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# Composition of Hydrocarbons in Diamonds, Garnet, and Olivine from Diamondiferous Peridotites from the Udachnaya Pipe in Yakutia, Russia

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ABSTRACT

Volatile components in diamonds, associated garnet (pyrope), and olivine from two extremely rare xenoliths of diamondiferous peridotites recovered from the Udachnaya kimberlite pipe in Yakutia, Russia, were analyzed by gas chromatography–mass spectrometry (GC–MS) using a Focus DSQ II Series Single Quadrupole GC–MS (Thermo Scientific, USA). These xenoliths are pyrope lherzolite and pyrope dunite based upon compositions of coexisting minerals. Unlike the pyrope lherzolite, which contained pyrope with moderate calcium (Ca)-component content (about 15 mol%), the dunite contained subcalcic chromium (Cr)-pyrope with low Ca-component content (less than 10 mol%). All investigated minerals contained dominating hydrocarbons and their derivatives represented by aliphatic (paraffins, olefins), cyclic (naphthenes, arenes), oxygenated (alcohols, ethers), and heterocyclic (dioxanes, furans) hydrocarbons; nitrogenated, chlorinated, and sulfonated compounds; carbon dioxide ($CO_2$); and water ($H_2O$). The relative concentration (rel%) of total hydrocarbon was 79.7 rel% for diamonds, 69.1 rel% for garnet, and 92.6 rel% for olivine, with a general amount of components ranging from 161 to 206. New data on volatiles in diamonds, associated garnet, and olivine suggest the presence of a wide spectrum of hydrocarbons along with nitrogen ($N_2$), $CO_2$, and $H_2O$ in some upper mantle areas.

## 1. Introduction

The nature and composition of fluids in the Earth's mantle and their role in magmatic and mineral formation are still one of the most controversial problems in geology, and continue to attract the attention of researchers. Despite considerable progress, many questions remain debatable concerning the composition of the fluid and the redox conditions in the deep geological processes associated with the nucleation and growth of diamond. Modern models of diamond formation, based on a complex of extensive mineralogical, geochemical, and experimental data, are constructed taking into account the significant role of C–O–H fluid in mantle mineral-forming processes.

The composition of fluids from the upper mantle is available for direct study in the form of fluid and melt inclusions in minerals of various deep xenoliths and natural diamonds [1–17].

Due to mechanical properties and chemical inertness, diamond is the best natural material for the conservation and transportation of mantle fluids to the surface [18,19]. Diamond is extremely important as the most reliable "container" that preserves high pressure inside the inclusions and retains its original chemical composition under room conditions [5–10]. Experimental studies carried out in recent years have shown that at the pressure–temperature (*P–T*) parameters of the upper mantle, it is possible to perform abiogenic synthesis of not only hydrocarbons corresponding to natural gas, but also hydrocarbons with a high molecular weight up to hexadecane ($C_{16}H_{34}$) [20–23].

Sobolev [24] was the first to advance the hypothesis of a significant role of deep hydrocarbons and carbon dioxide ($CO_2$) in the formation of natural diamonds. Hydrocarbons heavier than methane have been detected and studied using microthermometry, Raman spectroscopy, and infrared Fourier spectroscopy in primary fluid inclusions in diamond from placers and garnets from diamond-bearing eclogites from Yakutian kimberlite pipes, and in diamond from placers of the Urals (Fig. 1) [3,5,17]. The most recent chromatographic-mass spectrometric studies of olivines and picroilmenites from Yakutian kimberlite pipes and diamonds from northern Anabar placers have shown that they contain predominantly hydrocarbons and their derivatives: aliphatic
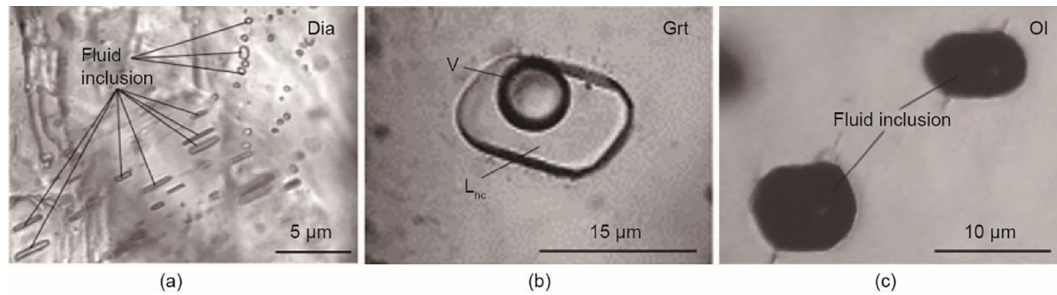
**Fig. 1.** Micrographs of primary fluid inclusions. (a) High-density fluid inclusions in super-deep diamond from the Ural alluvial deposits, Russia [5]; (b) partially decrepitated liquid hydrocarbon inclusion in garnet of the diamondiferous eclogite from the Udachnaya kimberlite pipe [3]; (c) partially decrepitated faceted fluid inclusions in the crystal of olivine from the Udachnaya kimberlite pipe [17]. Dia: diamond; Grt: garnet; Ol: olivine; V: gas; $L_{hc}$: liquid hydrocarbons.

(paraffins, olefins), cyclic (naphthenes, arenes), oxygenated (alcohols, ethers, aldehydes, ketones, and carboxylic acids), and heterocyclic (dioxanes, furans) hydrocarbons; and nitrogenated, chlorinated, and sulfonated compounds. Water ($H_2O$) and $CO_2$ are present in clearly subordinate quantities [11,12,15].

This paper presents the results of semi-quantitative determination of the composition of volatiles captured by diamonds, garnet, and olivine from two extremely rare and unusual xenoliths of diamondiferous peridotites from the Udachnaya pipe, Yakutia, by gas chromatography–mass spectrometry (GC–MS) in order to enable a better understanding of the fluid variability within the diamond stability field of the upper mantle, 150–200 km below the Earth's surface [19].

## 2. Samples

### 2.1. Diamonds and garnet (pyrope) from the diamondiferous lherzolite (sample U-331)

Diamond inclusion studies have established two main types of mantle environment for diamond formation: subcratonic lithosphere peridotitic and eclogitic [19].

A unique diamondiferous garnet peridotite xenolith was recovered from the Udachnaya pipe consisting of enstatite and lherzolite pyrope with lesser amounts of olivine [25,27]. The modal abundances of the minerals are (in vol%): diamond (9.5); enstatite (38); pyrope (35); olivine and chromdiopside (< 0.1); sulfides (4), including pyrrhotite, pentlandite and djerfisherite [26], with the remainder being alteration products along with the majority of diamonds (Figs. 2 and 3) [25]. This 10.5 g peridotite contains more than 30 000 colorless, octahedral microdiamonds with sizes ranging from 10 to 300 µm (Fig. 2), many of which occur in clusters [25].
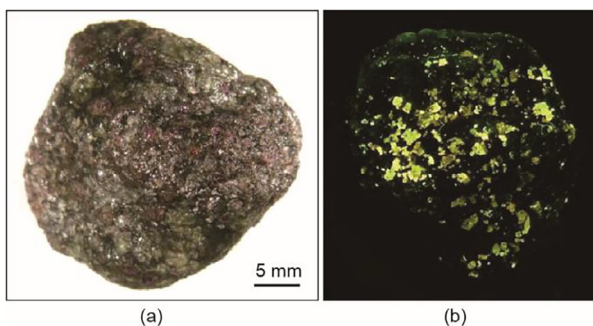


**Fig. 2.** Photographs of the unique diamondiferous lherzolite U-331 from the Udachnaya pipe with visible purplish garnets, (a) pale green enstatite and (b) yellow luminescent diamonds under a luminescent lamp [25].
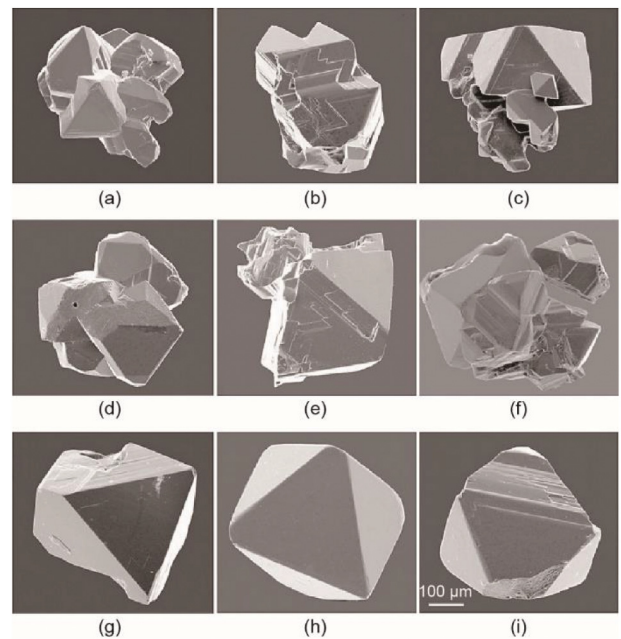


**Fig. 3.** (a–f) Typical polycrystalline diamond clusters and (g–i) microdiamonds crystals from the U-331 lherzolite xenolith. Note the totally euhedral morphology with perfect octahedrons. Reproduced from Ref. [25] with permission of Elsevier, © 2015.

This sample of diamondiferous pyrope lherzolite is a truly unique xenolith, mainly due to the thousands of microdiamonds present, which are rock-forming minerals. The $\delta^{13}C$ of the diamonds is −22.9‰, which is not characteristic of the mantle ($\delta^{13}C$, −2‰ to −8‰ Vienna Pee Dee Belemnite (VPDB)) [27,28]. The light carbon isotopic composition is consistent with a crustal signature resulting from the subduction of organic carbon [29]. The diamonds are Type IIa. Compositions of peridotitic pyropes from diamondiferous peridotite xenoliths from Russian and other kimberlites on a $Cr_2O_3$–CaO plot are presented in Fig. 4 [25].

### 2.2. Olivine from the diamondiferous dunite (sample Us-221)

An early study of the mineral inclusions in diamonds [30] established a harzburgitic (dunitic) assemblage without clinopyroxene but with subcalcic chromium (Cr)-pyrope. The latter was represented as megacrystalline rock, often consisting of large olivine macrocrysts with inclusions of diamonds, Cr-pyrope, and chromite. The first studied altered rocks of this type were recovered from the Aykhal pipe and contained Cr-pyrope, serpentine, diamond, and chromite [31].
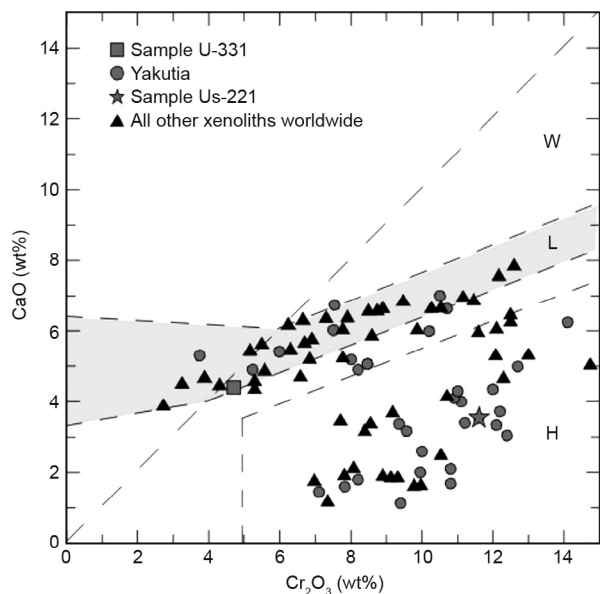
**Fig. 4.** Compositions of peridotitic garnets on a $Cr_2O_3$–CaO plot, from diamondiferous lherzolite xenoliths worldwide. Note the garnet composition for U-331, which plots just inside the lherzolitic field. Data sources are referenced in text. Solid boundaries for garnet parageneses as well as data source are from Ref. [25]. H: harzburgitic; L: lherzolitic; W: wehrlitic parageneses.

The available megacrystalline diamondiferous dunite is composed of large (2 cm) unaltered olivine with embedded diamond and two subcalcic Cr-pyrope grains. The diamond contains inclusions of olivine and chromite. The olivine inclusion in the diamond contains less FeO (6.35 wt%) than the host olivine (FeO, 6.70 wt%), indicating a higher forsterite content of this inclusion [32] and the syngenetic nature of the diamond. Sample Us-221 is a unique representative of a megacrystalline dunite containing olivines of different compositions; one grain is enclosed in diamond and major part of dunite is composed of host olivine [33], which was the reason for its selection for a volatiles study in completely unaltered olivine.

## 3. Experimental procedure

The volatiles were analyzed with the coupled GC–MS method using a Focus DSQ II Series Single Quadrupole GC–MS analyzer (Thermo Scientific, USA) [21,34,35]. The gas mixture was released from the sample by means of shock mechanical crushing in a custom-designed crusher. The crusher was heated to 160 °C and flushed with helium (He) to remove adsorbed volatiles. The released mixture was entrained in an He stream, without cryogenic focusing. Each analytical run was preceded and followed by blank analyses, which were later used in data processing.

The gas mixture was injected into the analytical column of the GC–MS instrument through a 6-port 2-position Valco (USA) valve thermostated at 290 °C, at a constant He flow rate of 1.7 mL·min$^{-1}$, using vacuum compensation. The GC–MS transfer line temperature was held at 300 °C. The gas mixture was separated in a Restek Rt-Q-BOND capillary column (100% divinylbenzene as a stationary phase; length 30 m; inner diameter 0.32 mm; film thickness 10 μm).

The temperature program of the GC separation comprised an isothermal stage (70 °C for 2 min) followed by two heating ramps (25 °C·min$^{-1}$ to 150 °C and 5 °C·min$^{-1}$ to 290 °C), followed by the final isothermal stage at 290 °C for 100 min. Total ion current (TIC) electron ionization spectra were collected on a quadrupole

mass-selective detector in the full scan mode at an electron energy of 70 eV and an emission current of 100 μA. Other experimental parameters included an ion source temperature of 200 °C, a multiplier voltage of 1500 V, positive ion detection, a mass range of 5–500 u; a scan rate of 1 scan per second and a mass rate of 506.6 u·s$^{-1}$. The start time of the analysis was synchronized with the shock crushing of the sample.

The procedure for preparing the sample for analysis excluded its contact with any solvents and other possible contamination. The input of the mixture extracted from the sample during the shock destruction was carried out online in the He flow without concentration including cryofocus. This method does not pyrolyze the sample, but heats it only in order to convert any water contained in the sample into a gas phase. In this case, it is a gas mixture that is analyzed *in situ* rather than pyrolyzate, which contains more oxidized compounds ($H_2O$, CO, $CO_2$, etc.) due to the reactions between the gas mixture compounds, gas mixture and accumulator surface, and gas phase compounds and sample. Blank online analyses were carried out before and after the "working" analysis. The previous analysis made it possible to control the release of gases sorbed by the sample surface, including atmospheric components, and to record the system blank at the end of the process. The degree and completeness of the elution of hydrocarbons and polycyclic aromatic hydrocarbons from the analytical column during temperature programming in a chromatograph thermostat were determined by the results of subsequent analysis. If necessary, the analytical column was thermoconditioned to achieve the required blank.

The collected spectra were interpreted using both automated mass spectral deconvolution and identification system (AMDIS) v. 2.73 software and manually, with background correction against spectra from the Wiley Registry 11th edition/ NIST 2017 mass spectral library (NIST MS Search 2.3). Peak areas in TIC chromatograms were determined using the ICIS algorithm Xcalibur (1.4SR1 Qual Browser). This method is suitable for the detection of trace volatile concentrations exceeding tens of femtograms. The relative concentrations (rel%) of volatile components in the studied mixture were obtained by normalizing the areas of individual chromatographic peaks to the total area of all peaks.

The reliability of this normalization method was verified using external standards; namely, certified Scotty Inc. NL34522-PI and 34525-PI gas standards of methane–hexane alkanes were injected into the gas stream, in the splitless mode, by means of a volumetric gas-tight syringe or a special valve with replaceable loops for volumes ranging from 2 to 500 μL. The calibration quality was assessed using the coefficients of determination $R^2$ of the relationships of the peak area versus the injected amount. The respective $R^2$ were: 0.9975 ($m/z$ 16, $n = 22$) for methane; 0.9963 ($m/z$ (26 + 30), $n = 16$) for ethane; 0.9986 ($m/z$ (29 + 43), $n = 15$) for propane; and 0.9994 ($m/z$ (29 + 43), $n = 17$) for butane. The concentration ranges of alkanes during the calibration were similar to the concentrations encountered in the experiments. The relative analytical uncertainty for $C_1$–$C_4$ alkane determination was below 5% ($2\sigma$) [22].

## 4. Results and discussion

### 4.1. GC–MS results from diamonds and garnet from the diamondiferous lherzolite (sample U-331)

The GC–MS results showed that the volatiles captured by the diamonds and garnets during their growth included hydrocarbons and their derivatives (79.7 rel% for diamonds and 69.1 rel% for garnets) (Figs. 5 and 6; Table 1; Tables S1 and S2 in supplementary data). Aliphatic (paraffins, olefins), cyclic (naphthenes, arenes),
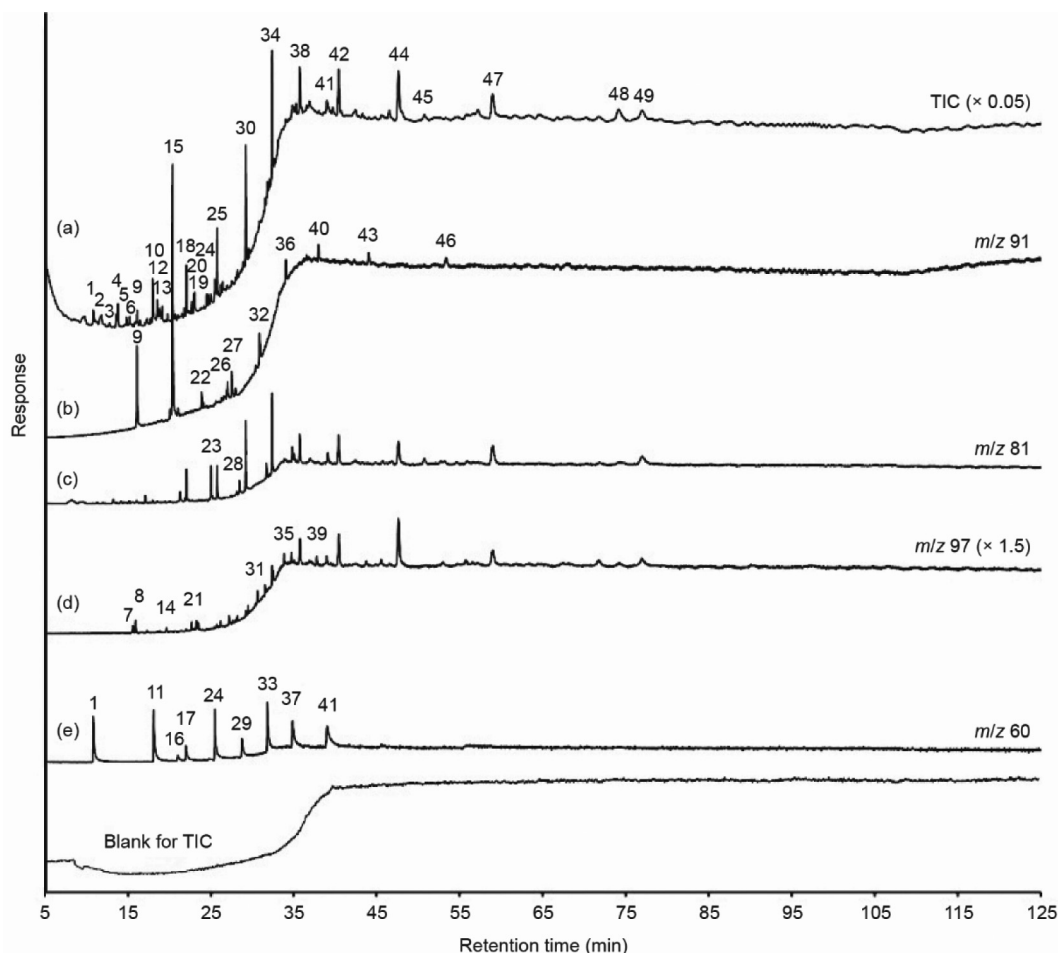
**Fig. 5.** Results of GC–MS analysis of volatiles extracted by mechanical shock crushing from diamonds from the diamondiferous lherzolite (U-331) of the Udachnaya pipe, Yakutia. (a) TIC chromatogram; (b–e) reconstructed ion current (RIC) chromatograms for $m/z$ 91, $m/z$ 81, $m/z$ 97, and $m/z$ 60, respectively. 1. Acetic acid ($C_2H_4O_2$); 2. benzene ($C_6H_6$); 3. 3-methylbutanal ($C_5H_{10}O$); 4. pentanal ($C_5H_{10}O$); 5. 1-heptene ($C_7H_{14}$); 6. heptane ($C_7H_{16}$); 7. 2-methylthiophene ($C_5H_6S$); 8. 3-methylthiophene ($C_5H_6S$); 9. toluene ($C_7H_8$); 10. hexanal ($C_6H_{12}O$); 11. butanoic acid ($C_4H_8O_2$); 12. 3-methyleneheptane ($C_8H_{16}$); 13. octane ($C_8H_{18}$); 14. 2-ethylthiophene ($C_6H_8S$); 15. ethylbenzene ($C_8H_{10}$); 16. 3-methylbutanoic acid ($C_5H_{10}O_2$); 17. pentanoic acid ($C_5H_{10}O_2$); 18. heptanal ($C_7H_{14}O$); 19. 1-nonene ($C_9H_{18}$); 20. nonane ($C_9H_{20}$); 21. 2-propylthiophene ($C_7H_{10}S$); 22. propylbenzene ($C_9H_{12}$); 23. 2-pentylfuran ($C_9H_{14}O$); 24. hexanoic acid ($C_6H_{12}O_2$); 25. octanal ($C_8H_{16}O$); 26. 1,2,4-trimethylbenzene ($C_9H_{12}$); 27. butylbenzene ($C_{10}H_{14}$); 28. 2-hexylfuran ($C_{10}H_{16}O$); 29. heptanoic acid ($C_7H_{14}O_2$); 30. nonanal ($C_9H_{18}O$); 31. 2-pentylthiophene ($C_9H_{14}S$); 32. pentylbenzene ($C_{11}H_{16}$); 33. octanoic acid ($C_8H_{16}O_2$); 34. decanal ($C_{10}H_{20}O$); 35. 2-hexylthiophene ($C_{10}H_{16}S$); 36. hexylbenzene ($C_{12}H_{18}$); 37. nonanoic acid ($C_9H_{18}O_2$); 38. undecanal ($C_{11}H_{22}O$); 39. 2-heptylthiophene ($C_{11}H_{18}S$); 40. heptylbenzene ($C_{13}H_{20}$); 41. decanoic acid ($C_{10}H_{20}O_2$); 42. dodecanal ($C_{12}H_{24}O$); 43. octylbenzene ($C_{14}H_{22}$); 44. tridecanal ($C_{13}H_{26}O$); 45. pentadecane ($C_{15}H_{32}$); 46. nonylbenzene ($C_{15}H_{24}$); 47. tetradecanal ($C_{14}H_{28}O$); 48. 2-pentadecanone ($C_{15}H_{30}O$); 49. pentadecanal ($C_{15}H_{30}O$).

oxygenated (alcohols, ethers, aldehydes, ketones, and carboxylic acids), and heterocyclic (dioxanes, furans) hydrocarbons were detected. Aliphatic hydrocarbons were more abundant in the garnets than in the diamonds (18.5 rel% and 14.9 rel%, respectively). Cyclic hydrocarbons—namely, naphthenes and arenes (3.7 rel% and 7.5 rel%, respectively)—were also detected (Fig. 7; Table 1).

Light molecular weight hydrocarbons, such as methane, ethane, propane, and butane, were present in the gas phase in a very small amounts (0.14 rel% for diamonds and 1.2 rel% for garnets). The share of methane was 0.001 rel% and 0.19 rel%, respectively. It was found that these diamonds and garnets contained medium ($C_5$–$C_{12}$, pentane ($C_5H_{12}$) to dodecane ($C_{12}H_{26}$)) and high molecular weight hydrocarbons. The heaviest were heavy molecular hydrocarbons ($C_{13}$–$C_{17}$, tridecane ($C_{13}H_{28}$) to octadecane ($C_{18}H_{38}$)), the amount of which was higher in the diamonds than in the garnets (5.4 rel% and 2.2 rel%, respectively).

Oxygenated hydrocarbons—namely, alcohols, esters, ethers, aldehydes, ketones, and carboxylic acids—comprised an essential fraction of the volatiles captured by the diamonds and garnets (55.6 rel% and 43.0 rel%, respectively) (Fig. S1 in supplementary data, Table 1). Aldehydes ($C_2H_4O$–$C_{16}H_{32}O$) and ketones

($C_3H_6O$–$C_{15}H_{30}O$) comprised approximately 78% of all oxygenated hydrocarbons in the diamonds. In contrast to the diamonds, alcohols, esters, ethers ($CH_4O$–$C_{18}H_{26}O_4$), and aldehydes ($C_2H_4O$–$C_{16}H_{32}O$) comprised approximately 75% of all the oxygenated hydrocarbons in the garnets (Table 1).

The gas phase in the diamonds and garnets also contained molecular nitrogen (0.07 rel% and 0.16 rel%, respectively), nitrogenated compounds (6.2 rel% and 1.3 rel%, respectively), and sulfonated compounds (2.26 rel% and 2.38 rel%, respectively) (Tables 1, S1, and S2). The nitrogenated components in the diamonds comprised pyridine ($C_5H_5N$), 1-isocyanobutane ($C_5H_9N$), pentanenitrile ($C_5H_9N$), hexanenitrile ($C_6H_{11}N$), 1H-pyrazole ($C_3H_4N_2$), isocyanobenzene ($C_7H_5N$), heptanonitrile ($C_7H_{13}N$), dichloropropanedinitrile ($C_3Cl_2N_2$), and a series from octanenitrile ($C_8H_{15}N$) to tetradecanenitrile ($C_{14}H_{27}N$) (Table S1). In the garnets, nitrogenated compounds were much less abundant and were mainly acetonitrile ($C_2H_3N$), 1H-pyrrole ($C_4H_5N$), pyridine, 1H-pyrazole, 2-pyridinamine ($C_5H_6N_2$), 3-pyridinamine ($C_5H_6N_2$), and 4-piperidone ($C_5H_9NO$) (Table S2). Tetradecanenitrile in diamonds (1.8 rel%) and 4-piperidone (0.55 rel%) in garnet prevailed among the nitrogenated compounds. The nitrogen in
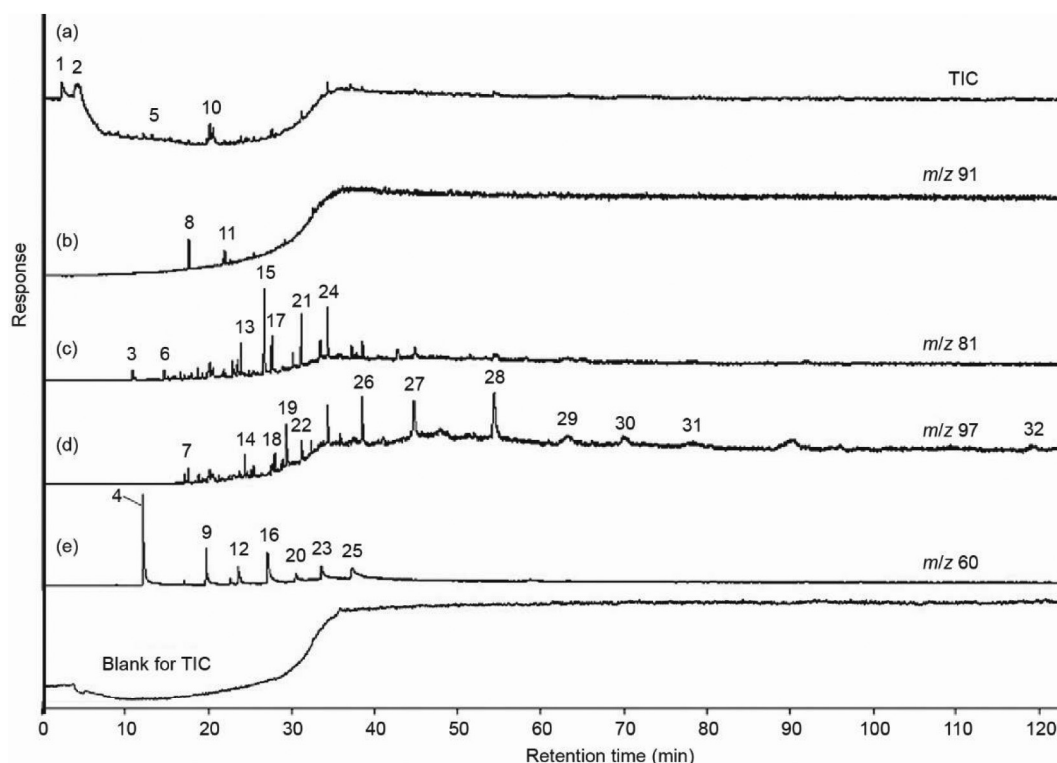
**Fig. 6.** Results of GC–MS analysis of volatiles extracted by mechanical shock crushing from garnet (pyrope) from the diamondiferous lherzolite (U-331) of the Udachnaya pipe, Yakutia. (a) TIC chromatogram; (b–e) RIC chromatograms for $m/z$ 91, $m/z$ 81, $m/z$ 97, and $m/z$ 60, respectively. 1. Carbon dioxide ($CO_2$); 2. water ($H_2O$); 3. 3-methylfuran ($C_5H_6O$); 4. acetic acid ($C_2H_4O_2$); 5. benzene ($C_6H_6$); 6. 2-ethylfuran ($C_6H_8O$); 7. 3-methylthiophene ($C_5H_6S$); 8. toluene ($C_7H_8$); 9. butanoic acid ($C_4H_8O_2$); 10. 2-ethyl-1-hexene ($C_8H_{16}$); 11. 1,4-dimethylbenzene (p-xylene) ($C_8H_{10}$); 12. pentanoic acid ($C_5H_{10}O_2$); 13. heptanal ($C_7H_{14}O$); 14. 1-nonene ($C_9H_{18}$); 15. 2-pentylfuran ($C_9H_{14}O$); 16. hexanoic acid ($C_6H_{12}O_2$); 17. octanal ($C_8H_{16}O$); 18. 1-decene ($C_{10}H_{20}$); 19. 2-butylthiophene ($C_8H_{12}S$); 20. heptanoic acid ($C_7H_{14}O_2$); 21. nonanal ($C_9H_{18}O$); 22. 1-undecene ($C_{11}H_{22}$); 23. octanoic acid ($C_8H_{16}O_2$); 24. decanal ($C_{10}H_{20}O$); 25. nonanoic acid ($C_9H_{18}O_2$); 26. undecanal ($C_{11}H_{22}O$); 27. dodecanal ($C_{12}H_{24}O$); 28. tridecanal ($C_{13}H_{26}O$); 29. γ-undecalactone ($C_{11}H_{20}O_2$); 30. tetradecanal ($C_{14}H_{28}O$); 31. γ-dodecalactone ($C_{12}H_{22}O_2$); 32. hexadecanal ($C_{16}H_{32}$).

**Table 1**
Composition of volatiles extracted by mechanical shock crushing of the diamond and garnet from the diamondiferous lherzolite (U-331) of the Udachnaya pipe, Yakutia.

| Name | Nominal mass | Diamond (rel%) | Garnet (rel%) |
|---|---|---|---|
| Aliphatic hydrocarbons | | 14.95 | 18.55 |
| Paraffins ($CH_4$–$C_{18}H_{38}$) | 16–254 | 10.14 | 8.67 |
| Olefins ($C_2H_4$–$C_{15}H_{28}$) | 28–208 | 4.81 | 9.88 |
| Cyclic hydrocarbons | | 7.55 | 3.77 |
| Cycloalkanes (naphthenes) ($C_4H_8$–$C_9H_{18}$) | 56–126 | 0.11 | 0.53 |
| Arenes ($C_6H_6$–$C_{16}H_{26}$) | 78–218 | 7.40 | 3.14 |
| Polycyclic aromatic hydrocarbons ($C_{10}H_8$–$C_{11}H_{10}$) | 128–142 | 0.04 | 0.10 |
| Oxygenated hydrocarbons | | 55.63 | 43.03 |
| Alcohols, esters, and ethers ($CH_4O$–$C_{18}H_{26}O_4$) | 32–306 | 6.45 | 17.03 |
| Aldehydes ($C_2H_4O$–$C_{16}H_{32}O$) | 44–240 | 28.59 | 14.33 |
| Ketones ($C_3H_6O$–$C_{15}H_{30}O$) | 58–226 | 14.89 | 4.95 |
| Carboxylic acids ($C_2H_4O_2$–$C_{13}H_{26}O_2$) | 60–214 | 5.70 | 6.72 |
| Heterocyclic compounds | | 1.59 | 3.79 |
| Dioxanes ($C_4H_8O_2$) | 88 | 0.01 | 0.27 |
| Furans (ethers) ($C_4H_6O$–$C_{13}H_{22}O$) | 70–194 | 1.58 | 3.52 |
| Nitrogenated compounds ($N_2$–$C_{14}H_{27}N$) | 28–209 | 6.27 | 1.46 |
| Sulfonated compounds (COS–$C_{14}H_{24}S$) | 60–224 | 2.26 | 2.38 |
| $CO_2$ | 44 | 0.33 | 9.52 |
| $H_2O$ | 18 | 11.42 | 13.93 |

The relative concentrations (rel%) of volatile components in the studied mixture were obtained by normalizing areas of individual chromatographic peaks to the total area of all peaks. COS: carbonyl sulfide.

the gas mixture occurred primarily in a bound form within the nitrogenated hydrocarbon compounds. As a result, the diamond sample did not contain significant amounts of nitrogen as a structural impurity, which was consistent with it being a Type IIa diamond.

Among the sulfonated compounds in the diamonds, in addition to sulfur dioxide ($SO_2$), carbon disulfide ($CS_2$), and dimethyl disulfide ($C_2H_6S_2$), a large number of thiophenes were found, from thiophene ($C_4H_4S$) to 2-decylthiophene ($C_{14}H_{24}S$). Hydrogen sulfide was not found in either the diamonds or the garnets (Tables S1 and S2).

Chlorinated compounds were also found in the diamonds and garnets (3.45 rel% and 0.7 rel%, respectively) in a series from 1-chlorobutane ($C_4H_9Cl$) to 1-chlorotetradecane ($C_{14}H_{29}Cl$) (Tables S1 and S2). The detection of chlorinated compounds in the diamonds and garnets indicates their stability under the conditions of the upper mantle.

### 4.2. GC–MS results from the olivine of the diamondiferous dunite (sample Us-221)

The GC–MS results showed that in the olivine from the diamondiferous dunite, as well as in the diamonds and garnets from the diamondiferous lherzolite, the main volatile components were hydrocarbons and their derivatives (92.6 rel%) (Fig. 8; Table 2; Table S3 in supplementary data).

The relative concentrations of volatile components in the studied mixture were obtained by normalizing areas of individual chromatographic peaks to the total area of all peaks.
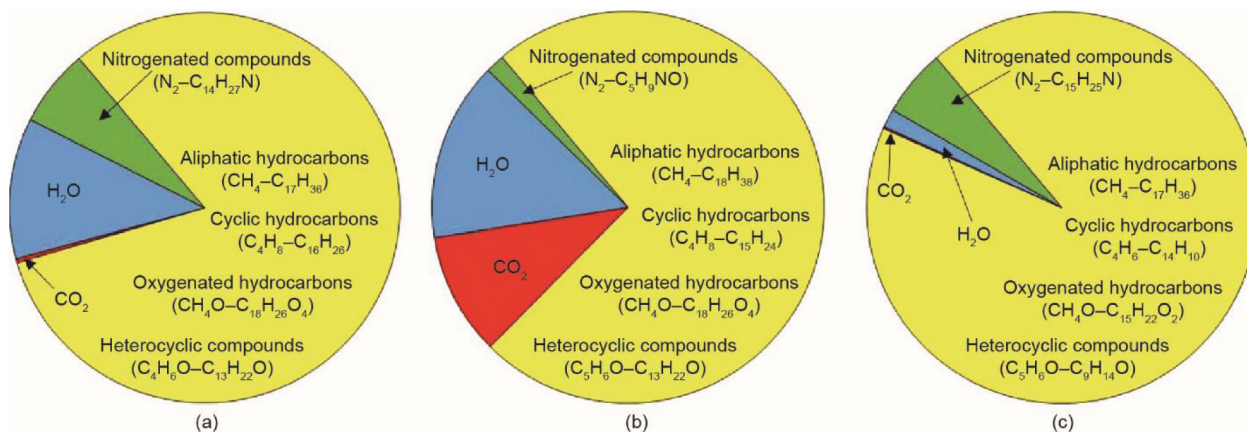
**Fig. 7.** Relative content of volatiles. (a) Diamond and (b) pyrope from diamondiferous lherzolite (U-331) from the Udachnaya pipe, Yakutia; (c) olivine from diamondiferous dunite (Us-221) from the Udachnaya pipe, Yakutia.
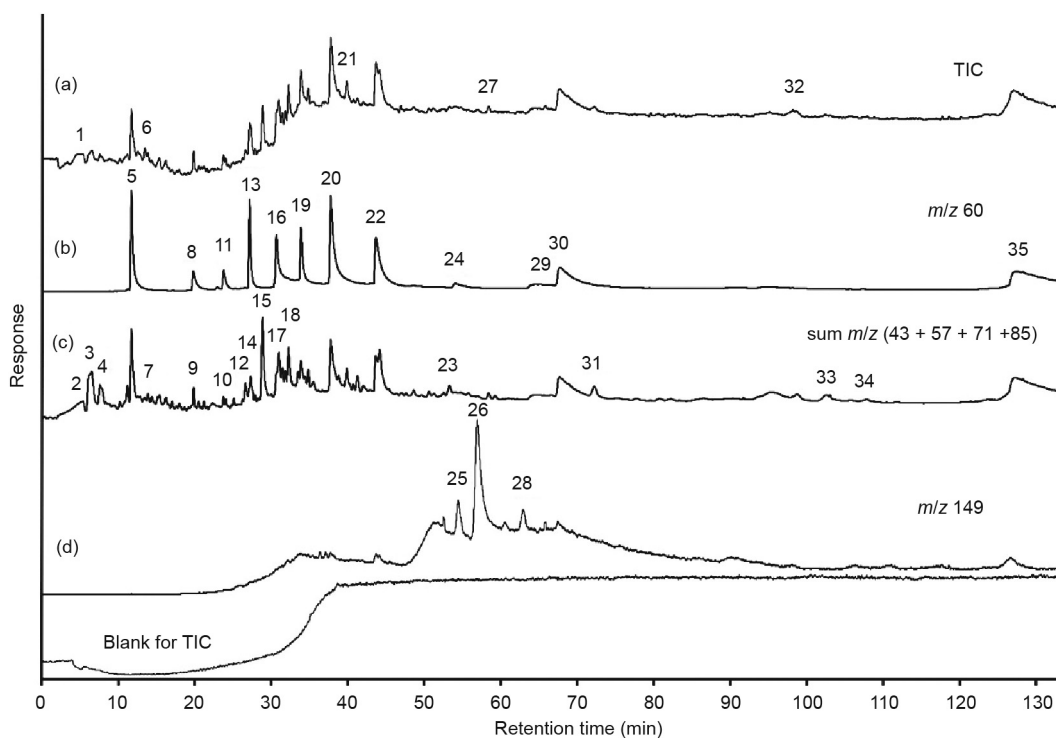


**Fig. 8.** Results of GC–MS analysis of volatiles extracted by mechanical shock crushing from olivine from the diamondiferous dunite (Us-221) of the Udachnaya pipe, Yakutia. (a) TIC chromatogram; (b–e) RIC chromatograms for $m/z$ 60, sum $m/z$ (43 + 57 + 71 + 85), $m/z$ 149, respectively. 1. 1-Propene ($C_3H_6$); 2. acetaldehyde ($C_2H_4O$); 3. 2-acetyltetrazole ($C_3H_4N_4O$); 4. 2-propanone ($C_3H_6O$); 5. acetic acid ($C_2H_4O_2$); 6. 1-butanol ($C_4H_{10}O$); 7. 3-methylbutanal ($C_5H_{10}O$); 8. butanoic acid ($C_4H_8O_2$); 9. hexanal ($C_6H_{12}O$); 10. 2-heptanone ($C_7H_{14}O$); 11. pentanoic acid ($C_5H_{10}O_2$); 12. 2-ethylhexanal ($C_8H_{16}O$); 13. hexanoic acid ($C_6H_{12}O_2$); 14. 2-pyrrolidinone ($C_4H_7NO$); 15. 2-ethyl-1-hexanol ($C_8H_{18}O$); 16. heptanoic acid ($C_7H_{14}O_2$); 17. nonanal ($C_9H_{18}O$); 18. undecane ($C_{11}H_{24}$); 19. octanoic acid ($C_8H_{16}O_2$); 20. nonanoic acid ($C_9H_{18}O_2$); 21. undecanal ($C_{11}H_{22}O$); 22. decanoic acid ($C_{10}H_{20}O_2$); 23. 5-methyltetradecane ($C_{15}H_{32}$); 24. undecanoic acid ($C_{11}H_{22}O_2$); 25. acetate 2-tert-butyl-4-methylphenol ($C_{13}H_{18}O_2$); 26. 2-(2-methylpropyl)-3,5-di(1-methylethyl)pyridine ($C_{15}H_{24}N$); 27. 1-pentadecene ($C_{15}H_{30}$); 28. phenylpropanamide ($C_9H_{11}NO$); 29. 2-methylundecanoic acid ($C_{12}H_{24}O_2$); 30. dodecanoic acid ($C_{12}H_{24}O_2$); 31. 2-hexyl-1-decanol ($C_{16}H_{34}O$); 32. 2-pentadecanone ($C_{15}H_{30}O$); 33. 1-heptadecene ($C_{17}H_{34}$); 34. heptadecane ($C_{17}H_{36}$); 35. tetradecanoic acid ($C_{14}H_{28}O_2$).

Aliphatic (paraffins, olefins), cyclic (naphthenes, arenes), oxygenated (alcohols, ethers, aldehydes, ketones, and carboxylic acids), and heterocyclic (dioxanes, furans) hydrocarbons were established. The aliphatic hydrocarbons in the olivines were much smaller (9.4 rel%) in comparison with those in the diamonds and garnets from the diamondiferous lherzolite (Figs. 7 and 8; Tables 2 and S3).

Light molecular weight hydrocarbons were present in the gas phase in a very small amount (0.07 rel%). The share of methane was 0.003 rel%. It was found that these olivines contained medium

($C_5–C_{12}$, pentane ($C_5H_{12}$) to dodecane ($C_{12}H_{26}$)) and high molecular weight hydrocarbons. The heaviest were heavy molecular hydrocarbons ($C_{13}–C_{17}$, tridecane ($C_{13}H_{28}$) to heptadecane ($C_{17}H_{36}$)). The amount of medium hydrocarbons in the olivines was much larger than that of heavy hydrocarbons (4.1 rel% and 1.5 rel%, respectively) (Table S3). Cyclic hydrocarbons—namely, naphthenes and arenes (1.7 rel%)—were also detected (Tables 2 and S3).

Oxygenated hydrocarbons (i.e., alcohols, esters, ethers, aldehydes, ketones, and carboxylic acids) comprised an essential fraction of the volatiles captured by the olivine (80.8 rel%)

(Fig. S2; Tables 2 and S3). Carboxylic acids ($C_2H_4O_2$–$C_{14}H_{28}O_2$) comprised approximately 65% of all oxygenated hydrocarbons in the olivine.

The gas phase in the olivine also contained molecular nitrogen (0.03 rel%) and a very large number (35) of nitrogenated compounds (5.5 rel%) (Tables 2 and S3).

Among the sulfonated compounds in the olivine (0.7 rel%), in addition to carbonyl sulfide (COS), sulfur dioxide ($SO_2$), carbon disulfide ($CS_2$), dimethyl disulfide ($C_2H_6S_2$), and thiophenes, 2-methyl-($C_5H_6S$) was found. Hydrogen sulfide was not found (Tables 2 and S3).

According to the calculated H/(O + H) ratios, diamonds from the diamondiferous lherzolite and olivine from the diamondiferous dunite crystallized under close redox conditions (Tables 1 and 2).

Modern models of diamond formation in the mantle mineral-forming processes have been constructed with regard to the significant roles of $CO_2$, $CH_4$, $H_2$, and $H_2O$ [36,37]. In addition, the important role of pH in diamond-forming systems with the participation of water ions has been shown by Sverjensky and Huang [38]. Investigation of the composition of volatiles in the diamonds, garnet, and olivine from the Udachnaya pipe showed that the crystallization of the examined diamonds in the Earth's upper mantle involved the active participation of aliphatic, cyclic, heterocyclic, and oxygenated hydrocarbons, whose content in the fluids was 92% or more, as well as nitrogenated, chlorinated, and sulfonated compounds. It is important to note that hydrocarbons—including high molecular weight hydrocarbons—have also been found in diamonds from the Pozdnyaya kimberlite pipe, Yakutia, and diamonds from placers of the Urals and in the northeastern part of the Siberian platform [5,15,39].

Undoubtedly, it is important that chlorinated compounds have been detected both in diamonds and garnets from the diamondiferous lherzolite, and in olivine from the diamondiferous dunite; this clearly indicates the possibility of the formation of chlorinated hydrocarbons and their stability under the conditions of the upper mantle. Chlorinated silicates—and sodalite in particular—have been found in the groundmass of kimberlites of the Udachnaya-East pipe [40], as well as in inclusions of phlogopite in diamonds of the same pipe [41] with a chlorine content of up to 0.5 wt%.

**Table 2**
Composition of volatiles extracted by mechanical shock crushing of the olivine from the diamondiferous dunite (Us-221) of the Udachnaya pipe, Yakutia.

| Name | Nominal mass | Olivine (rel%) |
|---|---|---|
| Aliphatic hydrocarbons | | 9.40 |
| Paraffins ($CH_4$–$C_{17}H_{36}$) | 16–240 | 5.67 |
| Olefins ($C_2H_4$–$C_{17}H_{34}$) | 28–238 | 3.73 |
| Cyclic hydrocarbons | | 1.73 |
| Cycloalkanes (naphthenes) ($C_6H_{10}$) | 82 | 0.03 |
| Arenes ($C_6H_6$–$C_{10}H_{14}$) | 78–134 | 1.06 |
| Polycyclic aromatic hydrocarbons ($C_{11}H_{10}$–$C_{14}H_{10}$) | 142–178 | 0.64 |
| Oxygenated hydrocarbons | | 80.83 |
| Alcohols, esters, and ethers ($CH_4O$–$C_{15}H_{22}O_2$) | 32–234 | 10.16 |
| Aldehydes ($C_2H_4O$–$C_{16}H_{32}O$) | 44–240 | 11.59 |
| Ketones ($C_3H_6O$–$C_{15}H_{30}O$) | 58–226 | 6.19 |
| Carboxylic acids ($C_2H_4O_2$–$C_{14}H_{28}O_2$) | 60–228 | 52.89 |
| Heterocyclic compounds | | 0.63 |
| Dioxanes ($C_4H_8O_2$) | 88 | 0.21 |
| Furans (ethers) ($C_5H_6O$–$C_9H_{14}O$) | 82–138 | 0.42 |
| Nitrogenated compounds ($N_2$–$C_{15}H_{25}N$) | 28–219 | 5.55 |
| Sulfonated compounds (COS–$C_5H_6S$) | 60–98 | 0.72 |
| $CO_2$ | 44 | 0.16 |
| $H_2O$ | 18 | 1.53 |

Moreover, the data obtained show that the upper mantle contains areas of low oxygen fugacity. Within these areas, abiogenic synthesis is probably possible for hydrocarbons. Alternatively, organic matter could eventually be transported with the slab during subduction. At certain depths, organic substances can react with ferrous iron-bearing minerals and can form hydrocarbon fluids [42,43]

## 5. Conclusions

The data obtained on volatiles in the studied mantle minerals confirm an earlier opinion [24] and suggest that hydrocarbons "heavier" than methane (from pentane to hexadecane) dominate in the fluid composition of some mantle areas.

Saturated hydrocarbons up to $C_{17}H_{36}$ and $C_{18}H_{38}$ were found by GC–MS not only in diamonds from studied peridotite, but also in several Russian diamonds from kimberlite. Very low methane presence was detected (< 0.1 rel%)

To a first approximation, the diamond-forming medium can be considered to be a specific ultrapotassic/carbonate/chloride/silicate/water/hydrocarbon fluid.

## Compliance with ethics guidelines

Nikolay V. Sobolev, Anatoly A. Tomilenko, Taras A. Bul'bak, and Alla M. Logvinova declare that they have no conflict of interest or financial conflicts to disclose.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eng.2019.03.002.

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