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Hydrocarbon components in carbonaceous meteorites

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Abstract—Currently, the presence of free *n*-alkanes and isoprenoid alkanes in carbonaceous meteorites is usually explained either by microbial contamination during the period between the meteorite fall and collection or by contamination from the environment of analytical laboratories and museums. The goal of this research was to repeat analysis of hydrocarbon components in meteorites and to investigate possible meteorite contamination routes discussed in the literature. Experimental analysis of free organic constituents in five carbonaceous meteorites by infrared spectroscopy (IR) and gas chromatographic (GC) methods confirmed the presence of extractable aliphatic components, n-alkanes in the $C_{15}H_{32}$–$C_{27}H_{56}$ range and isoprenoid alkanes (phytane, pristane, and norpristane), in some of these meteorites. The contents of these compounds vary depending on the source. Insoluble organic components of two meteorites (meteorite kerogens) were isolated, and their composition was analyzed by IR and cracking/GC methods. Comparison with the data on several terrestrial contamination sources proposed in the literature shows that the presence of free saturated hydrocarbons in meteorites and the composition of the meteorite kerogen could not be explained either by microbial contamination or by contamination from the laboratory environment. The types of the hydrocarbons in meteorites resemble those typical of ancient terrestrial deposits of organic-rich sediments, except for the absence of lighter hydrocarbons, which apparently slowly evaporated in space, and multi-ring naphthenic compounds of the biologic origin, steranes, terpanes, etc. The prevailing current explanation for the presence of free linear saturated hydrocarbons in carbonaceous meteorites, apart from contamination, is the abiotic route from hydrogen and carbon monoxide. However, the data on the structure of meteorite kerogens require a search for different routes that initially produce complex polymeric structures containing n-alkyl and isoprenoid chains which are attached, via polar links (esters, salts, etc.), to a cross-linked polymer matrix. Later, the polymer slowly decomposes with the liberation of free aliphatic hydrocarbons. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

A significant number of carbonaceous meteorites, stony meteorites containing from 0.5 to 5 wt.% of organic carbon, also contain small quantities of extractable hydrocarbons, saturated and aromatic compounds. The history of identification of these compounds in meteorites and the explanation of their origin underwent in the past a swing not typical for the studies of such an apparently straightforward subject.

The earliest chemical analyses of carbonaceous meteorites (reviewed by Vdovykin in 1967) were carried out in the middle of the nineteenth century. They showed that the meteorites contain a significant quantity, up to 0.5 to 0.6 wt.%, of a wax-like extractable material, a mixture of saturated and aromatic hydrocarbons. The modern period in the study of organic compounds in meteorites started in the mid-1950s after the development of new analytical techniques, infrared spectroscopy (IR), gas chromatography (GC), and mass spectrometry (MS). A large series of articles published by Meinschein (1965, 1963a, 1963b), Nagy et al. (1961), Briggs and Mamikunian (1963), Oró and Nooner (1967), Oró et al. (1966, 1968), Nooner and Oró (1967), Studier (1968), Studier et al. (1968), Hayes (1967), Hayes and Biemann (1968), and other researchers showed that many carbonaceous meteorites contain small quantities of linear and branched alkanes. The main subject of discussion during that period was the origin of the alkanes. The opinions included abiotic synthesis in space from CO and H_2 via the Fischer-Tropsch catalysis and even life outside of the Earth. The most potentially problematic subject was detection in the meteorites of two isoprenoid alkanes, phytane and pristane (Meinschein, 1963a, 1963b, 1965; Oró et al., 1966, 1968; Oró and Nooner, 1967; Nooner and Oró, 1967). These compounds, when found in terrestrial samples, clearly have the biologic origin; they are mostly the decomposition products of the phytol chain in chlorophyll. These compounds are not formed in Fischer-Tropsch catalytic reactions (Studier et al., 1968, Gelpi et al., 1970).

This avenue of research was interrupted after the publication of an article by Han et al. (1969). The article described organic compounds in the Pueblito de Allende (Mexico) meteorite. The meteorite was collected one week after its fall, in February 1969; it has a relatively low organic carbon content, 0.3%. An extract from the part of the meteorite under the fusion crust contained a small quantity of *n*-alkanes and isoprenoid alkanes, the same as those in other similar meteorites. However, no organic compounds of these types were found in the core of the meteorite. The external part of the meteorite also contained several ketones, esters, and fatty acids, including C_{16} and C_{18} fatty acids typical of biologic contamination. The principal conclusion of the article was: "It is clear that the organic material found on the surface layer of this meteorite is of biological origin and cannot be other than terrestrial contamination. . . . The speed with which this contamination was acquired. . .makes doubtful any interpretation of such organic

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materials. . .in meteorites of unknown, or at least considerably longer, terrestrial history.” The opinion that saturated hydrocarbons in meteorites are mostly terrestrial contamination persists to the present time, although the proposed contamination sources vary. For example, Cronin and Pizzarello wrote in 1990: “The presence in the meteorite extract of a suite of isoprenoid alkanes so similar to crude oils suggests contamination of the meteorite specimen with a petroleum product(s). The widespread laboratory use of oil-filled vacuum pumps and the common use of rock saws for cutting meteorites provide plausible sources of such contamination.”

Currently, the main subject of the meteorite research has shifted to the studies of polar organic compounds, including amino acids and their derivatives. A continuous improvement in the precision and sensitivity of various chromatographic techniques allowed Cronin and his coworkers to carry out an extraordinarily detailed analysis of such products in meteorites, to demonstrate their indigenous nature, and to develop a convincing mechanism of their formation through a series of abiotic reactions (Cronin et al., 1979, 1981, 1988; Cronin and Pizzarello, 1983, 1986; Cronin and Chang, 1993).

The main subject of this article is reinvestigation of the possibility of terrestrial contamination as the principal source of free aliphatic hydrocarbons in meteorites. Hydrocarbon constituents in carbonaceous meteorites have been examined very thoroughly (see reviews by Vdovykin, 1967; Cronin et al., 1988; Cronin and Chang, 1993); it is difficult to discover any principally new features of their structure. Instead, the research presented here was restricted to three subjects: (a) repeating GC and IR analysis of kerogens and free aliphatic hydrocarbons in several carbonaceous meteorites with a goal of evaluating dependability and reproducibility of such an analysis; (b) experimental analysis of structural features of hydrocarbons in terrestrial materials which are proposed in the literature as contamination sources of meteorites; and (c) discussion of arguments usually put forward as proofs of the contamination hypothesis.

2. MATERIALS AND METHODS

Samples of five carbonaceous meteorites were analyzed: one CI1, Orgueil (France) and four CM2, Cold Bokkeveld (South Africa), Mighei (Ukraine), Murchison (Australia), and ALH83100, Allan Hills (Antarctica). The first four samples were provided by Dr. M. Prinz, the meteorite curator at the American Museum of Natural History in New York. All these meteorites were collected within hours or a few days after their fall; they were kept in museums thereafter. The sample from the Antarctica meteorite was obtained from the Meteorite Working Group at the Johnson Space Center in Houston where a number of Antarctica meteorites are kept under sterile conditions. All meteorite samples (150 to 250 mg each) are black, very soft, easily pulverized rocks.

To prepare extracts of free hydrocarbons for GC analysis, 6- to 10-mg samples of a meteorite rock and 10 to 30 μL of a clean heavy solvent (*n*-butylcyclohexane or *n*-propylcyclohexane, GC standards of 99.9% purity) were placed in 2-mm glass ampoules, the rock was ground with a steel needle against the ampoule bottom, and the ampoules were rapidly sealed under vacuum. To avoid contamination through contact with the laboratory environment, the samples were sealed within a few minutes after opening their containers, and the vacuum was produced with a large syringe instead of a vacuum pump. The ampoules were kept at temperatures ranging from 25 to 150°C for periods from 24 to over 1000 h. GC analysis of the solvents showed that they did not contain heavy hydrocarbons and did not produce them when heated under the same conditions. The same procedure was used to prepare extracts from two materials representing possible terrestrial contamination in meteorites. The first sample was a small piece, 0.016 g, of a highly porous silicate stone which was exposed to the elements for 30 yr; a chip of a silicate brick from a house wall positioned 50 cm above the ground level. The second sample, a potential source of chlorophyll decomposition products, was a piece of vegetation (a maple leaf) dried for over 1 yr in air at room temperature.

Kerogens from two meteorites, Orgueil and Cold Bokkeveld, were separated from the inorganic matrix following the technique by Degens and Reuter (1964). Small quantities of rocks (0.05 and 0.1 g of Orgueil, 0.02 g of Cold Bokkeveld) were treated with 20 mL of conc. HF for 50 h, then washed with 100 mL of water, treated with 20 mL of 37% HCl for 50 h, and were finally washed twice with 100 mL of water.

Thermolysis of “whole” meteorite kerogens and thermolysis of meteorite rocks themselves were carried out in glass ampoules sealed under vacuum. There are several rationales for kerogen thermocracking without a prior removal of free alkanes. Bandurski and Nagy discussed some of them in 1976. Free alkanes constitute merely 2% to 3% of the total mass of the meteorite kerogen; their presence does not affect the results in situations when practically all kerogen is cracked to soluble products, as has happened in the experiments of Bandurski and Nagy and in the present experiments (see below). In addition, paraffins sublime easily under vacuum and separate from the insoluble part of kerogen. One more reason for avoiding the removal of free alkanes is a possibility of contamination. If the free alkanes are removed with a large quantity of a light solvent (a commonly used technique), a small amount of contaminants, which can be present even in purified solvents, can be deposited in the kerogen. If a heavy solvent is used for the extraction of free alkanes from the kerogen before thermolysis, a complete removal of the solvent from the kerogen is difficult, and the cracked products from the solvent may complicate analysis of kerogen fragmentation.

To interpret the results of the meteorite kerogen thermolysis, thermocracking of three model materials was carried out: an *n*-alkane, n-$C_{24}H_{50}$; an isoprenoid alkane, squalane (2,6,10,15,19,23-hexamethyltetracosane); and oil shale from Hazen, Colorado, USA. Small samples of the materials, 0.03 to 0.05 g, were sealed in glass ampoules under vacuum and heated at 350°C for 24 h. GC analysis of virgin vacuum-pump oil (Fisher-brand #19 Mechanical Pump Fluid) was carried out as well.

Gas chromatograms were recorded with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 60-m, 0.2-mm stainless-steel capillary column (MTX-1, Restek Co.) heated from 40 to 350°C at 4°C/min; the helium flow was 2 cm^3/min. Injected samples ranged from 3 to 7 μL. GC-MS data were produced with a Varian 3400 gas chromatograph equipped with a 0.32-mm, 50-m Chromopack

Al_2O_3-plot column heated from −20 to 380°C at 10°C/min and a high-resolution Finnigan MAT 8230 mass-spectrometer.

IR spectra of meteorites were recorded immediately after they were received from storage, without exposure to the laboratory environment. The Fourier transform infrared (FTIR) transmission spectra were recorded with a Perkin-Elmer Paragon 1000 FTIR spectrophotometer (4 cm^{-1} resolution, 256 scans) using KBr pellets and mulls in perfluorinated oil. The FTIR micro-reflectance spectra were recorded with a Nicolet Magna 750 IR spectrophotometer equipped with a Nic-Plan microscope (8 cm^{-1} resolution, 1024 scans). Electron-scanning microscopic data for meteorite kerogens were produced with a JEOL JSM-840A scanning electron microscope with a PGT Omega EDS detector.

3. EXPERIMENTAL RESULTS

3.1. Direct Identification of Hydrocarbon Constituents in Carbonaceous Meteorites

The IR technique provides the most straightforward means of observing hydrocarbon components in meteorites. Due to the low organic content in most carbonaceous meteorites, a number of earlier studies used organic or aqueous extracts (Vdovykin, 1967; Meinschein, 1963b; Briggs and Mamikunian, 1963; Kaplan et al., 1963). Modern FTIR instruments have high sensitivity and afford direct identification of aliphatic hydrocarbon groups in original meteorite rocks. IR transmission spectra of several meteorites, which were recorded immediately after they were received from storage, showed, in addition to intense broad bands due to inorganic minerals, four bands of aliphatic hydrocarbons in the 3000 to 2800 cm^{-1} range. The bands appear as small shoulders on the very intense broad ν(OH) band at 3700 to 2500 cm^{-1} from hydrous silicates. When the latter band is subtracted from the meteorite spectra using the IR spectrum of a silica sample containing a large quantity of siloxyl groups and adsorbed water, the presence of the IR bands due to the hydrocarbon groups becomes obvious. Fig. 1 shows three such difference spectra. The bands are assigned to the stretching modes of aliphatic CH_2 groups (2923 and 2855 cm^{-1}) and CH_3 groups (2957 and ~2870 cm^{-1}). No IR bands of mononuclear aromatic compounds in the 3060 to 3000 cm^{-1} range are observable.

The IR spectra afford a semiquantitative estimation of the relative quantities of CH_2 and CH_3 groups in the meteorites. The ratio of absorption coefficients for the 2957 and 2923 cm^{-1} bands in the IR spectra of alkanes and polar organic compounds with large alkyl groups (ketones, esters) ranges from ~2.3 to 3.2, depending on the branching degree of alkyl chains. Using these estimates and the values of the relative absorbance of the respective bands, one can calculate the CH_3/CH_2 ratio in organic components of meteorites. For the three meteorites in Fig. 1, the ratio is 0.20 to 0.27.

3.2. Extractable Organic Components of Meteorites

The most detailed information about the nature of free hydrocarbons is produced by GC analysis of organic extracts from the meteorites. The highest content of free alkanes in the meteorites listed in Table 1 was found in the Orgueil sample. Fig. 2 shows a part of the gas chromatogram of one of its extracts. Most peaks belong to three types of hydrocarbons: a suite of *n*-alkanes ranging from *n*-$C_{15}H_{32}$ to *n*-$C_{27}H_{56}$; three isoprenoid alkanes, phytane (2,6,10,14-tetramethylhexadecane), pristane (2,6,10,14-tetramethylpentadecane), and nor-pristane (2,6,10-trimethylpentadecane); and two aromatic hydrocarbons, phenanthrene (the major component) and 1,6-dimethyl-4-isopropylnaphthalene. Identification of all the GC peaks was based on their MS data (vs. the National Institute of Standards and Technology MS library), and was confirmed by a parallel GC analysis of various calibration mixtures and petroleum fractions (Kissin, 1987, 1993). The present results are in full agreement with the earlier published data on free hydrocarbons in meteorites (Oró et al., 1966; Oró and Nooner, 1967; Nooner and Oró, 1967).

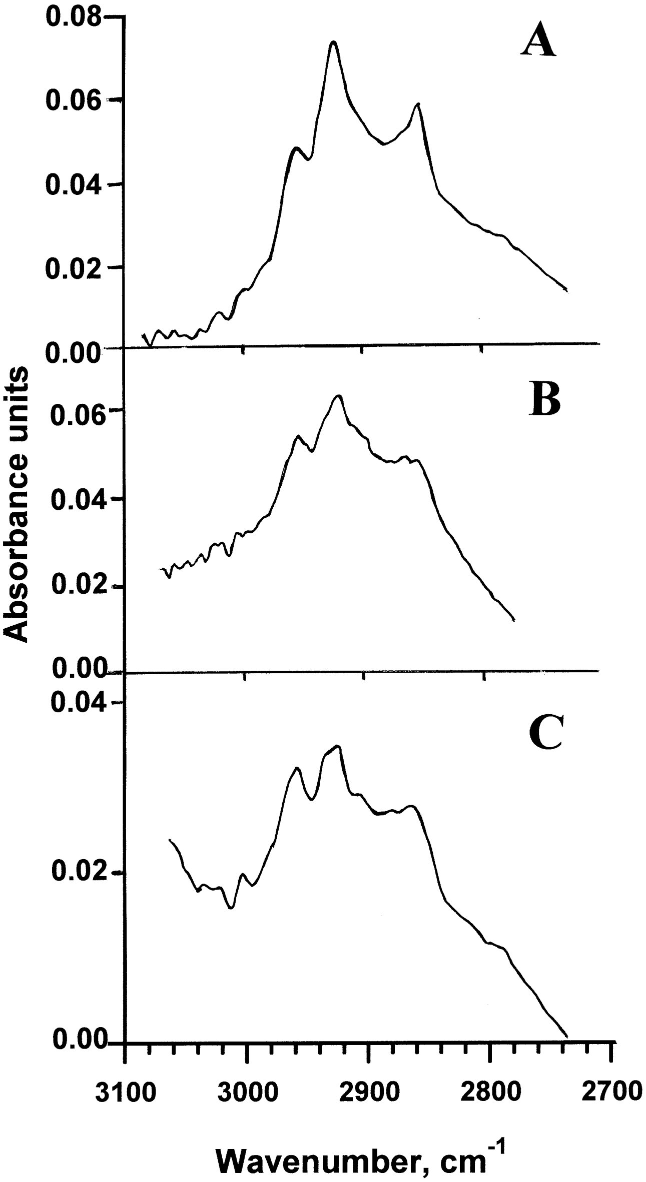

Fig. 1. IR spectra of three meteorites, Orgueil (A), Mighei (B), and Antarctica (C), in the 3200 to 2700 cm^{-1} range. Difference spectra are shown; the spectrum of silica is subtracted from the spectra of meteorite rocks.

Table 1. Content of heavy hydrocarbons in meteorites.

Meteorite	Place and date of fall	Extraction procedure	Free hydrocarbons, wt. %
Orgueil	South of	25°C, 1050 h	0.044
	France,	75°C, 528 h (two anal.)	0.054; 0.076
	May 1864	100°C, 336 h	0.11
Mighei	Ukraine,	75°C, 480 h	0.011
	June 1889	120°C, 90 h	0.026
Cold	South Africa,	75°C, 480 h	0.007
	Oct. 1838		
Bokkeveld	Oct. 1838	150°C, 94 h	0.0053
Antarctica	Allan Hills	120°C, 90 h	0.0035

Table 1 gives the estimates of the combined content of extractable hydrocarbons in the Orgueil meteorite. It increases with the severity of extraction conditions and can exceed 0.1 wt.% of the meteorite weight. Comparison with the total carbon content in the same meteorite, ~5 wt.% (Nagy et al., 1961; Mason, 1963a, 1963b), indicates that free hydrocarbons account for only a small fraction, ~2%, of the total organic carbon. Three other of the studied meteorites also contain suites of *n*-alkanes and isoprenoid alkanes, although in smaller quantities (Table 1). The present-day capillary GC analysis affords identification of these quantities of hydrocarbons in meteorites without difficulty or ambiguity.

Fig. 3 shows molar distributions of free *n*-alkanes in four meteorites. The data were normalized relative to the content of *n*-$C_{17}H_{36}$. Most distributions have two maximums, one at C_{15}–C_{17} and another at C_{21}–C_{23}. Overall, the distribution is shifted to the lighter end in the Antarctica meteorite and to the heavier end in the Cold Bokkeveld meteorite. All the *n*-alkane suites show no odd vs. even carbon atom (C_n) preference.

Three extraction experiments with our sample of the Murchison meteorite at a rock/solvent ratio of 0.4 g/mL at 25°C (362 h) and 75°C (41 and 400 h) followed by GC analysis showed that it contains only miniscule amounts of free saturated hydrocarbons, mostly *n*-alkanes in the C_{16}–C_{20} range. This result agrees with the finding of Cronin and Pizzarello (1990): their estimation gives the total *n*-alkane content in the meteorite as $\sim 1 \cdot 10^{-3}$ wt.%, four times less than in the Antarctica meteorite and 100 times less than in the Orgueil meteorite.

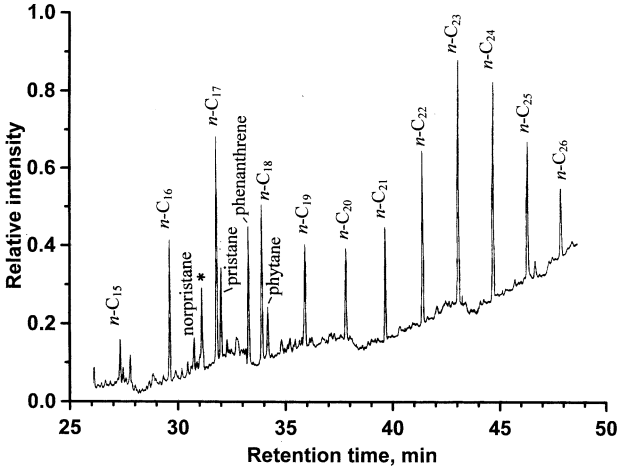

Fig. 2. Gas chromatogram (C_{14}–C_{27} range) of the organic extract from Orgueil meteorite. Extraction with *n*-butylcyclohexane (0.6 rock/solvent ratio) at 65°C for 528 h. *1,6-dimethyl-4-isopropylnaphthalene.

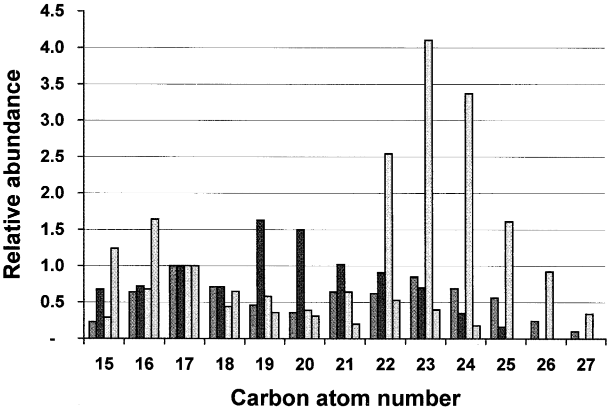

Fig. 3. Molar distributions of *n*-alkanes extracted from meteorites. Contents of all alkanes are normalized to that of *n*-heptadecane. The bars represent, left to right, Orgueil, Mighei, Cold Bokkeveld, and Antarctica meteorites.

3.3. Separation of Meteorite Kerogen and Its Analysis

The large difference between the total content of organic carbon in meteorites and the amount of the extractable organic material indicates that most organic constituents in carbonaceous meteorites are present in a form of the insoluble organic material called the meteorite kerogen (Vdovykin, 1967; Nagy, 1975; Bandurski and Nagy, 1976; Hayatsu et al., 1977; Cronin and Chang, 1993). This component from two meteorites, Orgueil and Cold Bokkeveld, was isolated using the method of Degens and Reuter (1964). Both kerogens are black, finely particular materials with density of ca. 1.0 g/cm^3. The Orgueil kerogen has a strong smell of sulfur-containing organic compounds. Electron-scanning microscope pictures of the material show that it consists of 0.5 to 3 μ globular particles. Most of the particles are clumped in larger agglomerates, 10 to 30 μ. Elemental mapping of the clumps showed that they contain, in addition to carbon, a noticeable amount of chlorine, probably an artifact due to the treatment with conc. HCl.

3.3.1. *IR Spectra of meteorite kerogen*

Fig. 4 shows the transmission IR spectrum of the Orgueil kerogen (KBr pellet). The reflectance IR spectrum of the material is similar. The spectrum, which is similar to those reported by Meinschein (1963a), Vdovykin (1967), and Wdowiak et al. (1988), contains several features which are also typical for terrestrial kerogens (Durand and Espitalie, 1976; Robin and Rouxhet, 1978; Kissin, 1987). The use of strong acids for dissolution of inorganic components of meteorites leaves a small quantity of inorganic impurities in the kerogens, mostly hydrated $CaSO_4$. Its contribution to the spectrum of the kerogen was evaluated by isolating this inorganic residue. A fraction of the Orgueil kerogen was subjected to extensive thermolysis at 250°C (see details below) followed by dissolv-

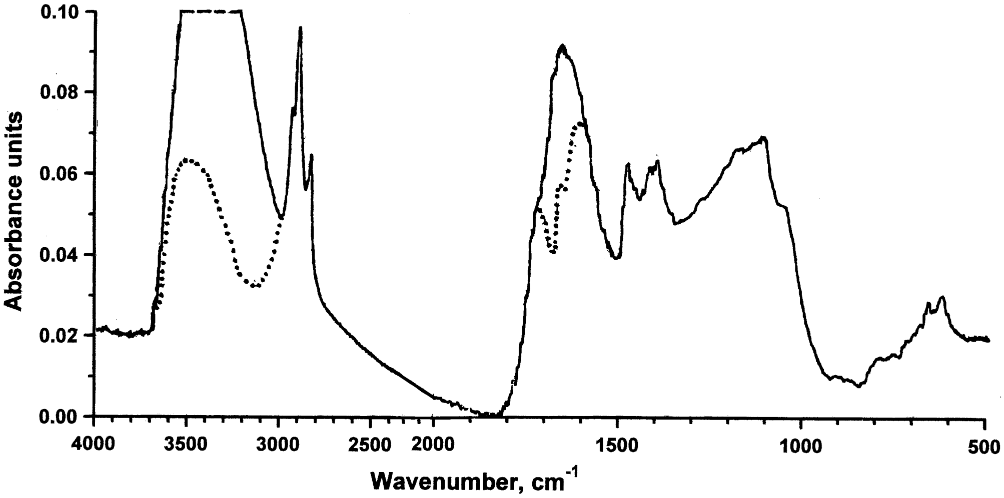

Fig. 4. IR spectrum of raw kerogen from Orgueil meteorite (KBr pellet). Dotted line: After subtraction of spectral features of inorganic impurities.

ing all organic decomposition products in CH_2Cl_2. The IR spectrum of a small solid residue showed that it is totally inorganic. Subtraction of the IR spectrum of the residue from the spectrum of the raw kerogen (Fig. 4, dotted line) allowed identification of the IR spectral features of the latter:

1. CH_2 and CH_3 groups: intense bands of 2953, 2924, 2868, 2854, 1459 cm^{-1}; the same as in the spectra of the meteorites themselves (Fig 1). The CH_3/CH_2 ratio in the kerogen is ~0.15 to 0.20.
2. Polar organic groups: hydroxyl groups [ν(OH) at ~3530 cm^{-1}; ν(C-O) at ~1100 cm^{-1}]; carboxylic acids [ν(C=O) at ~1705 cm^{-1}, δ(OH) at 1385 cm^{-1}, ν(C-O) at 1200 to 1180 cm^{-1}]; and carboxylic anions [$\nu(COO^-)$ at 1593 and ~1400 cm^{-1}].
3. A weak shoulder in the 1620 to 1600 cm^{-1} range, probably the overlap of bands due to quinones, unsaturated and multinuclear aromatic structures (Painter et al, 1983; Robin and Rouxhet, 1978).

3.3.2. Thermolysis of meteorite kerogen

In the case of terrestrial kerogens and bitumens, significant information about their structure can be obtained by subjecting the samples to mild thermocracking and by observing early fragmentation products (Kissin, 1987, 1993). Earlier, numerous researchers applied the same procedure to meteorite kerogens and to whole meteorites, both before and after removal of the soluble organic matter: see articles by Simmonds et al. (1969), Bandurski and Nagy (1976), Komiya et al. (1993), Sephton et al. (1998). In the present research, samples of the Orgueil kerogen were sealed in glass ampoules under vacuum, heated at 250 and 300°C, and analyzed by GC. The 250°C sample (very gentle conditions for thermocracking of organic compounds) produced two fractions. The first one is white semicrystalline powder sublimed in the upper part of the ampoule. Such materials were isolated and described over a century ago as meteorite wax (see review by Vdovykin, 1967). This fraction contains two types of products, the original free hydrocarbons in the meteorite (as was mentioned earlier, they constitute ~2% of the kerogen weight) and the early cracked products from the kerogen. The sublimate contains the following types of organic compounds:

1. Linear C_{13}–C_{24} alkanes with the maximum of the distribution at C_{17}–C_{18} These products account for ~20% of the sublimated mixture. They show no odd vs. even C_n preference.
2. Isoprenoid alkanes, phytane, pristane, and norpristane, in approximately the same relative quantities with respect to *n*-alkanes as in the organic extracts (Fig 2).
3. Several low-molecular-weight compounds in the C_8–C_{13} range whose GC peaks have the asymmetric shape with a trailing tail typical for GC peaks of alkanoic acids (Kissin, 1987); ~45%.
4. Elemental sulfur (~30%); it appears as two narrow peaks in the *n*-C_{23}–C_{26} range; confirmed by GC spiking.
5. Traces of light aromatic compounds (see discussion below).

The largest fraction of the 250°C thermolysis products is a black viscous mass. It is soluble in CH_2Cl_2, which indicates that prolonged mild thermocracking of a meteorite kerogen is sufficient for degrading it to a completely soluble material. (A small remaining insoluble part, according to IR analysis, is mostly hydrated $CaSO_4$.) The constituents of this organic mixture can be subdivided into two groups (Fig. 5A). The first group includes the same compounds as those present in the white sublimate: a suite of linear C_{14}–C_{27} alkanes, the three isoprenoid alkanes [their amounts are depleted by ~30% due to a higher reactivity in thermocracking reactions (Kissin, 1993)], phenanthrene (in a ~3 times higher ratio with respect to *n*-alkanes, compare Figs. 2 and 5A), and sulfur.

The second group of organic compounds in the degraded kerogen represents its main fragmentation and decomposition (dehydrogenation) products (Fig. 5A):

1. Light *n*-alkanes, C_6–C_{12}.
2. Light mononuclear aromatic compounds: benzene, toluene (both are outside of the GC range in Fig 5A), xylenes,

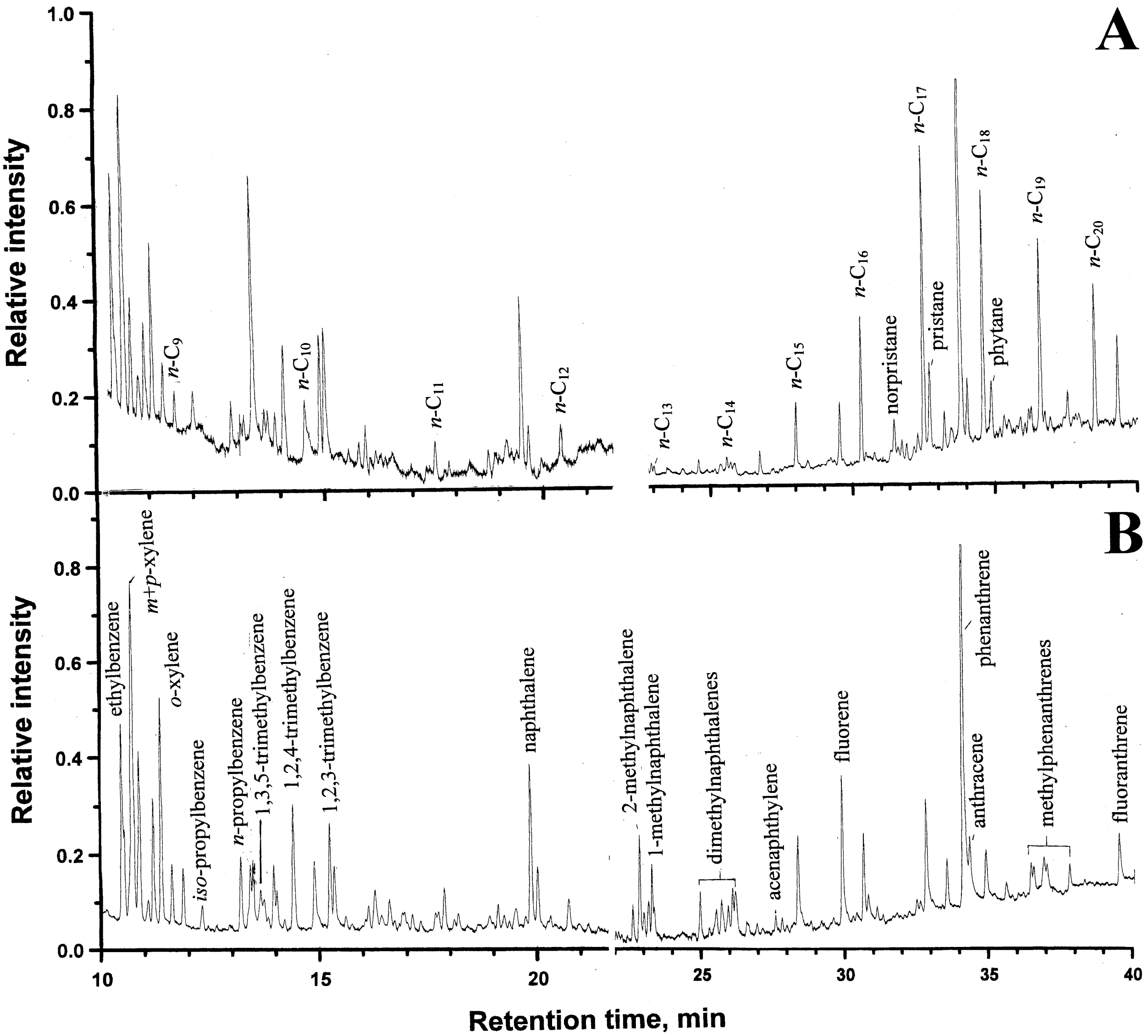

Fig. 5. Gas chromatograms (C_8–C_{21} range) of thermocracked material from kerogen of Orgueil meteorite. (A) 250°C for 242 h; (B) 300°C for 53 h.

methyl, ethyl-disubstituted benzenes, trimethyl-substituted benzenes, and small amounts of various C_4-substituted benzenes.

3. The lightest multinuclear aromatic compounds: naphthalene, mono- and dimethyl-substituted naphthalenes, fluorene, anthracene (the peak to the right of the phenanthrene peak), methyl-substituted phenanthrenes, and fluoranthrene No pyrene or heavier multinuclear aromatic compounds were detected.

All these light cracked products from meteorite kerogens, as well as from meteorites themselves, have been earlier reported by numerous researchers (Bandurski and Nagy, 1976; Levy et al., 1973; Komiya et al., 1993).

Our previous experience with cracking terrestrial kerogens (Kissin, 1987, 1993, 1998) suggests that when such reactions are carried out at higher temperatures, the conditions are too severe for identification of original structural elements in kerogens. Instead, the products of these reactions are mostly stable secondary cracked products. Fig. 5B shows the data for the 300°C products from the Orgueil kerogen. Comparison of Figures 5A and 5B shows the expected trends in thermocracking of complex organic mixtures under conditions of increasing severity:

1. Isoprenoid alkanes and kerogen fragments containing isoprenoid chains readily decompose at high temperatures due to the presence of tertiary C-H bonds. They completely disappear in the 300°C cracked products.
2. Thermocracking reactivities of *n*-alkyl chains increase with their carbon atom number. Therefore, heavy *n*-alkanes are present in much lower proportions in the 300°C sample. The heaviest of them, *n*-C_{22}–C_{26}, which are prominent in the meteorite extracts (Fig. 2), are present in lower quantities in the 250°C sample and completely disappear from the 300°C sample.
3. The yields of aromatic compounds are greatly increased in the 300°C sample, both those of mononuclear aromatics

(benzene, its mono-, di-, and polysubstituted methyl and ethyl derivatives) and multinuclear aromatic compounds, naphthalenes, fluorene, phenanthrene, anthracene, and fluoranthrene. Comparison of Figures 5A , 5B, and 2 suggests that only one of the multinuclear aromatics, phenanthrene, is present in a significant quantity in the meteorite itself, all others are the cracked products.

Similar results were obtained when samples of two meteorites, Orgueil and Murchison, rather than their kerogens, were heated at 300°C for 24 h. Thermolysis of the whole Orgueil meteorite produced the same products as those from pyrolysis of its kerogen. As mentioned previously, our sample of the Murchison meteorite contained a very low amount of free saturated hydrocarbons in the C_{16}–C_{20} range. Heating its dry rock at 300°C for 24 h released a large quantity of elemental sulfur (~0.8 wt.%), a small quantity of phenanthrene, and a variety of mono- and disubstituted benzenes. These results are consistent with previous pyrolysis experiments with this material (Sephton et al., 1998, 2000).

The pyrolysis results show that light aromatic compounds, which are often detected in thermolysis products of meteorites, are not present in the original specimens but are the decomposition products of indigenous organic components in the meteorites. To investigate possible organic precursors of the light aromatics, three model products, a heavy *n*-alkane (*n*-$C_{24}H_{50}$), a heavy isoprenoid alkane (squalane), and an ancient terrestrial hydrocarbon deposit (oil shale from Colorado, USA), were heated under vacuum at 350°C for 24 h, and their decomposition products were compared to those from the meteorite kerogen. The comparison confirmed that the three types of aromatic compounds, (a) all mononuclear aromatics, from benzene to trisubstituted benzenes, (b) all naphthalenes, and (c) anthracenes, are all the cracked products from the aliphatic components in meteorites. As an example, the relative yields of different xylenes, ethyl, methyl-disubstituted benzenes, and trimethyl-substituted benzenes, as well as the relative yields of naphthalene vs. its mono- and dimethyl-substituted analogs, are practically the same in all thermolyzed products, both from the meteorite kerogen and from the model compounds. These observations support the conclusion that all light aromatic compounds that are generated in thermolysis of meteorite kerogens are degenerate products in a sense that they do not reflect the structure of the kerogens. On the other hand, two compounds with mixed aliphatic/aromatic structures, fluorene and fluoranthrene, are present in the cracked products form the meteorite kerogen in much higher proportions (Fig. 5B). Apparently, the original polymeric structures in the kerogens contain fused five- and six-atom cycles which are thermolyzed to these two compounds. One can also assume that light aromatic compounds occasionally found in meteorites in small quantities (Hayes, 1967; Studier, 1968; Studier et al., 1968; Levy et al., 1970; Hayatsu et al., 1977; Kovalenko et al., 1992; de Vries et al., 1993; Sephton et al., 1998) could be generated from the aliphatic kerogen in their outer layers when the meteorites were flash-heated during their passage through the air.

3.4. GC Analysis of Possible Sources of Terrestrial Contamination in Meteorites

In the literature, assignment of free *n*-alkanes and isoprenoid alkanes in meteorites to terrestrial contamination proposes several contamination sources and routes. To evaluate their plausibility, three most often cited contamination sources were analyzed by GC.

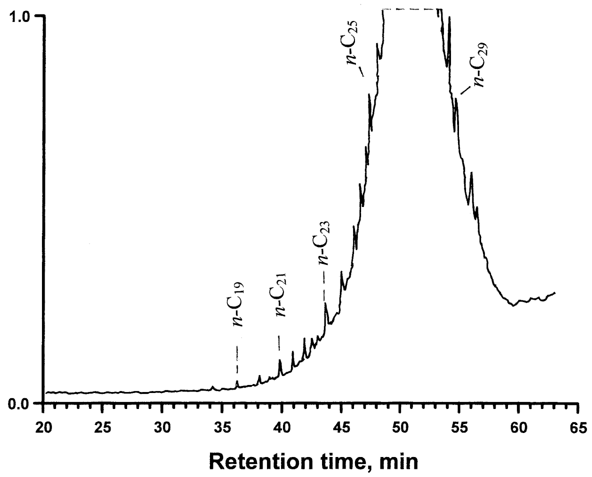

Fig. 6. Gas chromatogram of neat vacuum-pump oil.

1. Vacuum oils. The gas chromatogram of common vacuum-pump oil was recorded in parallel with the GC analysis of the meteorite alkanes (Fig. 6). It shows a broad “band” starting at C_{21}–C_{22} and extending to C_{33}–C_{35}. This band is the overlap of GC peaks of a large variety of heavy branched and multi-ring naphthenic hydrocarbons typical for dewaxed petroleum distillates (Kissin, 1990). None of the meteorite extracts have this GC feature.
2. Heavy organic compounds due to microbial contamination. A piece of a highly porous silicate stone that was exposed to the elements for 30 yr was chosen as a model of the combined microbial and heavy airborne terrestrial contamination outside of laboratory. Organic contaminants were extracted from the stone at 75°C (530 h) and 200°C (73 h). Fig. 7A shows the GC results for the first extract. Both extracts contain peaks of numerous organic compounds in the C_{11}–C_{14} range (retention times 20 to 26 min in the figure). Such compounds are completely absent from the meteorite extracts. In addition, the extracts contain over 30 organic compounds in the C_{15}–C_{30} range, together amounting to ~0.01% of the sample weight. None of their GC peaks match peak positions of *n*-alkanes or isoprenoid alkanes.
3. Degradation products of the phytol chain in chlorophyll as the source of isoprenoid alkanes. Extracts from a specimen of dried vegetation were examined for the presence of isoprenoid alkanes in the early decomposition products of chlorophyll. Extraction with *n*-butylcyclohexane at 100°C for 5 h (Fig. 7B) produced numerous light organic compounds in the C_{11}–C_{14} range and two heavy alkanes, *n*-$C_{25}H_{52}$ and *n*-$C_{27}H_{56}$, in a 1:3.3 ratio. Virtually no heavy isoprenoid alkanes or *n*-alkanes lighter than *n*-$C_{25}H_{52}$ were detected. When the extraction at 100°C continued for 64 h, it produced, in addition to the two *n*-alkanes, over 80 minor products in the C_{11}–C_{40} range, nearly all with peak positions different from those in the gas chromatograms of meteorite

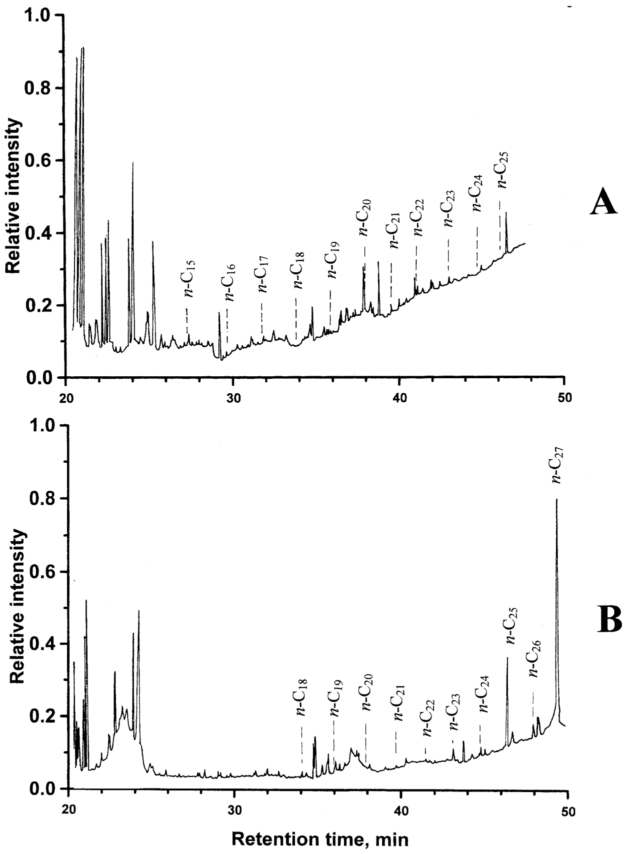

Fig. 7. Gas chromatograms of possible terrestrial contamination sources. (A) Exposed porous silicate rock, extraction at 75°C for 22 d. (B) Dry vegetation, extraction at 100°C for 5 h.

extracts. Only minuscule quantities of C_{15}–C_{22} *n*-alkanes and isoprenoid alkanes typical of meteorites were present in the latter extract as well.

4. DISCUSSION

Carbonaceous meteorites contain three types of organic components. The main part is the meteorite kerogen. This component is observable in whole meteorites (Fig. 1); it can be isolated from the meteorites by dissolving their inorganic components in conc. HF and HCl. The kerogen contains, in addition to carbon and hydrogen (Fig. 1), various heteroatoms, mostly oxygen, as well as nitrogen and sulfur (Vdovykin, 1967). The polar groups are easily detected by IR (Fig. 4). The amount of kerogen in carbonaceous meteorites can reach 5 to 6 wt.%. The indigenous nature of this material in meteorites was never challenged. The IR features of saturated hydrocarbon groups very similar to those in meteorites were also identified in interplanetary particles collected under conditions when terrestrial contamination was excluded (Swan et al., 1987).

The second group of organic compounds includes extractable indigenous polar organic compounds: mono- and dicarboxylic acids and their anions, sulphonites, phosphonates, amino acids, etc.; see reviews by Vdovykin, 1967; Cronin et al., 1988; Cronin and Chang, 1993. This fraction may be contaminated with synthetic organic compounds such as plasticizers (alkyl phthalates) and antioxidants (Cronin and Pizzarello, 1990).

The third group of organic compounds is a mixture of free *n*-alkanes, isoprenoid alkanes, and a few heavy aromatic compounds (Fig. 2). They constitute a small part of the overall organic material in meteorites, from 2 to 3 to <0.1 wt.%. Some meteorites, such as the Murchison meteorite (Cronin and Pizzarello, 1990; the data in the present study), contain very low quantities of free high-molecular-weight *n*-alkanes, although the meteorite contains a significant quantity of kerogen (Levy et al., 1973; Sephton et al., 1998). Comparison of the free alkane content measured in the Cold Bokkeveld meteorite 20 yr after its fall (Wöhler, 1858) and recently (Table 1) indicates that these compounds did not accumulate in the rock during storage.

The presence of free alkanes in many carbonaceous meteorites is beyond doubt; the only issue is their origin. The following discussion is limited to aliphatic constituents of kerogen and to free aliphatic hydrocarbons. It is separated into two subjects: (a) the possibility and the proposed sources of terrestrial contamination in meteorites, and (b) the principal structural features of aliphatic hydrocarbon groups in meteorites.

4.1. Possibility of Terrestrial Contamination

Currently, most researchers in the field view free alkanes in meteorites as terrestrial contamination; the opinion not shared by the present author. The following three arguments are usually cited in favor of contamination:

1. The quantity of heavy *n*-alkanes in meteorites is the highest in outer area under the crust and the lowest near the center. This distribution suggests penetration of impurities through the meteorite surface (Han et al., 1969; Cronin and Pizzarello, 1990).
2. Isoprenoid alkanes, first of all, phytane and pristane, are typical of terrestrial petroleum. Because these isoalkanes are nearly always found in meteorites together with *n*-alkanes, the latter are also terrestrial contamination.
3. The measurement of the $^{13}C/^{12}C$ ratio in individual compounds in the process of their GC analysis is an important technique for the analysis of terrestrial organic materials. A recent measurement of the $^{13}C/^{12}C$ ratio in *n*-alkanes extracted from several carbonaceous meteorites showed that this ratio (commonly represented as a $\delta^{13}C$ value with respect to the terrestrial Pee Dee belemnite carbonate fossil) is in the −25.3 to −38.7‰ range (Sephton et al., 2001). The $\delta^{13}C$ values for terrestrial alkanes are similar; they vary from −28 to −33‰ in ancient terrestrial sediments (Uzaki et al., 1993; Simoneit and Schoell, 1995; Odden et al., 1998) and in recent sediments (Huang et al., 1997). The use of this argument as a proof of terrestrial contamination is complicated, however. The $\delta^{13}C$ measurements for some meteorite kerogens (undoubtedly, indigenous materials) and for several lightest products of their thermolysis gave similar results, −25 to −33‰ (Alexander et al., 1998; Sephton et al., 1998, 2000).

From the viewpoint of terrestrial contamination, the period between a meteorite fall and its analysis in the laboratory should be separated into three stages: (a) time a meteorite spent on the ground before collection, (b) time spent in a museum or storage, and (c) time spent in a laboratory before and during analysis. Correspondingly, different sources of contamination should be assigned and discussed separately. The duration of the first period depends greatly on the size of a meteorite and the place of its fall. Relatively large meteorites (Orgueil, Cold Bokkeveld, Mighei) were noticed as bright bolides when they were passing through the air (Vdovykin, 1967); they were collected within a few hours afterward and kept in museums since. Some meteorites were collected within several days after their fall, whereas Antarctica meteorites spent thousands of years embedded in ice. The duration of storage before analysis can last from a few weeks to over 160 yr.

Some carbonaceous meteorites contain quite significant quantities of extractable organic material. The presence of extractable organic components in several large carbonaceous meteorites was determined relatively soon after their collection: by Wöhler (1858) and by Wöhler and Hornes (1859) in the Kaba and the Cold Bokkeveld meteorites, by Berthelot (1868) in the Orgueil meteorite. Quantities of semicrystalline meteorite waxes in some cases exceeded 0.6 wt.%; they were sizable enough to measure, even at that time, their overall chemical composition and physical properties (Vdovykin, 1967). It is difficult to imagine a level of contamination that would leave such quantities of soluble organic material in meteorites after microbial exposure for several hours or days. It should be mentioned also that these earlier studies were conducted well before the laboratory environment could be a potential source of heavy petroleum hydrocarbons.

4.1.1. "Man-made" contamination sources

Studier et al. (1968) proposed automobile exhaust products as a source of alkanes and aromatic compounds in meteorites. This contamination route, either before collection or during storage, can be easily excluded: exhaust gases of automobiles, apart from CO_2, CO, and the products of partial oxidation of hydrocarbons, contain only light aliphatic components (C_5–C_{10}) typical of gasoline whereas aliphatic hydrocarbons extracted from meteorites do not contain any hydrocarbons lighter than C_{14}. Airborne combustion-derived polycyclic aromatic hydrocarbons (PAH) can potentially contaminate meteorites as well. However, their typical composition (see examples in Youngblood and Blumer, 1975; Ishiwatari et al., 1994b) shows prevalence of heavy multinuclear compounds such as fluoranthrene, pyrene, crysene, and benzofluoranthrenes. This composition is radically different from the composition of multinuclear aromatics in meteorites, mostly phenanthrene.

Cronin and Pizzarello (1990) proposed the second possible man-made airborne source of terrestrial contamination: vacuum oils, lubricating fluids for saws, etc. (they all are petroleum distillates), and mixtures of plasticizers and stabilizers for plastics (e.g., substituted phenols, organic esters). Plasticizers and stabilizers can be easily detected by GC/MS. Large meteorites collected before 1900 (including Orgueil, Cold Bokkeveld, and Mighei in this study, see Table 1) and in Antarctica were not exposed to this source before collection and during a large part of their storage time. Ubiquitous aliphatic materials in modern chemical laboratories, vacuum and lubricating oils, should be also dismissed as a source of alkane contamination. Commercial lubricating and vacuum oils are usually dewaxed and are formulated with a goal of retaining relatively constant viscosity over a wide temperature range, a very low vapor pressure, and so forth. As our GC analysis shows (Fig. 6), such oils contain heavy branched and multi-ring naphthenic hydrocarbons in a relatively narrow range, C_{21}–C_{33} (see also Kissin, 1990). These oils contain very small fractions of heavy *n*-alkanes and do not contain any C_{18}–C_{20} isoprenoid alkanes. It should be noted that the meteorite samples examined in this particular study were not exposed to the laboratory environment at all.

One more cited source of possible *n*-alkane contamination for porous solids in museums and in the laboratory environment is floor wax. In the past, floor waxes were natural products; they were mostly mixtures of aliphatic esters with alkyl groups of a particular length (Banthorpe, 1992). Currently, floor waxes are heavy petroleum fractions. Both the fractionation data (Bennett, 1975) and high-temperature GC analysis (Quadrex Corp., New Haven, Conn.) show that these solids mostly contain linear C_{25}–C_{40+} alkanes, i.e., much heavier hydrocarbons than those found in meteorites (Fig. 3). Isoprenoid alkanes are not present in floor waxes. A part of floor wax in museums is eventually converted to dust and settles on furniture. Oró et al carried out analysis of several samples of this dust in 1966. As expected, the duct contains heavy *n*-alkanes with a distribution maximum at C_{25}–C_{27}; it does not contain any alkanes lighter than C_{20} and does not contain isoprenoid alkanes (compare to Figs. 2 and 3).

In the experience of this author, the most probable sources of small quantities of man-made terrestrial contamination in laboratory are light solvents such as methanol, benzene, toluene, and hexane. These materials, when bought in bulk, may have contact with paraffin-covered surfaces, such as seals in bottle caps. They may also have contact with plastic tubing containing stabilizers and plasticizers. This type of contamination can be quite persistent, even after solvent distillation. This contamination source can be avoided if heavier solvents, such as GC analytical standards (which are usually handled in glass), are used for the extraction. In general, a low level of contamination due to the laboratory environment is a serious concern but preparing appropriate blank samples using exposed porous materials and analyzing them can always estimate its nature and the level.

4.1.2. Biologic contamination sources

Han et al. (1969) and Cronin and Chang (1993) regarded microorganism invasion into meteorites during the period from their fall to collection as the most obvious potential source of contamination with organic compounds. Indeed, microorganism invasion into meteorites was experimentally detected (Steele et al., 1999). When discussing a possibility of terrestrial microbial contamination, both before collection or during storage, one should take into account that microbial organic matter is predominantly a complex mixture of polar, oxygen-containing, high-molecular-weight compounds (cell membranes, fatty substances, etc.) and biopolymers. Transformation of these materials into aliphatic hydrocarbons requires anaerobic conditions, increased temperatures, and at least 10^7 yr (Tissot and

Welte, 1984). Conditions under which meteorites are kept in museums and laboratories are not conducive to such transformations. Even a single-point evaluation of organic components in a contaminated porous material (see the experiment above, Fig. 7A) shows that the accumulated organic matter does not contain heavy linear or isoprenoid alkanes, especially in significant quantities reported in the earlier studies (Vdovykin, 1967), in the studies carried out in the 1960s, and in this paper.

n-Alkanes derived from terrestrial biologic sources always exhibit a strong odd vs. even C_n preference (Rieley et al., 1991; Uzaki et al., 1993; Tissot and Welte, 1984; Ishiwatari et al., 1994a; Yamada and Ishiwatari, 1999). A noticeable odd-C_n preference persists for millions of years; it was detected even in subbituminous coals that are 2 to $3{\cdot}10^6$ years old (Nelson, 1987) and in bitumens extracted from terrestrial kerogens (Kissin, 1987). In contrast, *n*-alkane distributions in meteorite extracts (Figs. 2 and 3) do not exhibit any odd vs. even C_n preference that would suggest recent biologic contamination.

The presence of heavy isoprenoid alkanes in meteorite extracts is usually regarded as an important evidence of terrestrial contamination with biologic materials because pristane and phytane are degradation products of the phytol chain in chlorophyll. However, phytane and pristane are very rare “natural” terrestrial contaminants. They are not present in soils or in microorganisms in significant quantities. Phytane is found on Earth only in crude petroleum and oil shales, and pristane is found, in addition to petroleum, only in a few recent marine sediments (Tissot and Welte, 1984; Banthorpe, 1992). Chlorophyll, the terrestrial precursor of phytane and pristane, is, of course, abundant in plants, but transformation of its phytol chain into isoprenoid alkanes is a very slow process, as the simple experiment with dried vegetation described above confirmed (Fig. 7B). On the other hand, accidental contamination of numerous meteorites collected in different places and kept in different museums, with crude oils or middle-range petroleum distillates (petroleum fractions containing pristane and phytane) is not very plausible.

The results published by Han et al in 1969 are usually cited as the most evident proof of terrestrial contamination of meteorites. These data can be reevaluated in the view of the present discussion. The Pueblito de Allende meteorite described by Han spent 7 d on the ground and was analyzed shortly afterwards. The only source of contamination considered by Han was biologic contamination on the ground. The outside part of the meteorite under the crust contained 0.1 ppm of fatty acids, with two of them, saturated C_{16} and unsaturated C_{18} acids, accounting for ca. 90% of the total acid content. This pattern is indeed typical for terrestrial biologic contamination. However, the same sample contained a five times higher quantity of the alkane/isoalkane mixture typical for other carbonaceous meteorites as well. This mixture exhibited no C_n preference shown by the fatty acids (a $C_nH_{2n+1}COOH$ acid mostly decarboxylates to a C_nH_{2n+2} alkane) and typical for *n*-alkanes in recent terrestrial sediments in general. These two facts—a large relative quantity of alkanes and the absence of the most prominent feature of terrestrial alkanes of the biologic origin, the odd vs. even C_n preference—suggest that the alkanes in this meteorite are not recent terrestrial contamination but are indigenous.

4.2. Relationship between Kerogen and Free Alkanes in Meteorites

Kerogen is the indigenous material in carbonaceous meteorites; it is present is some of them in very significant amounts. Infrared spectra of the kerogens (Fig. 4) and the meteorites themselves (Fig. 1) show that they contain a large fraction of aliphatic hydrocarbon structures. Thermolysis of meteorite kerogens under very mild conditions produces aliphatic fragments of different sizes which are derived from linear and isoprenoid alkyl groups in the kerogen. The kerogen apparently also contains fused five- and six-member carbon rings, predecessors of fluorene and fluoranthrene. The similarity between the C_n distributions of free hydrocarbons extracted from meteorites (Fig. 2) and those evolved from the meteorite kerogen thermolyzed at 250°C (Fig. 5A) supports the assertion that free aliphatic hydrocarbons in meteorites do not have a terrestrial origin as well.

4.3. Nature of Organic Components in Meteorites

Principal scientific results of the present study can be formulated as follows:

1. The presence of a suite of free heavy *n*-alkanes and isoprenoid alkanes in some carbonaceous meteorites, first researched in the mid-1960s, is confirmed in this study, as well as in many recent studies (eg., Cronin and Chang, 1993; Sephton et al., 2001). The quantities of these compounds vary depending on the source (Table 1). Very few free aromatic hydrocarbons are present in the examined meteorites in significant quantities, mostly phenanthrene.
2. IR spectral features of the meteorite kerogen (Fig 4) and the nature of its thermolysis products generated at relatively low temperatures (Fig. 5A) show that the kerogen contains *n*-alkyl and isoprenoid fragments attached (via polar links, judging by the IR data) to the predominantly aliphatic polymer matrix.
3. Various light aromatic compounds produced during thermocracking of organic components of meteorites and described by Vdovykin (1967), Simmonds et al. (1969), Bandurski and Nagy (1976), Hayatsu et al. (1977), Cronin and Chang (1993), Komiya et al. (1993), Alexander et al. (1998), Sephton et al. (1998, 2000), as well as in the present study (Fig. 5B), are typical thermolysis products from any aliphatic organic material, irrespective of its origin or composition. These aromatic compounds are a poor source of information about the original structure of the meteorite kerogen.
4. IR spectral features of the meteorite kerogen (Fig 4) and the nature of its thermocracked products (Fig. 5A) are, in some respects, similar to those of terrestrial kerogens. In particular, gas chromatograms of free aliphatic hydrocarbons extracted from meteorites, such as that shown in Fig. 2, are similar to the alkane suites from *thermocracked* terrestrial kerogens and bitumens, except for (a) the absence of lighter hydrocarbons which apparently slowly evaporated in space, (b) the absence of large quantities of methyl-substituted isoalkanes, which are formed in terrestrial organic deposits in cracking/isomerization reactions of heavy *n*-alkanes catalyzed by acidic clays (Kissin, 1987), and (c) the absence of

multi-ring naphthenic compounds typical for terrestrial biologic sources, such as steranes and terpanes (Tissot and Welte, 1984).

Many researchers, starting with Bandurski and Nagy (1976), reached similar conclusions about similarities of meteorite and terrestrial kerogens. The original terrestrial diagenic materials, precursors of kerogens, contain relatively few free acyclic hydrocarbons, with a strong odd vs. even C_n preference for *n*-alkanes. Slow evolution of free hydrocarbons from them (Tissot and Welte, 1984) and a gradual change of their *n*-alkane distributions to the smooth distributions typical for mature crude oils (Kissin, 1987) occurred when the kerogens aged for millions of years under conditions typical for petroleum maturation, at temperatures in the 80 to 150°C range. Alternatively, free aliphatic hydrocarbons evolve from terrestrial kerogens and bitumens when the latter are subjected to accelerated aging at 250 to 300°C (Johns et al., 1966; Philippi, 1965, 1974; Tissot and Welte, 1984; Kissin, 1987).

Based on the data on kerogen thermolysis, one can suggest that the original meteorite kerogens are mostly polymeric materials and do not contain significant fractions of free hydrocarbons. The final ratios between free hydrocarbons and insoluble kerogen in meteorites (although these ratios are always low) depend on their thermal and radiation history, similarly to terrestrial samples. Carbonaceous meteorites are small black bodies; they may spend a significant time in orbits around the Sun not much different from the Earth orbit, and the temperature on their surface can be, intermittently, quite high (the temperature on the Moon surface at noon is $>100°C$). Depending on their preimpact orbits, some carbonaceous meteorites may have their kerogen partially decomposed to light products or may completely lack soluble organic compounds despite a significant kerogen content. In this model, the extent of kerogen cracking is the highest in the outer layers of the meteorites and decreases with depth. If this assumption is correct, the Fischer-Tropsch route for abiotic synthesis of free *n*-alkanes in space should be discounted. Instead, different routes should be explored that may lead directly to polymeric structures containing long *n*-alkyl and isoprenoid substituents which are attached, via polar links, to a cross-linked polymer matrix consisting of cycloalkyl and aromatic fragments.

These conclusions require uncompromising hypotheses about the origin of saturated hydrocarbons in meteorites and, by inference, in asteroids. (The data presented here cannot discriminate between different proposed origins of kerogen in meteorites; they merely question the possibility of its terrestrial origin.) If plausible abiotic routes to various hydrocarbon groups in meteorite kerogens are found, they may have significant implications for the discussion of the origin of terrestrial aliphatic hydrocarbons in general. Abiotic synthesis of amino acids and components of ribonucleic acids on the surface of the primordial anaerobic Earth was proved to be feasible (Cronin et al., 1979; Cronin and Chang, 1993). In contrast, original abiotic sources of membrane materials of cells, fatty and isoprenoic acids and esters are not known. Terrestrial biologic routes to the synthesis of linear alkyl chains are very complex. The latter are formed in a series of reactions starting with digestion of carbohydrates, converting them to acetic acid and proceeding via acetyl-, acetoacetyl-, and capronyl-coenzymes A. Isoprenoid chains are also formed in enzyme-assisted reactions starting from the acetate ion and progressing via δ-dioxy-β-methylvaleric acid and isopentenyl pyrophosphate. Development of these multi-step enzymatic routes is difficult to rationalize based on the current understanding of the early-Earth chemistry. However, polar compounds with alkyl chains (e.g., fatty acids and esters) could be originally delivered to the Earth in meteorites, they could dissolve in water, form simple micelles, and could be used as membranes in first single-cell organisms. Later, terrestrial organisms could develop complex biosynthetic routes to *n*-alkyl and isoprenoid chains to replicate the structures of the substances essential for their survival.

5. CONCLUSIONS

Experimental analysis of soluble organic components in five carbonaceous meteorites by the GC method confirmed the presence of free aliphatic compounds, heavy *n*-alkanes and isoprenoid alkanes, in some of the meteorites. These results are in full agreement with numerous published data on extractable organic constituents in such meteorites. The quantities of these compounds vary depending on the source.

Currently, the presence of free *n*-alkanes and isoprenoid alkanes in carbonaceous meteorites is usually explained either by microbial contamination in a period between a meteorite fall and collection or by contamination from the environment of analytical laboratories and museums. Experimental evaluation of the plausibility of these contamination routes, by analyzing a contaminated terrestrial porous rock, a source of phytol, and the most often proposed laboratory contamination source, vacuum oil, shows that the presence of free saturated hydrocarbons in meteorites cannot be explained either by terrestrial microbial contamination or by contamination from the laboratory environment.

Insoluble organic components of two meteorites (meteorite kerogens) were isolated, and their composition was analyzed by IR and cracking/GC methods. The early aliphatic cracked products from the kerogen (generated under mild cracking conditions) are heavy *n*-alkanes and isoprenoid alkanes with the same carbon atom numbers as those in the free hydrocarbons extracted from the meteorites.

GC and thermocracking data suggest that the most abundant indigenous aromatic compound in the meteorites is phenanthrene. Most other aromatic compounds, both mono- and multinuclear, generated in the process of kerogen thermolysis are stable secondary products of thermocracking reactions involving aliphatic components in the kerogen. These aromatic compounds are a poor source of information about the kerogen structure.

The types of free hydrocarbons in meteorites resemble those of thermocracked ancient terrestrial organic sediments (kerogens, bitumens), except for the absence of lighter hydrocarbons, which apparently slowly evaporated in space, and the absence of multi-ring naphthenic compounds derived from terrestrial biologic sources such as steranes or terpanes.

The prevailing current explanation for the presence of free linear saturated hydrocarbons in carbonaceous meteorites (apart from contamination) is the abiotic route from gases relatively abundant in space, H_2 and CO. However, the produced data on the structure of meteorite kerogens require a search for different formation routes of free hydrocarbons. These routes should initially lead to complex polymeric structures containing *n*-alkyl and isoprenoid chains which are attached, via polar links (esters, salts, etc.), to a cross-linked polymer matrix. Free alkanes in meteorites are apparently formed as a result of slow thermo-decomposition of the cross-linked polymer.

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