoprenanes). The

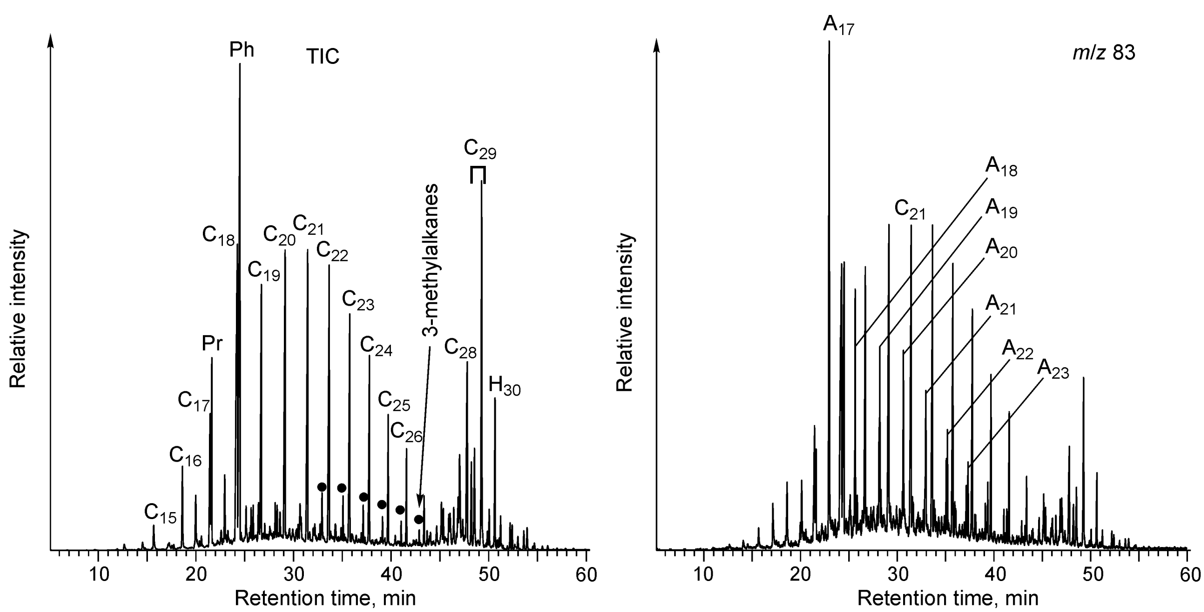

Fig. 2. Chromatogram of total ion current (TIC) for saturated hydrocarbons and mass fragmentogram of alkylcyclohexanes (*m/z* 83) of oil from the Uzon caldera. C_{15}–C_{26}, *n*-alkanes; C_{28}, C_{29}, steranes; H_{30}, hopane; Ph, phytane; Pr, pristine; $A_{17–A23}$; alkylcyclohexanes.

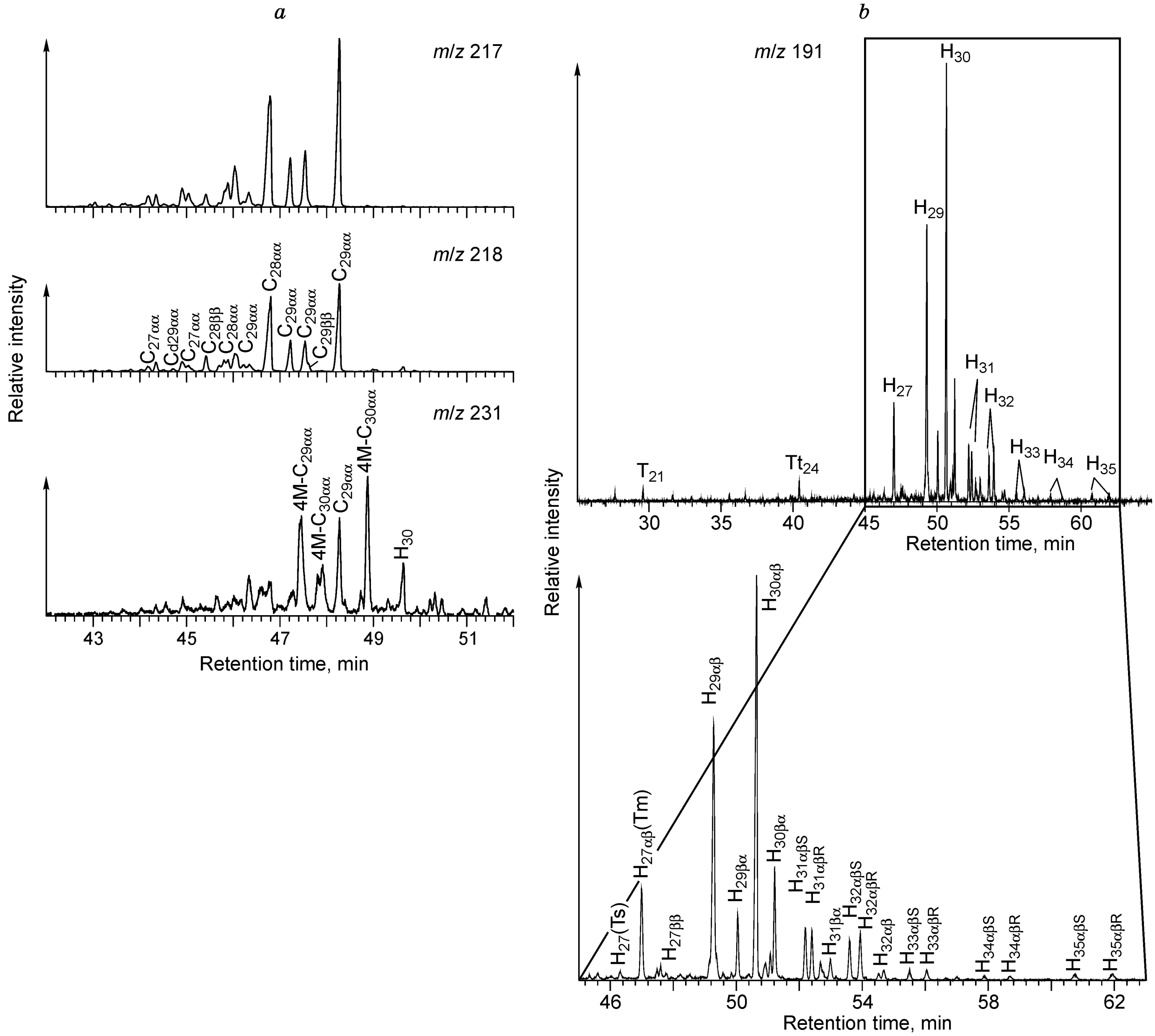

Fig. 3. Mass fragmentogram of steranes (*a*) and terpanes of the saturated fraction of oil from the Uzon caldera (*b*). T_{21}, tricyclane; Tt_{24}, tetracyclane.

Pr/Ph ratio in the oil shows is <0.5. The concentration of normal alkanes is three times greater than that of isoprenanes. The monomethylalkanes have the highest concentrations of 3-methylalkanes (Fig. 2).

The high-molecular weight cycloalkanes in the caldera oil are represented by steranes, terpanes, and hydrocarbons of homologous series of alkylcyclohexanes. The latter are well seen in *m/z* 83 mass fragmentograms (Fig. 2).

In the examined oil shows, the concentrations of steranes and normal alkanes are close (Fig. 3, *a*). Ethylcholestanes (C_{29}) dominate in steranes (C_{27}–C_{30}). C_{27}, C_{28}, C_{30} steranes, in decreasing order of concentrations, form the following series: $C_{28} > C_{27} > C_{30}$ (Fig. 3, *a*). The C_{29}/C_{27} ratio is higher than 2.5. In the C_{27}/C_{29} hydrocarbons of homologous series of steranes, αα-isomers account for to 85% of the total isomers (Fig. 3, *a*). As seen from Fig. 3, in the examined oil, methyl-, and ethylcholestanes contain ββ-isomers, while they are absent from the cholestane composition. The *m/z* 231 mass chromatogram shows the presence of 4-methyl-αα-C_{29}–C_{30} steranes, the precursors of which generally are synthesized by diatoms (Fig. 3, *a*).

The terpanes (C_{19}–C_{35}) have the highest concentrations of hopanes (49–77% of the total terpanes) (Fig. 3, *b*). The content of tricyclanes (C_{19}–C_{31}) accounts for from 6 to 35% and that of moretanes from 6 to 15% of the total terpanes. The hopanes (C_{27}–C_{35}) and the moretanes (C_{29}–C_{32}) show the maximum concentrations of C_{30} hydrocarbons (30–41% of the total hopanes and 47–51% of the total moretanes). The Ts/Tm hopane ratio is <0.1 that indicates the low level of their thermal maturity (see Fig. 3, *b*).

The tricyclanes have the maximum concentrations of C_{19}–C_{20} hydrocarbons (23–33% of the total tricyclanes). The content of C_{23}–C_{26} tricyclanes accounts for 25–27% of the total tricyclanes. The C_{28}–C_{31} hydrocarbons account for from 12 to 33% of the total tricyclanes. The $(2(C_{19} + C_{20})/\Sigma C_i;\ i = 23, 24, 25, 26)$ tricyclane index (Kontorovich, 2000) is >2 in oil shows.

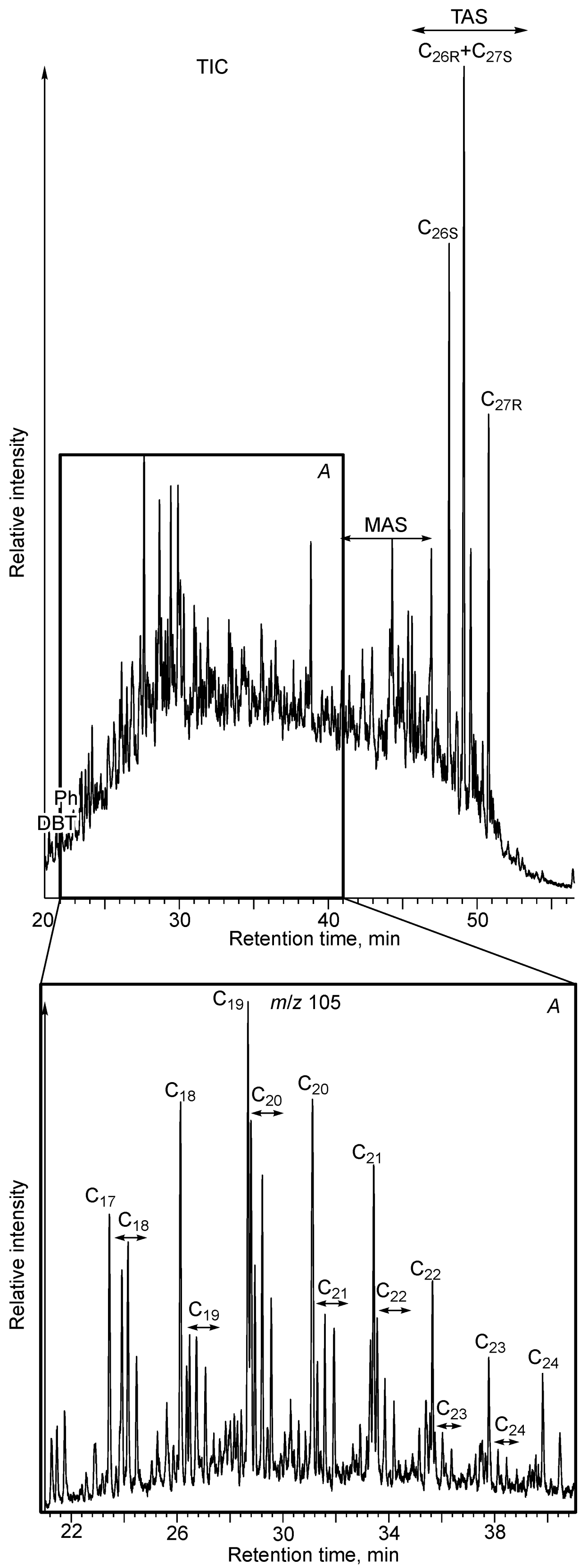

Fig. 4. Chromatogram of total ion current (TIC) for aromatic hydrocarbons and mass fragmentogram of methylbenzenes (*m/z* 105) of oil from the Uzon caldera. DBT, dibenzothiophene; Ph, phenanthrene; MAS, monoaromatic steroids; TAS, triaromatic steroids.

In the *m/z* 178, 192, 184, 198, 253, 231 mass fragmentograms of the aromatic fraction of oil shows, phenanthrenes, methylphenanthrenes, mono-, and triaromatic steroids are present, as well as dibenzothiophenes. The concentrations of triaromatic steroids are predominant among these compounds (51.96–80.40%). The value of triaromatic/monoaromatic steroid concentration ratio varies from 1.18 to 4.39. The concentration of phenanthrenes and dibenzothiophenes does not exceed 2.69 and 0.91% of the total polycyclic aromatic compounds. Alkylbenzenes (*m/z* 92), methylbenzenes (*m/z* 105), biaromatic hydrocarbon (*m/z* 205), and triaromatic dinosteroids (*m/z* 245) have been identified in the aromatic fraction. The concentrations of alkylbenzenes and methylbenzenes are comparable with those of alkycyclohexanes (Figs. 2 and 4).

Living matter as the source for Uzon oil

The composition of saturated and aromatic hydrocarbons in oil shows of the Uzon caldera shows that they have been derived from lipids of the remains of land plant brought in sediments (the C_{29}/C_{27} sterane concentration ratio >2.5, the tricyclane index $2(C_{19} + C_{20})/\Sigma C_i$ (i = 23, 24, 25, 26) >2.0, relatively high concentration of triaromatic steroids), aquabionts, inhabitants of caldera sediments and bottom waters (ratio of n-C_{27}/n–$C_{17} < 0.2$, Pr/Ph < 0.5), and the living matter of bacteria (hopanes). This source for lipids of initial living matter is also confirmed by the carbon isotope composition of fossilized organic matter ($\delta^{13}C = -28.3$‰).

The above-described results of investigations of the caldera oil composition agree with the earlier geochemical studies (Bazhenova et al., 1998; Simoneit et al., 2009).

Judging from the composition of biomarker hydrocarbons of oil, the level of initial organic matter maturity corresponds the very beginning of the main phase of oil generation. This is also indicated by the ratio of even to odd *n*-alkanes (close to unity), high concentrations of $\alpha\alpha$-steranes and at the same time, the absence of biohopanes higher than C_{27}, the predominance in homohopanes of *S*-isomers over *R*-isomers, low values of the Ts/Tm hopane concentration ratio, low values of phenathrene and dibenzothiophene indices (0.6–1.1 and 0.3–1.2, respectively) (Kontorovich et al., 2004).

Uzon caldera as a natural laboratory of the present-day oil generation

The Uzon caldera is a natural system, in which, owing to the discharge of high-temperature hydrotherms, sediments almost from the very surface are heated to temperatures that in the classic petroliferous basins occur at depths of 2–3 km and deeper. Under these conditions, on real-time basis, organic matter destruction and generation of hydrocarbons and heterocyclic compounds of oil occur in Pliocene–Lower Quaternary sediments of the Uzon volcano caldera. The specific character of forming hydrocarbons, due to a short duration of this experiment of Nature and relatively low temperatures, is that the bulk of oil hydrocarbons from the Uzon caldera inherit the hydrocarbon skeleton and lipid stereochemistry of the initial living matter. In these "young" formations, the biomarker abundance becomes apparent to a greater degree than in "normal" oils. Using the methods of ^{14}C isotopic geochronology, the age of Uzon oil has been estimated at 940 ± 40 ka (Simoneit et al., 2009).

In other words, the Uzon caldera represents a natural laboratory of recent generation of oil from the organic matter of Pliocene–Lower Quaternary sediments.

Attempts to consider the compounds forming these oil shows as a product of abiogenic synthesis of hydrocarbons are absolutely unfounded (Simoneit et al., 2009). The foregoing confirms M.K. Kalinko's hypothesis (1975) stated earlier that due to the impact of hydrotherms, oil is generated from the recent organic matter buried in sediments at the present moment of geological time.

Uzon volcano caldera (Kamchatka) is a unique natural laboratory of the present-day naphthide genesis.

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