

LETTER

A search for C₆₀ in carbonaceous chondrites

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Abstract—Analysis of interior samples of the Murchison meteorite by two routes yielded an upper limit of 2 ppb for its C₆₀ content, as compared to parts per million levels for individual polycyclic aromatic hydrocarbons (PAHs). Provided the samples contain an interstellar component, which is probable since Murchison hydrocarbons contain excess deuterium, this result argues against the ubiquitous presence of C₆₀ in the interstellar medium. A possible explanation for the absence of C₆₀ was found in experiments showing how PAHs replace fullerenes as stable end products when hydrogen is present during carbon condensation. As a secondary result we found high molecular weight PAHs in the Murchison and Allende meteorites. Coronene and its methyl derivatives are especially interesting since features in the coronene spectrum have been shown to match some of the unidentified interstellar infrared emission bands.

INTRODUCTION

AFTER THE UNIQUE STABILITY and inertness of the C₆₀ cluster were discovered and attributed to a highly symmetric cage structure by KROTO et al. (1985), predictions appeared stating that this species would be distributed ubiquitously in the Galaxy (KROTO, 1988; KROTO and MCKAY, 1988). This hypothesis was based on the exceptional photochemical and thermal stability of the C₆₀ molecule, which would make it "the lone survivor" of interstellar processing (KROTO, 1990), and on conditions in the outflow of red giant carbon stars which were supposed to be favorable for its formation. It was therefore expected that some of the ubiquitously observed interstellar spectroscopic features, in particular the unidentified infrared emission bands, would turn out to be due to C₆₀ or its ions. So far this expectation has not been fulfilled. C₆₀ in bulk has been isolated in the laboratory, but its spectroscopy doesn't match astronomical observations (KRÄTSCHMER et al., 1990)

Another way to test for interstellar C₆₀ is to search for it in carbonaceous meteorites. These primitive objects contain polycyclic aromatic hydrocarbons (PAHs) whose extraterrestrial origin was established by analysis of fresh samples of the new-fallen Murchison meteorite (PERING and PONNAMPERUMA, 1971; ORO et al., 1971; STUDIER et al., 1968). While the provenance of these meteoritic PAHs was not firmly established, a link may exist with PAHs observed in the interstellar medium; deuterium excess which has been found in meteorite organic matter (KERRIDGE, 1983; YANG and EPSTEIN, 1983; EPSTEIN et al., 1987) is consistent with interstellar processing (WATSON, 1976; TIELENS, 1983). Like C₆₀, interstellar PAHs are thought to be formed in the outflow of

carbon stars (LEGER et al., 1986; ALLAMANDOLA et al., 1985; FRENKLACH and FEIGELSON, 1989). Thus, they should be found together. We have therefore looked for C₆₀ in two representative meteorites, the Allende and Murchison, in the latter by two independent tests of increasing sensitivity.

METHODS

Since the fullerenes C₆₀ and C₇₀ are readily isolated from soot by vacuum sublimation at about 400°C (KRÄTSCHMER et al., 1990; MEIJER and BETHUNE, 1990), we applied this procedure to carbonaceous residues obtained by acid demineralization of interior Murchison and Allende samples as described previously by KERRIDGE et al. (1987). Using stainless steel cells with 1 mm orifices, sublimation fractions were collected at 300, 450, and 600°C as spots on a Au-plated sample bar. The collecting surface was at or slightly above room temperature; thus, volatile components such as phenanthrene, fluoranthene, and pyrene which are found to be most abundant by extraction methods are underrepresented in the sublimate. Allende samples yielded less sublimate than Murchison, consistent with relative abundances of PAHs detected by earlier workers. The deposits were analyzed by 2-step laser mass spectrometry with jet cooling (MEIJER et al., 1990), using 248 nm (KrF) pulses for vaporization and 193 nm (ArF) for ionization. This method is specific for aromatic compounds and fullerenes which have the necessary, long-lived intermediate electronic states for stepwise excitation (ZENOBI et al., 1989; HAHN et al., 1988; MEIJER and BETHUNE, 1990). It should be pointed out that ionization efficiencies vary to a moderate degree for different PAHs and thus the peak heights in Figs. 2, 3, and 4 do not accurately reflect relative concentrations.

Deuterium excess measurements of the sublimation fractions were carried out by secondary ion mass spectrometry (SIMS), as discussed by MCKEEGAN et al. (1985). Each sublimate measurement was made in conjunction with analysis of a microtome thin section of an epoxy resin (LR White) with known D/H ratio (δ SMOW = -100‰, relative to Standard Mean Ocean Water). The resin samples were located adjacent to the sublimate and were analyzed under identical instru-

ment conditions in order to obtain corrections for instrumental, mass-dependent bias in H and D detection efficiencies. Both the standard deviation based on Poisson counting statistics and the standard error of the mean over many measurement cycles were calculated. Although the two types of standard deviations were approximately the same in all cases, the higher value was used for further calculations. The sublimate and reference (LR White) measurement errors were propagated into the final result.

RESULTS AND DISCUSSION

The sublimate showed characteristics previously observed in solvent extracts of the same meteorites. In particular, the Murchison sublimation fractions at 300, 450, and 600°C yielded deuterium enrichments of $+990 \pm 20$, $+1400 \pm 20$, and $+650 \pm 30\%$ when analyzed by SIMS. These values extend beyond the range of $+483$ to $+1066\%$ previously obtained from bulk analysis of Murchison acid residues by ROBERT and EPSTEIN (1982), YANG and EPSTEIN (1983), and KERRIDGE et al. (1987). They are in reasonable agreement with the results of KRISHNAMURTHY et al. (1992) for the bulk hydrocarbon fraction, which is the most appropriate comparison since the acid residues are known to be isotopically distinct from the soluble organic compounds.

Following KOLODNY et al. (1980), the deuterium enrichments are interpreted as signatures of an interstellar component. The excess deuterium in the bulk residues resides in both aliphatic and aromatic moieties, with possibly the aliphatic hydrogen being more strongly enriched in deuterium (KERRIDGE et al., 1987). In principle the deuterium enrichment in the PAHs can be obtained separately by isotope-selective ionization of the jet-cooled molecules with a tuneable laser, using the large blue shift of the d_1 species. We did not attempt this analysis in the present work.

An infrared spectrum of Murchison acid residue sublimated onto KBr at 600°C (Fig. 1) shows features probably arising from PAHs at 3000 to 3100 and 1490 to 1620 cm^{-1} ,

accompanied by others at 2960, 2926, 2870, 1699, 1449, and 1378 cm^{-1} which have been observed in a whole benzene-methanol extract and attributed to polycyclic, aliphatic hydrocarbons and their carbonyl derivatives by CRONIN and PIZZARELLO (1990). From a comparison with model compounds, the ratio of aliphatic to aromatic CH bonds in the sublimate was estimated to be 4 ± 1 .

Figure 2 shows mass spectra of the 600°C sublimation fractions of Allende and Murchison. Other fractions were qualitatively similar, the molecular weight of observed PAHs generally increasing with sublimation temperature. None showed any evidence of C_{60} . Mass spectra of all fractions are contained in a preliminary report by DE VRIES et al. (1991). Our observations are summarized in Table 1 and give clear evidence of PAHs in the C_{21} to C_{26} range which have not previously been identified. However, ionization with the fixed 193 nm wavelength cannot distinguish between the possible isomers listed in Table 1. The Murchison mass spectrum shows the presence of alkyl-substituted rings, lower molecular weight examples of which have been observed earlier by BASILE et al. (1984) and by HAHN et al. (1988). The PAHs of Allende appear relatively depleted in the more volatile species relative to Murchison, consistent with abundant evidence that Allende experienced higher temperature than Murchison.

Looking for possible reasons why C_{60} is not detected in these experiments, we found that the photoionization cross-section of C_{60} at 193 nm is substantially lower than that of the PAHs observed. We therefore carried out a second, more sensitive test for C_{60} in Murchison. Toluene extraction of soot as described by HAUFLE et al. (1990) has become the standard method of bulk preparation of C_{60} . We applied this procedure to a ground-up, interior sample of the Murchison meteorite. After treatment with colloidal copper to remove elemental sulfur, the extract was evaporated to dryness in a stream of N_2 at room temperature.

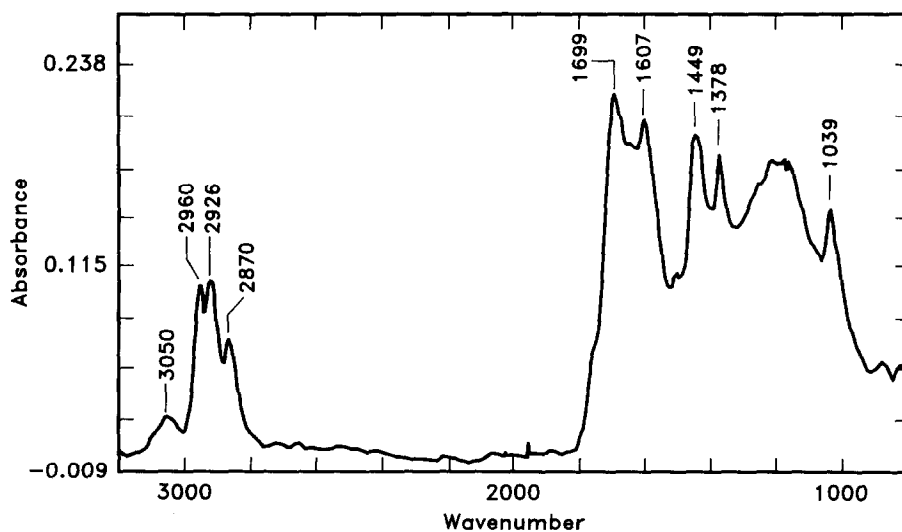


FIG. 1. Infrared absorption spectrum of Murchison acid residue sublimated onto KBr at 600°C.

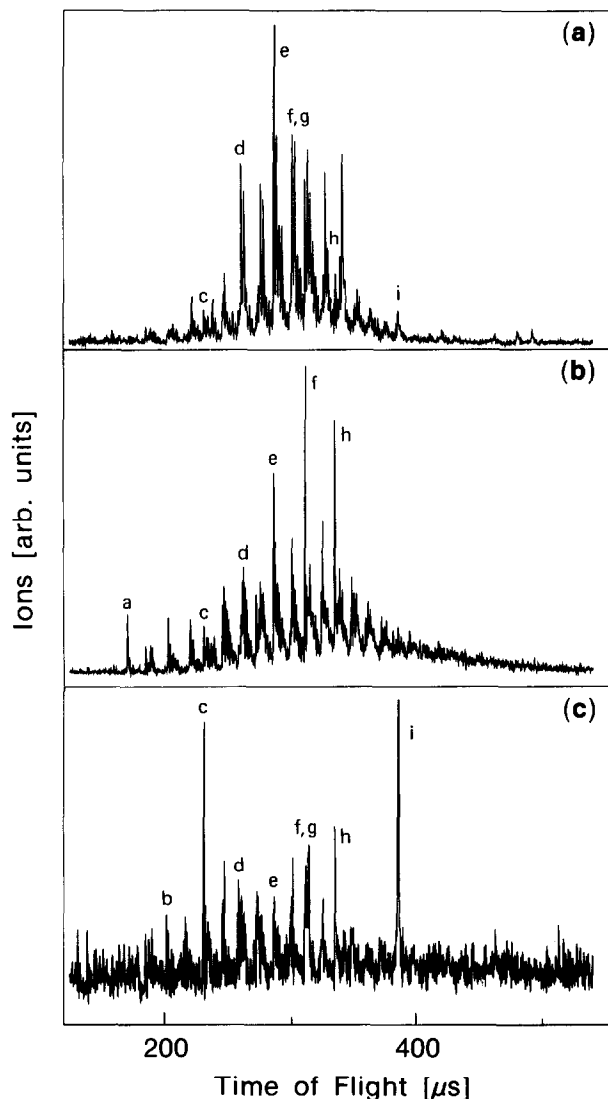


FIG. 2. Time-of-flight mass spectra obtained from (a) Allende acid residue sublimated at 600°C, (b) Murchison acid residue sublimated at 600°C, and (c) soot collected from laser ablation of graphite in an atmosphere of 450 Torr Ar and 50 Torr H₂. The labels refer to the parent PAHs listed in Table 1. Peaks corresponding to their alkyl-substituted derivatives are not labeled.

Analysis of this sample was carried out in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, again using 248 nm and 193 nm laser pulses for vaporization and ionization, respectively. A survey spectrum (Fig. 3a) shows the range of PAHs already detected in the sublimate, but also reveals the presence of PAHs with higher masses extending to 800 amu, with a secondary maximum around 520 amu. Such high molecular weight components have not been observed before, but their presence in the interstellar medium has been inferred from the infrared emission spectrum (ALLAMANDOLA et al., 1989). Both low volatility and

lower abundance relative to compounds identified in Table 1 are probably responsible for the absence of these high masses in the sublimate time-of-flight spectrum (Fig. 2b). Low concentration and the large number of possible isomers prevented us from making any definitive structural assignments of these high molecular weight PAHs. We were able to estimate the meteorite's content of perylene/benzopyrene isomers at 1 ppm, based on a 5 ppm measurement for anthracene/phenanthrene obtained by HAHN et al. (1988), by spiking the sample with anthracene and perylene. The spiking procedure automatically takes into account the variable response of different PAHs.

Unlike the PAHs, C₆₀ does not fragment at high 193 nm ionization intensities which therefore can be used to advantage for its detection. The presence of a large number of PAH and fragment ions, however, drastically reduces the detection sensitivity of FTICR for C₆₀. Therefore, an ion ejection and isolation scheme using the "stored waveform inverse Fourier transform" (SWIFT) technique of CHEN and MARSHALL (1987) was used for sensitivity enhancement. Figure 3b shows an ion-isolated mass spectrum (718 to 722 amu) with 10 ppb of C₆₀ added to the toluene extract, giving the expected peak at 720 amu (which at higher resolution shows the correct ¹²C/¹³C ratio with 721 amu). The absence of any detectable peak in the unspiked sample under the same conditions (Fig. 3c) leads to an upper limit of 2 ppb for the C₆₀ content of

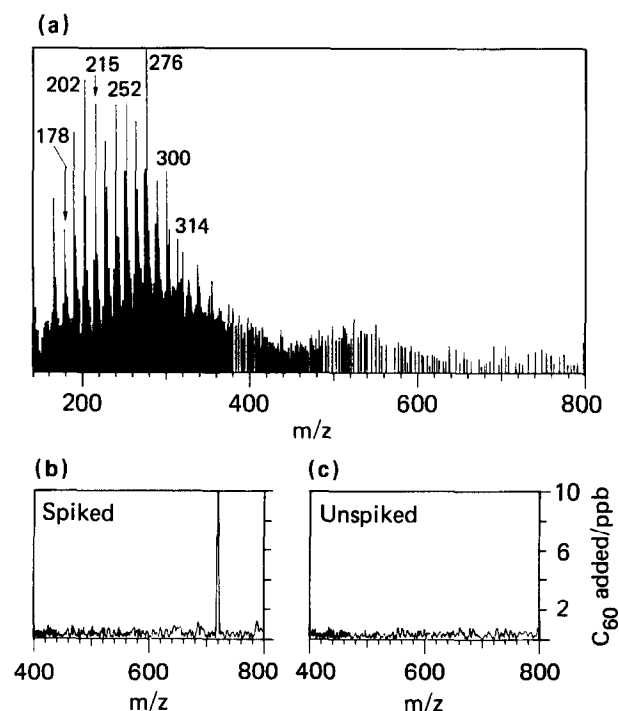


FIG. 3. FTICR mass spectra from a toluene extract of Murchison. (a) Survey spectrum, (b) selective excitation (SWIFT) spectrum from $m/z = 718$ to 722 amu of extract spiked with 10 ppb C₆₀, (c) same as (b) but not spiked with C₆₀.

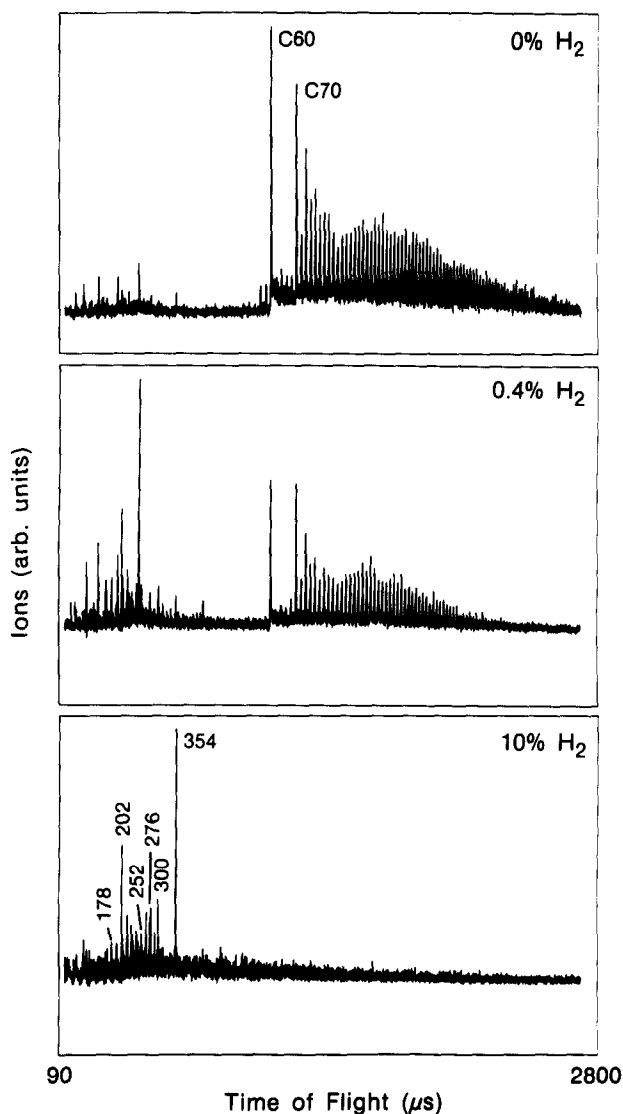


FIG. 4. Time-of-flight mass spectra of fullerenes and PAHs resulting from laser ablation of graphite in Ar with different concentrations of H_2 . Fullerene peaks starting at C_{56} are 24 amu apart. The bottom panel is compared with meteorite acid residue sublimates in Fig. 1.

Murchison (signal/noise = 2). All parts per billion figures are based on the anthracene/phenanthrene content of 5 ppm determined by HAHN et al. (1988) and are upper limits because some of the anthracene/phenanthrene may have been lost due to its volatility.

Why is there no detectable C_{60} in Murchison? It has long been realized that there will be complications with the proposed growth mechanism of fullerenes in the presence of hydrogen (KROTO and MCKAY, 1988). The formation of hydrogenated fullerenes ("fulleranes") was investigated in a cluster source by ROHLFING (1990), but neither have the chemically stable end products been collected nor have the competition between PAH and fullerene formation been ex-

plored. We therefore carried out some experiments analyzing the deposits formed on a room temperature collecting surface when graphite is ablated with a laser in an atmosphere of Ar and H_2 , at 500 Torr total pressure. The method of analysis was the same as for the acid residues. In a crude way this experiment simulates condensation on dust grains of molecular matter ejected from a carbon star.

The results are shown in Fig. 4. With no H_2 present, we find the stable, even-numbered carbon clusters up to at least C_{220} , starting with prominent C_{60} and C_{70} signals. With 0.4% H_2 , fullerene formation is reduced while not altered in its distribution; at the same time prominent PAHs appear in the 100 to 400 amu mass range. With 10% H_2 present, PAHs are the only products collected, and no more fullerenes are observed. This case is also included in Fig. 2 to show the similarity of its PAH distribution with those of the meteorite residue sublimates. The analogy extends to the largest PAHs including coronene, and includes methyl derivatives. A prominent product at 354 amu which may also be present in Allende is probably bianthrlyl or one of its isomers.

We found no evidence for fulleranes in the products obtained with added H_2 . However, this does not disprove their presence. A control experiment with a sample of partially hydrogenated fullerenes, kindly supplied by Dr. G. W. Schriver of Exxon Research, showed that these species cannot be detected by two-photon ionization at 193 nm. The sample contained the compounds C_{60} , $C_{60}H_2$, $C_{60}H_4$, and so on in monotonously decreasing abundance, as determined by CI mass spectrometry. Since the hydrides have much lower thermal stability than the fullerenes themselves, it is possible that the intermediate hot triplet formed by absorption of the first 193 nm photon decomposes, rather than being ionized by the second photon as in the case of C_{60} . If this is true, hydrides would not be stable in interstellar space.

CONCLUSIONS

Provided there is interstellar material in our meteorite samples, which is probable in view of the observed deuterium excess in the sublimates, our results are incompatible with the hypothesis that C_{60} is ubiquitous and abundant in the interstellar medium. A possible reason for this is suppression of the fullerene growth mechanism by hydrogen, the most abundant co-reactant in those stellar atmospheres which are considered likely sources of fullerenes. ALLAMANDOLA et al. (1989) have suggested that a similar mechanism limits the size of PAHs. If this is true, the growth of carbon grains may also take a path different from the one suggested by KROTO (1988) based on the cage structure of fullerenes.

While looking for C_{60} in meteorites we have found some large PAHs of which coronene and its alkyl-substituted derivatives are especially interesting. IR emission bands of coronene were thought to "give an impressive fit to the observed" unidentified interstellar IR emission bands by LEGER and PUGET (1984), a fit which improved when spectra were obtained at higher temperature (FLICKINGER and WDOWIAK, 1990).

Table 1.

(1)	amu	(2)	PAHs (3)
a	154	M	acenaphthene*
b	178	S	anthracene*, phenanthrene*
c	202	A,M,S	pyrene*, fluoranthene*
	216	A,M,S	methyl - c benzfluorene
	230	A,S	dimethyl - c
	244	A,S	trimethyl - c
d	228	A,M,S	benzanthracenes*, benzophenanthrenes*, chrysene*, triphenylene
	242	A,M,S	methyl - d
e	252	A,M,S	benzopyrene*, perylene, benzofluoranthenes
	266	A,M	methyl - e
	280	A,M	dimethyl - e
f	276	A,M,S	benzoperylene, indenopyrene, anthranthene
	290	M,S	methyl - f
	304	M	dimethyl - f
g	278	A,S	dibenzanthracenes, dibenzophenanthrenes, pentacene
	292	A	methyl - g
	306	A	dimethyl - g
h	300	A,M,S	coronene
	314	A,M,S	methyl - h
	328	A,M,S	dimethyl - h
	340	A,M,S	trimethyl - h
i	354	A,S	bianthryl, biphenanthryl

- (1) These are the labels for unsubstituted PAHs used in Fig. 1.
- (2) Masses found in the following samples: A: Allende, M: Murchison, S: Soot from laser-vaporized graphite.
- (3) The prefixes "dimethyl" and "trimethyl" are used to designate any alkyl derivatives with two resp. three CH₂ groups added to the parent.
- PAH's previously identified by combined gas chromatography-mass spectrometry (PERING and PONNAMPERUMA, 1971; ORO et al., 1971; STUDIER et al., 1968 and 1972; BASILE et al., 1984).

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