Aliphatic hydrocarbons of the Murchison meteorite*

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Abstract—The indigenous organic compounds of carbonaceous chondrites have been difficult to characterize because of problems arising from terrestrial contamination. The fall of the Murchison meteorite (CM2) provided pristine samples which allowed the resolution of some prior ambiguities as, for example, in the case of the amino acids. However, the nature of the aliphatic hydrocarbons has remained unclear. Shortly after the Murchison fall, one laboratory found them to be mainly cycloalkanes; another found, in order of abundance, branched alkanes, olefins, and cycloalkanes; while a third reported predominantly *n*-alkanes followed by methyl alkanes and olefins. We have reinvestigated this question using benzene-methanol as the extraction solvent, silica-gel chromatography for fractionation of the extract, and GC-MS, and IR and NMR spectroscopic techniques for the analyses. When interior samples were obtained and the analyses carried out under conditions that minimized environmental contaminants, we have found the principal aliphatic components of the Murchison meteorite to be a structurally diverse suite of C_{15} to C_{30} branched alkyl-substituted mono-, di-, and tricyclic alkanes. Comparative analyses were carried out on the Murray (CM2), Allende (CV3), and New Concord (L6) chondrites that illustrate the nature of the contamination problem encountered with carbonaceous chondrites.

INTRODUCTION

THE NATURE OF THE ALIPHATIC hydrocarbons of the Murchison meteorite has been a matter of some controversy. Soon after the meteorite fell in Australia in 1969, analyses of these compounds were done in three laboratories. KVENVOLDEN et al. (1970) extracted a powdered meteorite sample with benzene-methanol (9:1), fractionated the extract on a silica gel column, and analyzed the hexane eluate (aliphatic compounds) by gas chromatography (GC), mass spectrometry (MS), and combined GC-MS. Although discrete compounds were not identified by these analyses, the aliphatic compounds appeared to be dominated by cycloalkanes. The authors suggested decahydronaphthalenes with short-chain hydrocarbon substituents as possible structures. The fact that the GC traces had the appearance of a relatively smooth bell-curve or hump and were generally devoid of discrete peaks suggested that the aliphatic components of this meteorite comprised a mixture of considerable structural complexity, i.e., a mixture of isomeric and closely related homologous compounds in comparable amounts.

ORO et al. (1971) used a similar procedure to analyze the Murchison hydrocarbons. They fractionated a benzene: methanol (3:1) extract on silica gel and analyzed the aliphatic fraction by GC-MS. Using a 150 m capillary column, they were able to separate the mixture into many discrete components. The most abundant of these were reported to be the branched alkanes (monomethyl and dimethyl isomers) followed in abundance by olefins and cycloalkanes.

Finally, STUDIER et al. (1972) published results of analyses of the Murchison hydrocarbons. As part of a comprehensive study, they analyzed benzene-methanol (3:1) extracts of the meteorite both before and after silica gel chromatography

and used a capillary GC-MS system of higher resolution than ORÓ et al. (1971). They found normal alkanes to be the most prominent aliphatic hydrocarbons, followed by several series of methyl and dimethyl alkanes and olefins. In contrast with KVENVOLDEN et al. (1970) and ORÓ et al. (1971), they emphasized the remarkable structural specificity of this suite of compounds and have often raised this point in support of the Fischer-Tropsch type process as a formation mechanism for meteorite organic compounds (STUDIER et al., 1972; ANDERS et al., 1973; HAYATSU and ANDERS, 1981; LEWIS and ANDERS, 1983).

To the best of our knowledge, these contradictory findings have not been satisfactorily resolved, although STUDIER et al. (1972) attributed the difference between their results and those of KVENVOLDEN et al. (1970) to the difference in resolution between the GC systems employed.

Recently, we prepared hydrocarbon fractions from the Murchison meteorite for stable isotope analyses. It was necessary to carry out GC-MS analyses of these fractions in order to assess the extent of terrestrial contamination. In the course of this work we learned how pervasive aliphatic hydrocarbons are in laboratory and/or curatorial environments, and how difficult it can be to exclude them as contaminants when working with small meteorite samples which may contain indigenous hydrocarbons at a concentration of only a few tens of ppm or less. These data, which we believe are relevant to the question of the nature of the indigenous aliphatic hydrocarbons of carbonaceous chondrites, are the subject of this paper. Results of the isotopic analyses will be published separately.

In summary, our results indicate that the most abundant aliphatic hydrocarbons of the Murchison meteorite are a structurally complex suite of substituted cycloalkanes. The *n*-alkanes and methyl alkanes, if indigenous to the meteorite, appear to be only minor components.

MATERIALS AND METHODS

A Murchison stone (specimen 1) obtained by S. Epstein from the Field Museum, Chicago, was broken at Caltech, and an interior piece brought to Arizona State University. This piece was then broken and interior fragments weighing 7.82 g total were crushed in a steel press and ground to a fine powder in a mortar. The powdered sample was weighed and placed in a container with 30 ml of benzene-methanol (9:1). The container was evacuated, sealed, and maintained at 90–110°C for 24 h. After removal of the meteorite residue by centrifugation, the extract was concentrated using a rotary evaporator and passed through a 3.5 × 0.5 cm column of Cu powder (J. T. Baker). (The large sulfur peak observed at about 35 min in the chromatogram shown in Fig. 1 indicates that this desulfurization procedure was not completely effective.) The combined eluate and column rinses were evaporated to dryness on a rotary evaporator and redissolved in dry, redistilled hexane (HPLC grade). The hexane solution was applied to a 21 × 1 cm column of dry silica gel (J. T. Baker, 40 μm, dried at 200°C) and the column was sequentially eluted with 1.5 column volumes of redistilled hexane, redistilled benzene, and redistilled methanol. The eluates were concentrated by rotary evaporation and aliquots were transferred and dried on a solid injector (S.G.E.). Gas chromatography was carried out using a Hewlett-Packard (HP) 5880 A series gas chromatograph connected to an HP 5970 mass selective detector with data acquisition by an HP 59970 C ChemStation. Separation was achieved on a 12 m × 0.2 mm fused silica capillary column coated with a 0.33 μm layer of HP high-performance cross-

linked methyl silicone gum. The column temperature was initially held at 70°C for 3 min, and then increased to 220°C at 3°/min. The injector and interface temperatures were, respectively, 220 and 280°C.

All subsequent analyses were carried out on meteorite specimens supplied by the Center for Meteorite Studies from the collections of Arizona State University: Murchison specimen 2 (#828.6), Murray (#635), Allende (#818), and New Concord (#202). Each stone was broken, sampled by drilling, and the sample transferred to the extraction solvent in a 27 × 37 in polyethylene glove bag, through which a continuous flow of He was maintained. Drilling was done with a Dremel Moto-Flex tool equipped with a diamond bit. The drill motor and control unit were located outside the bag, and only the bit and chuck, connected to the motor by a flexible shaft, were in the bag. The drilled powder was transferred to a vial containing 5 ml of a benzene-methanol mixture (9:1), sealed under vacuum, and kept at 100°C for 20 to 24 h. Benzene was distilled using a Vigreaux column and then sublimed under vacuum. All other solvents were redistilled HPLC grade. After centrifugation the extract was removed with a glass syringe with Teflon plunger and transferred to a second vial containing 1–1.5 g Cu powder (Aldrich, submicron) which had been rinsed with the extraction solvent. After standing overnight, the suspension was centrifuged and the supernatant concentrated to about 300 μl using a rotary evaporator which was protected by an activated charcoal filter in the air inlet and a dry ice-acetone trap in the vacuum line. For analyses of the whole extract, aliquot portions were transferred to the solid injector in the He glove bag. GC-MS analyses were carried out as described previously with the exception that the gas chromatograph was fitted with a 30 m × 0.25 mm glass capillary coated with a 0.25 μm layer of OV-17 (50% phenyl, surface bonded and cross-linked, J&W Scientific). The column temperature-program was 70 to 230°C at 1°/min followed by 70 min at 230°C. The injector was maintained at 230°C and the interface at 280°C. Fractionated extracts were obtained as described previously with the exceptions that the entire process was carried out in a He-filled glove bag and a 1 × 15 cm silica gel column was used.

An unfractionated benzene-methanol extract obtained using the He glove-bag procedure was used for infra-red (IR) spectroscopy. An aliquot representing the extract from 32.6 mg of Murchison powder was dried on a small area at the center of a 25 × 5 mm KBr disc. The disc was mounted in the sample compartment of a Nicolet MX-1 FT-IR spectrometer and data were accumulated for 8 min. The 1-alkene standards (1-hexadecene, 1-octadecene, 1-eicosene, and 1-docosene) were dissolved in benzene and the spectrum obtained in the same way.

A silica-gel hexane fraction obtained using the He glove-bag procedure was used for nuclear magnetic resonance (NMR) spectroscopy. The hexane eluate from 480 mg of Murchison meteorite was dried and redissolved in benzene-d$_6$ (Aldrich, 99.5 atm% D). A Bruker AM 400 MHz spectrometer operating with a 5 mm proton probe was used, and spectra were acquired for the solvent, a procedural blank, and the sample using the identical number of scans, transmitter pulse width, and receiver gain. The three individual spectra were transformed using an identical normalization constant and exponential weighting of 1 Hz. The benzene-d$_6$ spectrum was subtracted from both the procedural blank and the sample spectra, and the corrected procedural blank was then subtracted from the solvent-corrected sample spectrum to give the ultimate corrected sample spectrum.

The simultaneous equations generated by the type analyses of LUMPKIN (1956) were solved by iteration using a Bull HN desk top computer.

RESULTS

GC-MS Analyses of Hydrocarbon Extracts of the Murchison Meteorite

Figure 1 shows the total ion chromatogram resulting from GC-MS analysis of the hexane eluate obtained when a powdered Murchison stone (specimen 1) was extracted with benzene-methanol and the extract was fractionated on silica gel. The hexane fraction is expected to contain all the saturated
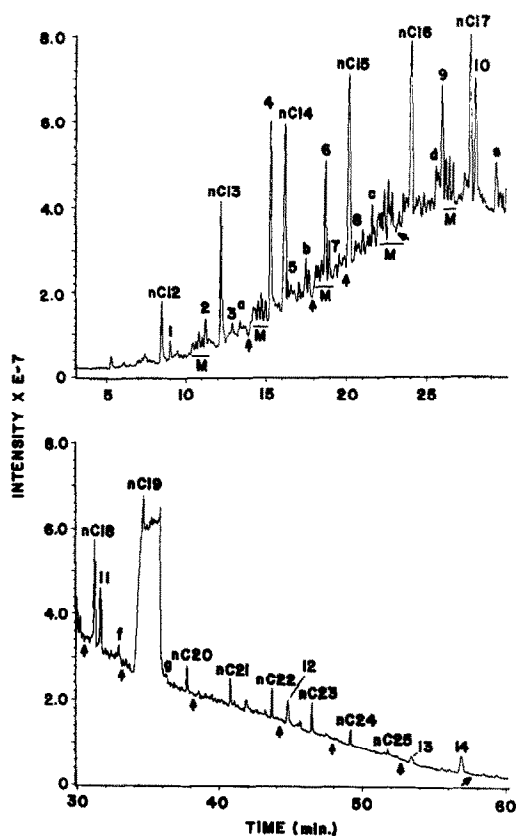

FIG. 1. Total ion chromatogram of the aliphatic hydrocarbons (silica gel hexane fraction) extracted from Murchison specimen 1. Numbers 1–14 denote isoprenoid hydrocarbons which are identified in Table 1. Letters a–g indicate the elution position of a series of alkyl cyclohexanes having the C number of the immediately following n-alkane. The bars marked by the capital letter M denote the elution ranges of monomethyl alkanes of the same C number as the respective following n-alkanes.

hydrocarbons of the original extract, including branched and cyclic forms (MEINSCHEIN et al., 1963). From analyses of retention times and mass spectra it was possible to identify suites of (1) n-alkanes, (2) monomethyl alkanes, (3) isoprenoid alkanes, and (4) cyclohexyl- and methylcyclohexyl alkanes. In addition, an envelope comprised largely of unresolved cycloalkanes was eluted across the entire chromatogram, as indicated by baseline mass spectra acquired, for example, at the retention times marked by the arrowheads in Fig. 1 (vide infra). The aliphatic compounds in total amounted to about 15 μg/g meteorite and about 20% by weight of the total material extracted with benzene-methanol. Both figures are in general agreement with earlier work (KVENVOLDEN et al., 1970; HAYES, 1967).

The finding of phthalate esters in the silica gel methanol eluate (data not shown) indicated that the meteorite specimen was not free of terrestrial contaminants. Consequently, it was important to inquire to what extent the hexane eluate, i.e., the aliphatic hydrocarbons, might also include material of terrestrial origin. The isoprenoid hydrocarbons were particularly telling in this regard. Those tentatively identified in the hexane fraction are listed in Table 1. Each identification implies that both the mass spectrum and expected retention time for the compound in question were obtained. Although comparison standards were not used, the mass spectra of branched alkanes can be predicted given the fact that cleavage with charge retention occurs mainly at the branched carbon atoms with preferential loss of the largest alkyl group (MCLAFFERTY, 1980). Retention times were derived from relative retention factors calculated according to Kissin and coworkers (KISSIN and FEULMER, 1986; KISSIN et al., 1986). The presence of isoprenoid hydrocarbons is in itself suggestive of terrestrial contamination. The C chain structures of other classes of meteorite organic compounds commonly show branching but do not show the branch point regularity of isoprenoid hydrocarbons (CRONIN et al., 1988). Furthermore, the structural homology with phytane shown by most of the compounds listed in Table 1 strongly suggests that they are

decomposition products of phytol or phytol esters, although a few appear to have originated in higher structures such as squalane. Isoprenoid alkanes are common components of crude oils, and most of those listed in Table 1 have already been identified therein (PETROV, 1987). The absence of C_{17} homologs (see Table 1) is characteristic of the isoprenoid distribution observed in crude oils and has been attributed to the lack of a probable cleavage mode for the principal precursors, pristane and phytane (TISSOT and WELTE, 1984). The presence in a meteorite extract of a suite of isoprenoid alkanes so similar to those of 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.

The apparent terrestrial origin of the isoprenoid alkanes raised the question whether other hydrocarbons of the hexane fraction (i.e., the n-alkanes, monomethyl alkanes, and cycloalkanes) might also be terrestrial or, at least, include a terrestrial contribution. All three of these classes of hydrocarbons are major components of crude oils (TISSOT and WELTE, 1984) and it is unlikely that contamination by isoprenoid alkanes could occur without contamination by other petroleum components as well. If oil is the source of the isoprenoid alkanes, an even greater contamination by n-alkanes would be expected since, in general, they occur in crude oils in greater amounts than do the isoprenoid alkanes (TISSOT and WELTE, 1984). In a survey of fractionated petroleum products that were considered to be potential sources of organic contaminants of ocean floor core samples, all those found to contain the isoprenoid alkanes, phytane and pristane, also contained n-alkanes (DUNHAM, 1987).

Since terrestrial contaminants should be located primarily on and near the surface of a meteorite stone, an experiment was done in which the sample was obtained by drilling into a Murchison stone (specimen 2) and collecting finely ground material from well below the surface. In order to minimize exposure to airborne contaminants, the sampling procedure and all subsequent operations were carried out either in a glove-bag with continuous He flow or in a closed container, e.g., a sealed, evacuated vial as used in the extraction step. Extracts of both an interior sample, obtained as described above, and a surface sample, obtained by using the drill to grind off surface material, were analyzed by GC-MS. In this experiment the extracts were analyzed directly without prior fractionation on silica gel. The results are shown in Fig. 2. The upper trace was obtained from the extract of the exterior sample and is quite complex. In addition to the saturated aliphatic compounds found in the silica gel hexane fraction, the unfractionated extract contains aromatic and heterocyclic compounds along with a number of environmental contaminants, plasticizers being the most prominent of the latter. The contaminants are easily recognized from a comparison of the GC-MS trace of the exterior sample with that of the interior sample (inverted in Fig. 2). The peaks corresponding to contaminants are either missing or greatly diminished in the interior trace. Peaks 13, 15, 29, 35, and 36, which represent various phthalate esters, are particularly dramatic examples. The n-alkanes, which are quite prominent in the exterior extract, are also markedly diminished in the interior

TABLE 1. Isoprenoid hydrocarbons (silica gel hexane eluate) found in the Murchison meteorite, specimen 1.

| Fig. 1 number	Isoprenoid hydrocarbon	Phytyl chain cleavage product
1	2,6-dimethyl undecane	+
2	2,6,10-trimethyl undecane	+
3	3,7-dimethyl dodecane	+
4	2,6,10-trimethyl dodecane (farnesane)	+
5	2,6-dimethyl tridecane	
6	2,6,10-trimethyl tridecane	+
7	3,7,11-trimethyl tridecane	+
8	2,6-dimethyl tetradecane	
9	2,6,10-trimethyl pentadecane	+
10	2,6,10,14-tetramethyl pentadecane (pristane)	
11	2,6,10,14-tetramethyl hexadecane (phytane)	
12	2,6,10,15,19-pentamethyl eicosane	
13	C_{28} isoprenoid	
14	C_{30} isoprenoid (squalane ?)	
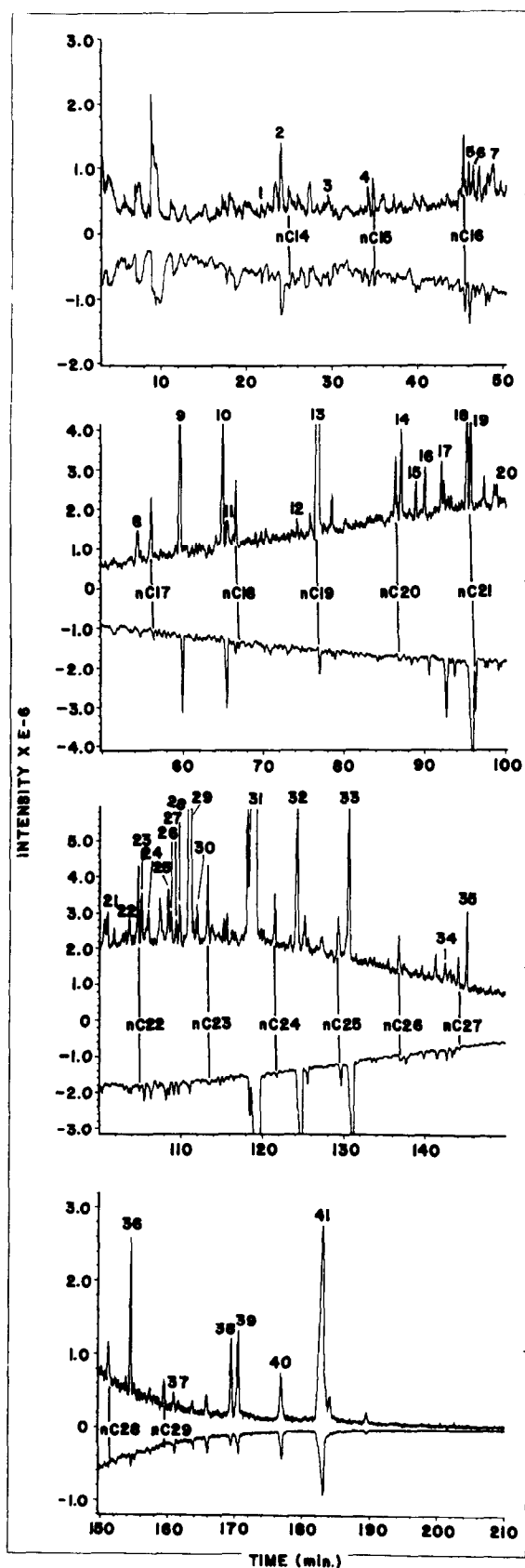
FIG. 2. Total ion chromatograms of whole benzene-methanol extracts of interior (inverted) and exterior samples of Murchison specimen 2. The numbered compounds were tentatively identified as

sample. A large decrease in abundance is observed for each n-alkane from C number 14 to 28. In a few cases where the decrease does not appear to be as pronounced, a coeluting component contributes substantially to the peak in the interior extract trace: a phthalate residue at C_{19}, phenanthrene and anthracene at C_{21}, and an unknown compound with base peak at m/z 208 in the case of C_{25}. Whether the small amounts of n-alkanes in the interior extract are indigenous or represent contamination that has diffused into the interior of the stone is not known. However, it is clear that if the n-alkanes are indigenous, they are not the predominant compounds, as has been previously claimed (STUDIER et al. 1972).

GC-MS Analyses of Hydrocarbon Extracts of the Murray Meteorite

The Murray meteorite is very similar to the Murchison meteorite but has had a terrestrial exposure period about twice as long. (The Murray fall was in 1950, Murchison in 1969.) Exterior and interior samples of this meteorite were obtained by drilling, respectively, at the surface and into the interior of a fragment that had been obtained some time ago when a larger stone was broken. Benzene-methanol extracts of these samples were prepared and analyzed as was done with Murchison specimen 2. Both extracts contained abundant n-alkanes along with clear indications of terrestrial contamination in the form of isoprenoid alkanes and phthalate esters. The distribution of the n-alkanes in the extract of the interior sample is illustrated by the m/z 57 single ion chromatogram shown in Fig. 3. The maximum abundance of this ion, which is very intense in the mass spectra of acyclic alkanes, occurs at the retention time of n-heptadecane and declines continuously through n-octacosane. It is interesting to note that this distribution is very similar to that observed for the n-alkanes of the gas-phase fraction of residential city air (CAUTREELS and VAN CAUWENBERGHE, 1978).

In an attempt to obtain samples at a greater distance from the surface, a second drilling experiment was carried out with a larger Murray stone. In this experiment, surface material, much of which was fusion crust, was initially ground off. Next, material drilled out of the interior was collected between the fresh surface and 1.2 cm (interior 1), and then from 1.2 cm to 2.5 cm (interior 2) into the stone. Each of these samples was obtained and worked up in a protected environment as described above. The content of n-alkanes in these samples was lower by about a factor of 10 in comparison with the

follows: (1) branched alkane, (2) naphthalene, (3) branched alkane, (4) methyl naphthalene, (5) acenaphthene, (6) 2,6-t-butyl-1,4-benzoquinone, (7) branched alkane, (8) branched alkane, (9) ?, (10) ?, (11) branched alkane, (12) tributyl phosphate, (13) diethyl phthalate, (14) 4-hydroxyl-3,5-di-t-butyl benzaldehyde, (15) methylbutyl phthalate, (16) methyl hexadecanoate, (17) fluoren-9-one, (18) phenanthrene, (19) anthracene, (20) anthracene-9-one, (21) and (22) methyl dibenzothiophenes, (23), (24), (26), and (27) methylphenanthrenes/methylanthracenes, (25) methyl octadecanoate, (28) dimethyl naphthothiophene, (29) dibutyl/diisobutyl phthalate, (30) dimethyl naphthothiophene, (31) ?, (32) fluoroanthene, (33) pyrene, (34) methyl pyrene, (35) butoxyethylbutyl phthalate, (36) di-sec-octyl phthalate, (37) naphthacene/chrysene/triphenylene, (38) ?, (39) bis(2-ethylhexyl)/dioctyl sebacate, (40) ?, (41) erucamide ?.
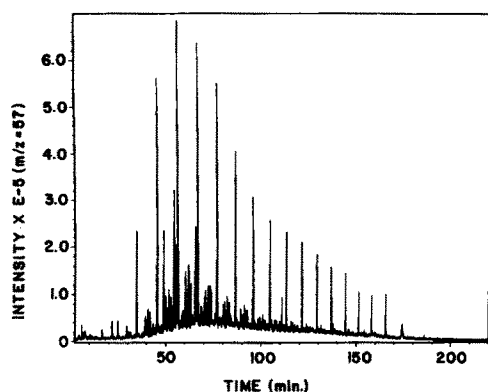
FIG. 3. Single ion chromatogram (m/z 57) of a whole benzene-methanol extract of an interior Murray sample. The series of intense peaks represent the n-alkanes; the intensity maximum corresponds to n-heptadecane.

previous Murray analyses. Interestingly, the distribution of n-alkanes varied significantly among the surface and the two interior samples. The intensity of the n-alkane peaks in the m/z 57 mass fragmentograms is plotted in Fig. 4. A feature unique to the n-alkanes of these samples is a component having a distribution with a maximum at n-tetradecane. In each case this distribution is superimposed on a suite of heavier alkanes having distribution maxima at $\geq C_{28}$ (exterior sample), C_{21} (interior 1), and C_{17} (interior 2). When the intensities of the n-alkane peaks of these three samples are summed, the total intensity distribution is similar to that observed for the first Murray samples analyzed, except for the addition of the light fraction peaking at C_{14}. Ignoring for the moment the light fraction, the shift of the distribution

maxima of the remainder of the alkanes toward lighter members of the series as sampling proceeded inward suggests the possibility that airborne hydrocarbons, which accumulated on the surface of the stone, diffused inward, with the lighter, more mobile components reaching the greatest depth.

The presence of phthalates in the sample taken at greatest distance from the surface shows that, even at a depth of 1.2 to 2.5 cm below the surface, the Murray specimen is not free of contaminants. The phthalates in this sample are made evident by a m/z 149 (phthalate base peak) single ion chromatogram, as displayed in Fig. 5a. Moreover, the more abundant isoprenoids, phytane, pristane, etc., are also present, suggesting a substantial terrestrial contribution to the alkanes, in general (see Fig. 5b).

The behavior of the phthalate diester contaminants in these samples is similar to that of the n-alkanes. All three samples contain the principal members of this class of compounds, diethyl-, dibutyl-, and di-2-ethylhexyl phthalate. The total concentration of these three compounds drops off smoothly as one proceeds from the surface to the interior, and in the innermost sample is about 40% of that at the surface. However, the concentration of diethyl phthalate, the lightest of these compounds, is nearly the same in all three samples, whereas the 2-ethylhexyl diester drops sharply from the exterior to the first interior sample—a result that may reflect the effects of diffusion.
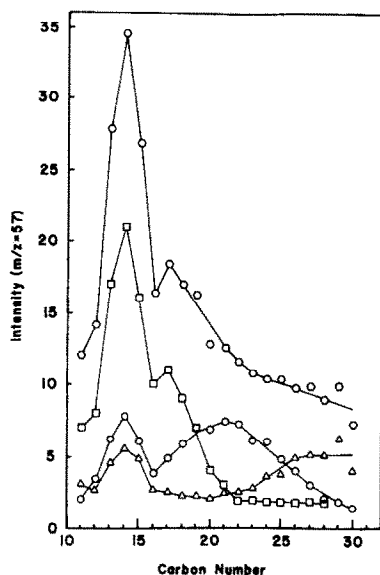

FIG. 4. Normal alkane abundances in whole benzene-methanol extracts of the Murray meteorite: triangles, exterior sample, mainly fusion crust; circles, interior sample 1 taken from surface (after removal of fusion crust) to 1.2 cm; squares, interior sample 2 taken from 1.2 cm to 2.5 cm below surface; hexagons, sum of exterior and two interior samples.
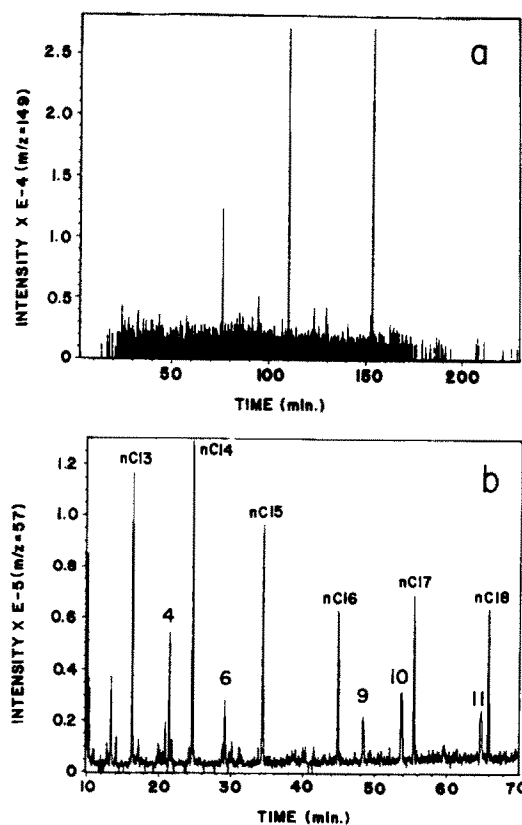

FIG. 5. Single ion chromatograms of the whole benzene-methanol extract of an interior (1.2 to 2.5 cm depth) Murray sample. (a) m/z 149; (b) m/z 57. The isoprenoid alkanes are numbered as in Table 1.

The light fraction of *n*-alkanes with a distribution maximum at *n*-tetradecane is most abundant in the most interior fraction (Fig. 4). However, inferences drawn from quantitative comparisons of alkanes in this molecular weight range are not warranted because the abundance of *n*-alkanes of C chain length up to about C_{18} can be dependent on the temperature and pressure used for concentration and/or drying (NOONER and ORÓ, 1967). In our procedure, small differences in the extent to which the extract was concentrated and later dried on the solid injector could have had significant quantitative effects.

GC-MS Analyses of Hydrocarbon Extracts of the Allende Meteorite

In an attempt to obtain an unambiguous look at the alkanes which can contaminate carbonaceous chondrites, several analyses were carried out on samples of the Allende meteorite, a C3V chondrite that was carefully analyzed immediately after its fall and shown to be nearly devoid (≤ 0.1 ppb) of extractable organic compounds (HAN et al., 1969). Three different stones from the Arizona State University collection were analyzed. One had for many years been kept as a hand specimen in the office of one of us (J.R.C.). This hand specimen and one of the other stones was sampled by drilling; the remaining stone was broken and fragments originating in the interior and others retaining exterior surface were collected. In all cases, sampling and all subsequent manipulations were carried out in a protected environment and procedural blanks were analyzed in parallel with the meteorite extracts. The results were as follows:

1) In each sample the *n*-alkanes were the predominant compounds present.
2) The content of *n*-alkanes was substantially less in the interior samples than in exterior samples.
3) The distribution of *n*-alkanes was different in each specimen, with maxima at (a) n-C_{15}; (b) primary at n-C_{21},

secondary at n-C_{15}; and (c) primary at n-C_{27}, secondary at n-C_{20-21}.
4) Each sample contained phthalates and the total content of *n*-alkanes correlated well with the total phthalate content.

The decreased content of *n*-alkanes in interior samples and the correlation of their abundance with phthalate content clearly mark the *n*-alkanes as contaminants. However, their presence in all of the Allende interior samples and the qualitative variation among the samples was surprising. The fact that of all the samples analyzed, only an interior sample of the New Concord meteorite, an ordinary chondrite (L6), was free of *n*-alkane and other organic contaminants suggests a particular affinity of the carbonaceous chondrites for airborne hydrocarbon contaminants. The presence in carbonaceous chondrites of insoluble carbonaceous phases may account for this. The variation in the *n*-alkane distribution patterns seems to indicate different contamination sources even among stones originating in the same collection.

Infra-red Absorption Spectroscopy of the Murchison Hydrocarbons

Figure 6 shows the IR absorption spectrum of a benzene: methanol extract that is identical to the extract of uncontaminated Murchison interior sample that gave the GC-MS analysis shown in Fig. 2. For comparison, the spectrum of a mixture of standard alkenes (1-hexadecene, 1-octadecene, 1-eicosene, and 1-docosene) is also shown. Several significant inferences can be drawn from a comparison of these spectra. First, they confirm the GC-MS results indicating the near absence of *n*-alkanes. The IR spectrum gives no indication of long *n*-alkyl groups in general, whether in the form of alkanes or attached to aryl or other functional groups. Long chain *n*-alkyl groups, if present, would be apparent from a spectral band at 730–720 cm^{-1} that arises from rocking modes of polymethylene sequences (KISSIN, 1987). This spectral
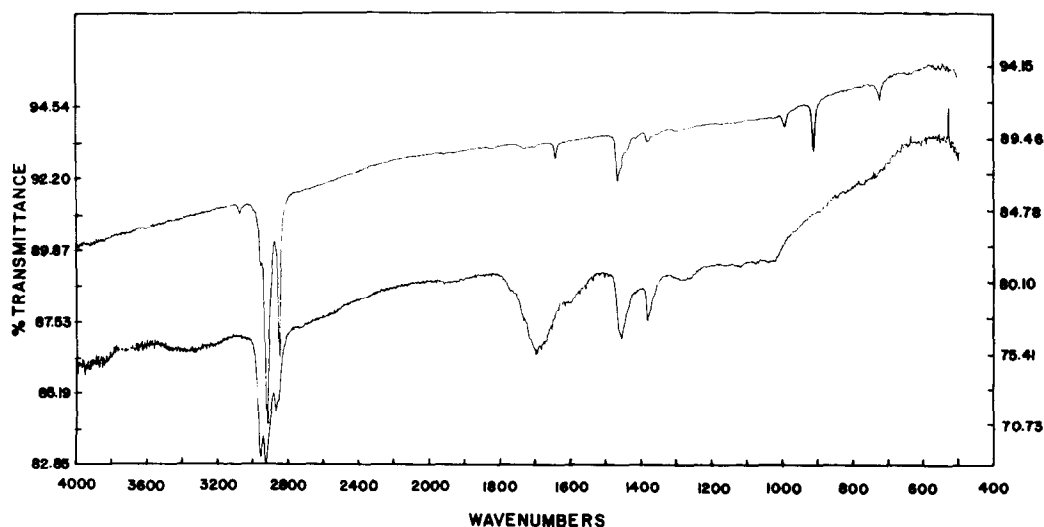

FIG. 6. Infra-red spectra of (i) a whole benzene-methanol extract of Murchison specimen 2 (lower trace, left scale) and (ii) a standard composed of 1-hexadecene, 1-octadecene, 1-eicosene, and 1-docosene (upper trace, right scale).

feature, clearly apparent in the standard, is absent from the meteorite extract.

Secondly, the alkyl groups appear to be highly branched. This is clearly seen in the intense absorption band at 2900–2800 cm^{-1}. This spectral feature is composed of two sets of bands arising from CH stretching vibrations of, respectively, methyl and methylene groups. The methyl bands lie at slightly higher wavenumbers than the methylene bands (CROSS, 1960). The absorption bands arising from the methylene groups are clearly dominant in the alkene standard, which has an overall methylene:methyl ratio of 16. The meteorite extract, in contrast, has methyl bands that are roughly equal in intensity to those of the methylene groups. The relative abundance of methyl groups is also seen from the intensity and absorption maximum of the spectral feature near 1400 cm^{-1} (CROSS et al., 1950). Methylene groups give rise to a weak doublet, as seen in the spectrum of the standard; however, with increasing methyl content, the extinction increases and the absorption maximum shifts to a slightly higher wavenumber. The spectrum of the Murchison extract is clearly of the latter type.

Third, reasonably intense absorption bands around 3100 and from 1000 to 700 cm^{-1} would provide evidence for olefinic structures, if present (CROSS, 1960). However, none of these bands were observed in the IR spectrum of the meteorite extract. Hydrogenation of the Murchison extract with a Pd/BaSO$_4$ catalyst was also carried out with the intention of revealing n-alkenes. A mixture of n-alkenes containing multiple positional and geometrical isomers and their close homologues would be manifest on GC-MS as a broad hump in intensity due to the large number of compounds with similar retention times. Hydrogenation of such a mixture would convert these compounds to n-alkanes, and the chromatographic hump to a series of intense n-alkane peaks. However, such a result was not observed by GC-MS analysis. Although hydrogenation gave rise to reduction products derived from aromatic compounds, such as octahydrophenanthrene, the hump persisted and no increase was observed in the content of n-alkanes.

Finally, a broad absorption feature lying between 1800 and 1550 cm^{-1} in the IR spectrum of the meteorite extract suggests the presence of carbonyl groups (CROSS, 1960). The fact that this feature largely disappears from the spectrum obtained after hydrogenation is consistent with the presence of aldehydes and/or ketones. Several quinoid compounds have been identified in the silica-gel methanol fraction of the extract and may contribute to this spectral feature (unpubl. results).

Proton NMR Spectroscopy of Murchison Alkanes

The question of chain branching was also addressed by NMR spectroscopy. A benzene-methanol extract was obtained as before (GC-MS analysis of Fig. 2; IR analysis of Fig. 6). In order to focus on the alkanes, the extract was fractionated on silica gel and the hexane eluate was analyzed. The proton NMR spectrum is shown in Fig. 7. Two major absorption features are seen with maxima, respectively, at 0.91 and 1.32 ppm. A shoulder on the second, or more downfield, peak ranges from about 1.4 to 2.0 ppm. The peaks
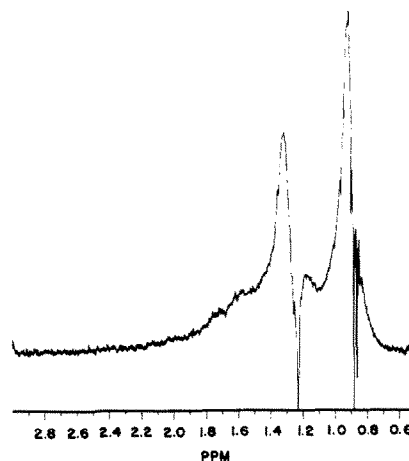

FIG. 7. Proton NMR spectrum of the aliphatic hydrocarbons (silica gel hexane fraction) extracted from Murchison specimen 2.

are fairly broad, indicating considerable structural heterogeneity in the sample. Both peaks are slightly distorted by negative excursions of the trace, resulting from the fact that extraneous features in the sample spectrum are not perfectly compensated by corresponding features in the solvent and procedural blank. The more upfield of the two major peaks covers a chemical shift range that is characteristic of relatively unshielded methyl protons, e.g., as found at the ends of C chains. The chemical shift range of the second peak corresponds to that of relatively unshielded methylene protons. The shoulder covers a chemical shift range characteristic of ring methylene protons and unshielded methene protons. Integration of the spectrum gives values of 44, 42, and 14% of the total intensity, respectively, for the methyl, methylene, and methene/ring methylene protons. The intensity of the methyl proton feature is rather striking. The methyl proton:methylene proton ratio calculated from these integration data is 1.05 (a second experiment gave a slightly higher value, 1.18). For alkanes to give methyl:methylene ratios of this order, it is necessary for there to be chain branching at about every third to fourth C atom of the main chain. The subtraction artifact at about 1.2 ppm causes the methylene peak to be slightly underestimated in these spectra, but it does not appear that the general conclusion of extensive chain branching would be altered significantly by a better correction.

Cycloalkanes of the Murchison Meteorite

It was pointed out above that chromatograms of the silica-gel hexane fraction display an envelope of intensity apparently arising from unresolved cycloalkanes. The presence of these compounds can be inferred from the mass spectra observed at intensity minima in the total ion chromatogram of the hexane fraction, e.g., at the retention times marked by the arrowheads in Fig. 1. A typical mass spectrum taken at the retention time marked by the earliest arrowhead in Fig. 1 is shown in Fig. 8. The most prominent fragment ions belong to a C$_n$H$_{2n-1}$ series (m/z = 55, 69, 83, 97, 111, . . .) that declines in intensity with increasing m/z.

Mass spectra obtained at progressively later retention times, as indicated by the additional arrowheads in Fig. 1, are similar

to the spectrum shown in Fig. 8. However, the mass range in these spectra extends to higher m/z values, indicating an increase in molecular weight, and, secondly, the C_nH_{2n-3} and C_nH_{2n-5} ion series become increasingly significant in the later mass spectra. The latter observation suggests the presence of two- and three-ring condensed alicyclic compounds, respectively.

We have used the procedure of LUMPKIN (1956) for mass spectrometric type analysis to estimate the relative proportions of acyclic alkanes, single-ring cycloalkanes, and two-ring through six-ring condensed cycloalkanes in the silica gel hexane fractions of Murchison specimens 1 and 2. The results are shown in Table 2. It can be seen from the proportions calculated for the hexane fraction of Murchison specimen 2, which we believe to be nearly free of contamination, that single-ring cycloalkanes dominate the material of low retention time followed in abundance by acyclic alkanes. At later retention times, cycloalkanes account for about 90% of the material, with single-ring and two-ring condensed cycloalkanes being present in roughly comparable amounts, followed by significantly smaller amounts of three-ring condensed cycloalkanes and acyclic alkanes.

Similar mass spectra are observed at intensity minima in the total ion chromatograms of unfractionated extracts, such as that shown in Fig. 2. However, these spectra are more complex and cannot be subjected to type analysis because of contributions from both alkyl-substituted aromatic ring compounds and alkyl heterocyclic compounds.

DISCUSSION

Taken together, the results of these analyses indicate that a structurally diverse suite of branched, alkyl-substituted cycloalkanes ranging in C number from about 15 to 30 is the predominant component of the aliphatic fraction of the Murchison meteorite. This result is in good agreement with the earlier findings of KVENVOLDEN et al. (1970) but contrasts with the results of STUDIER et al. (1972).

The identification of cycloalkanes in this work and earlier by the Kvenvolden and Oró groups is based entirely on mass spectral evidence and, it should be added, on mass spectra of mixtures containing multiple, albeit closely related, com-

FIG. 8. Mass spectrum recorded at the first arrowhead in Fig. 1 (retention time = 13.9 min).

TABLE 2. Percentage distribution of aliphatic components at selected retention times throughout GC-MS analysis of fractionated (hexane) Murchison extracts and in standards.

	Percent						
	Acyclic Alkanes	Cycloalkanes condensed ring number					
		1	2	3	4	5	6
Retention time (min.)							
Murchison specimen 1							
13.9	17	37	28	16	2	0	0
21.9	14	34	12	27	13	0	0
29.1	8	24	32	19	12	5	0
43.5	6	17	26	13	17	15	6
Murchison specimen 2*							
35.3-37.7	22	71	6	1	0	0	0
79.7-83.3	10	52	38	0	0	0	0
145.0-147.0	7	40	48	5	0	0	0
167.8-171.0	9	43	35	13	0	0	0
Standards							
n-dodecylcyclohexane	0	100	0	0	0	0	0
n-octacosane	98	0	0	1	0	1	0
2,6,10-trimethyl dodecane	99	0	1	0	0	0	0
2,6,10,14-tetramethyl pentadecane (pristane)	99	0	1	0	0	0	0

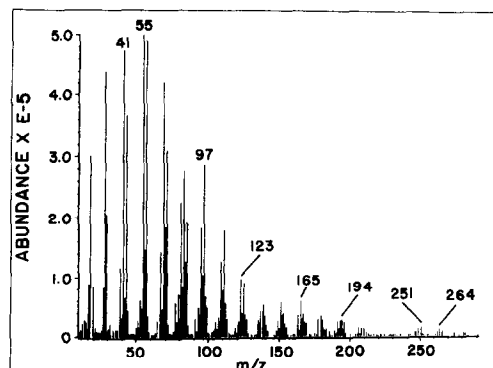*Mass spectra averaged over the retention time periods given.

ponents. Nevertheless, the evidence seems compelling. The silica gel chromatographic step should have removed the more polar compounds, such as fatty alcohols or thiols which, if present, could have given similar C_nH_{2n-1} ion series. However, long chain alkenes could be present in the silica gel hexane fraction and give mass spectra which in mixtures might be mistaken for those of cycloalkanes. Our IR and NMR spectroscopic analysis and hydrogenation studies provided no evidence for alkenes, although they could have escaped detection if present in relatively small amounts. KVENVOLDEN et al. (1970) may have removed small amounts of unsaturated compounds from the hexane eluate by $AgNO_3$ chromatography, although they did not directly identify them. Likewise, ORÓ et al. (1971) attribute the C_nH_{2n-1} ion series observed early in the GC elution to olefins.

Structural diversity in the cycloalkanes is inferred from an inability to achieve their chromatographic resolution. KVENVOLDEN et al. (1970) drew this inference from the hump observed in their gas chromatograms, but were criticized by STUDIER et al. (1972) who stated that these results were more likely a reflection of the poor resolution of the packed column GC system employed by KVENVOLDEN et al. (1970) than of the nature of the meteorite aliphatic mixture. The results reported here support the findings of KVENVOLDEN et al. (1970). We consistently observed a featureless intensity envelope or hump when the hexane eluate was analyzed by high resolution capillary GC. Our spectroscopic evidence for

a rather high methyl:methylene ratio provides an obvious explanation for the structural diversity: the degree of branching required by a methyl:methylene ratio of this magnitude offers enormous possibilities for ring substitution and chain isomerism.

STUDIER et al. (1972) found the Murchison extract to consist of a few homologous alkane and alkene series with normal alkanes being most prominent, followed by methyl and dimethyl alkanes. The difference between the results reported here and those of STUDIER et al. (1972) may arise largely from the tendency of the latter to focus on the lower homologues, i.e., the alkanes of C number less than about 16. They state that the heavier alkanes were present only in low abundance. However, as we have seen, the lower alkanes can contaminate even interior samples of carbonaceous chondrites, and rather extreme measures are required if aliphatic contaminants, in general, are to be avoided. In carbonaceous chondrites with long terrestrial histories it may be very difficult, if not impossible, to avoid them completely. The failure of STUDIER et al. (1972) to detect the complex suite of cycloalkanes, which we believe are the dominant aliphatic components indigenous to the meteorite, may be a result of (1) their tendency to focus on the n-alkanes ($<C_{16}$) which elute before the maximum in the cycloalkane intensity hump is reached, and (2) their use of a chromatographic system of such high resolution that the hump was spread over a broad elution range and effectively flattened to near invisibility. We observed the latter when a Murchison extract was run on a 92 m Apiezon L capillary column using a temperature program of 0.5°C per min.

It is interesting to compare our results with the very comprehensive pre-Murchison analyses of NOONER and ORÓ (1967). The aliphatic hydrocarbons of some 20 carbonaceous chondrites, including all three major petrologic types, were analyzed by methods similar to those used in this work. The results were similar to those reported here for what we consider to be contaminated samples. Homologous series of each of the four classes of aliphatic compounds that we found in Murchison specimen 1 (i.e., n-alkanes, monomethyl alkanes, cyclohexyl alkanes, and isoprenoid alkanes) were also reported by GELPI and ORÓ (1970). They found that the amounts varied both within and between meteorites, and in some instances bimodal distributions of alkanes were observed. The similarity between these compounds and those of petroleum crudes and derived products was apparent, and GELPI and ORÓ (1970) somewhat despairingly suggested that these contaminants masked any trace of indigenous extractable material.

The problem of recognizing the indigenous hydrocarbons of carbonaceous chondrites with long terrestrial exposures is a serious one, to which our inability to obtain uncontaminated interior samples of the Murray meteorite attests. It may be that only the Murchison meteorite, which now has had a terrestrial exposure of 20 years, can provide pristine samples. If so, the protection of specimens of this meteorite from additional contamination should be seriously considered.

GELPI and ORÓ (1970) found isoprenoid alkanes in 19 of the 20 carbonaceous chondrites analyzed. Both HAYES (1967) and WASSON (1974) used the data of Oró and his coworkers (NOONER and ORÓ, 1967; GELPI and ORÓ, 1970) to make log-log plots of the n-alkane vs. isoprenoid content of carbonaceous chondrites. The correlation of n-alkane content with isoprenoid content in the data is rather striking. In view of the recognition by GELPI and ORÓ (1970) that the meteorite isoprenoids are terrestrial, their correlation with n-alkanes surely raises a doubt as to the origin of at least some portion of the n-alkanes. In light of these results, our inability to detect significant amounts of n-alkanes, isoprenoid hydrocarbons, or other compounds common to crude oils in interior Murchison samples is not a surprising result even considered apart from the earlier Murchison analyses of KVEN-VOLDEN et al. (1970) and ORÓ et al. (1971). It is prudent to note in this regard that cycloalkanes, which appear by mass spectrometric analysis to be similar to those of the Murchison meteorite, are also found in oils. However, it should also be noted that the IR spectrum of vacuum pump oil, which by GC-MS shows a substantial content of cycloalkanes, suggests a significantly lower methyl:methylene ratio than was found for the Murchison cycloalkanes. How cycloalkanes alone (i.e., without accompanying n-alkanes, isoprenoids, etc.) could come to contaminate interior samples of a meteorite is not at all clear, and it seems safe to assume that the cycloalkanes are in fact the predominant indigenous aliphatic compounds.

In a recent review, we noted that almost all classes of chondritic organic compounds seem to share certain characteristics, one of which is the abundance of branched-chain isomers (CRONIN et al., 1988). When this review article was written, the supposed predominance of n-alkanes within the higher molecular weight aliphatic hydrocarbons seemed to set the latter apart when judged by this criterion. The results of the present work, which suggest highly branched structures for these compounds, resolve this apparent inconsistency.

The formation mechanism(s) for the branched cycloalkanes is an intriguing question. Isotopic analyses of chondritic amino acids (EPSTEIN et al., 1987) have led to the hypothesis that the organic compounds of carbonaceous chondrites are derived from interstellar precursors by way of nebular and/or parent body reactions, e.g., hydrogenation and/or aqueous phase chemistry. The formation of the aliphatic hydrocarbons of carbonaceous chondrites should be considered in this context and will be discussed in a subsequent paper describing additional isotopic analyses (KRISHNAMURTHY et al., 1990).

CONCLUSIONS

1) The predominant aliphatic components of the Murchison meteorite are C_{15} to C_{30} branched-alkyl-substituted mono-, di-, and tricyclic alkanes.

2) The n-alkanes, methyl alkanes, and isoprenoid alkanes found in some extracts of this meteorite are terrestrial contaminants.

3) Carbonaceous chondrites are highly susceptible to hydrocarbon contamination from various terrestrial sources. Contaminant-free indigenous hydrocarbons can be obtained only from the interior of meteorite stones, and then only when the sampling, extraction, and analytical work-up are done under conditions that rigorously exclude procedural and air-borne contaminants.

4) Previous arguments that the formation process for chondritic hydrocarbons was highly selective for straight-chain

compounds as, for example, the Fischer-Tropsch type process, can no longer be considered valid.

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