Reports

Interstellar Polycyclic Aromatic Hydrocarbons and Carbon in Interplanetary Dust Particles and Meteorites

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Both interplanetary dust particles (IDPs) and meteorites may contain material that is similar to polycyclic aromatic hydrocarbons (PAHs). The Raman spectra of IDPs and meteorites show features that are similar in position and relative strength to interstellar infrared emission features that have been attributed to vibrational transitions in free, molecular-sized PAHs. The Raman spectra of some IDPs also show red photoluminescence that is similar to the excess red emission seen in some astronomical objects and that has also been attributed to PAHs and hydrogenated amorphous carbon. Moreover, a part of the carbonaceous phase in IDPs and meteorites contains deuterium to hydrogen ratios that are greater than those for terrestrial samples. Deuterium enrichment is expected in small free PAHs that are exposed to ultraviolet radiation in the interstellar medium. Taken together, these observations suggest that some of the carbonaceous material in IDPs and meteorites may have been produced in circumstellar dust shells and only slightly modified in interstellar space.

MANY PARTICLES FROM AIRBORNE impaction collectors (which are flown at altitudes of 18 to 20 km) are extraterrestrial in origin (*1, 2*). Although similar to meteorites in their bulk chemistry, these interplanetary dust particles (IDPs) form a distinct class of extraterrestrial material (*3, 4*). Most chondritic IDPs fall into two major categories, both of which are characterized by the presence of silicate minerals (*4, 5*). The mineral phases present are usually in chemical disequilibrium with each other and show evidence of a complex history [see (*6*) for a recent review]. Some of the particles contain a carbonaceous phase that has large deuterium to hydrogen (D/H) enrichments (*2, 7*). These enrichments and the large degree of chemical heterogeneity in IDPs suggest that they have not been substantially altered since their initial formation. Thus IDPs may contain at least some relatively unaltered interstellar material. They may even contain molecules that are almost unchanged since their formation in the circumstellar envelopes of distant stars.

Most IDPs contain 2 to 10% carbon by weight (*8*) in a variety of physical forms, including amorphous material that contains minor amounts of oxygen and nitrogen (*4, 9*). Some of the carbon must be in the form of hydrogenated organic compounds since the deuterium concentration in IDPs correlates with the carbon concentration (*2*). Virtually all IDPs are optically black (*8*), presumably because the dominant silicates are masked by carbonaceous coatings whose structure is not well characterized.

Table 1. Properties of some aromatic hydrocarbons.

Compound	Formula	C/H ratio	Number of vibrational modes	Approximate C–H dissociation energy threshold*	Structure
Benzene	C_6H_6	1.00	30	41,600	
Naphthalene	$C_{10}H_8$	1.25	48	53,000	
Anthracene	$C_{14}H_{10}$	1.40	66	65,600	
Pyrene	$C_{16}H_{10}$	1.60	72	69,500	
Chrysene	$C_{18}H_{12}$	1.50	84	77,200	
Perylene	$C_{20}H_{12}$	1.67	90	83,300	
Benzoperylene	$C_{22}H_{12}$	1.83	96	(88,000)	
Coronene	$C_{24}H_{12}$	2.00	102	(92,000)	
Ovalene	$C_{32}H_{14}$	2.29	132	($\geq$110,000)	
Hexabenzo-coronene	$C_{42}H_{18}$	2.33	174	(>110,000)	

*Values for benzene through perylene are taken from (*30*). The parenthetical values for benzoperylene through hexabenzocoronene are extrapolated from (*30*). This parameter represents the minimum vibrational energy content required for the C–H bond rupture rate to equal the radiative relaxation rate.

Because of the recent suggestion that polycyclic aromatic hydrocarbons (PAHs) and related materials are ubiquitous and abundant in interstellar space (*10, 11*), the presence of hydrogenated organic compounds in IDPs is of particular interest. PAHs are extremely stable, planar molecules composed of fused-hexagonal rings (see Table 1). The interstellar medium probably contains a mixture of PAH-related species that consist of (i) free molecules in neutral, ionized, and radical form; (ii) small clusters of PAHs with some of the individual subunits bound physically and others bound chemically; and (iii) larger clusters of PAHs and particles, which are probably similar to materials referred to as "hydrogenated amorphous carbon" (HAC) or "glassy carbon," a disordered form in which the aromatic subunits are irregularly cross-linked. The free aromatic molecules, which are thought to be formed in stellar outflows and account for a few percent of all interstellar carbon, are more abundant than all the other interstellar polyatomic molecules together (*11*).

In this report we note the striking spectral and chemical similarities between the carbonaceous component in IDPs and meteorites and those expected if interstellar PAHs are present. The vibrational and electronic spectral similarities are presented first and are followed by a discussion of the deuterium enrichments.

First-order Raman scattering from graphite (a material that consists of highly ordered, symmetric aromatic sheets) produces one intense band at 1581 Δcm^{-1}. For glassy carbon this peak is shifted to higher relative wavenumbers and an additional, much broader peak at about 1355 Δcm^{-1} appears (*12*) (Fig. 1). The second-order Raman bands between 2200 and 3300 Δcm^{-1} obtained from glassy carbon are considerably wider and more complex than those obtained from graphite. The reduced symmetry of the amorphous carbon induces this additional Raman activity.

The first Raman spectra of individual IDPs that showed the presence of amorphous carbon were reported in 1982 (*13*). Recently obtained micro-Raman spectra of many IDPs (*14*) show significant spectral variation (Fig. 2). These data show that amorphous carbon with different degrees of short-range order is present in most IDPs. Although similar statements can be made about the Raman spectra of many bulk

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meteorite samples (*13, 15*), we will restrict our discussion to the new IDP spectra presented in Fig. 2.

In the spectra of the IDPs Essex and Attila, which have strong bands at about 1350 and 1600 Δcm^{-1}, second-order Raman activity is apparent between 2200 and 3300 Δcm^{-1} (Fig. 2). Moreover, the region between the first-order bands is partially filled and the second-order Raman feature appears as a broad plateau instead of three or four resolved peaks (compare to Fig. 1). These details in the Raman spectra show that the amorphous carbon in IDPs is less ordered than in glassy carbon, which implies that domains smaller than 25 Å are present. Some of the IDP spectra also show a hint of spectral structure between the major Raman bands. For example, both Essex and Attila contain a minor band in the region from 1450 to 1490 Δcm^{-1}.

Raman spectra of IDPs show a striking similarity to interstellar infrared emission spectra. For example, Fig. 3 shows the Raman spectrum from 1000 to 2000 Δcm^{-1} of the IDP Essex and the corresponding emission spectrum of the Orion nebula. Many interstellar spectra contain a broad plateau that extends from about 2700 to 3100 cm^{-1} (*16*) that resembles the second-order Raman feature in the IDP spectra. Some astronomical objects also show a minor feature at 1450 to 1480 cm^{-1} (*17*) that is similar in position to the weak C–C stretch band seen in the Raman spectra of Essex and Attila.

The peak positions of the IDP Raman band near 1600 Δcm^{-1} also indicate that the carbonaceous component in IDPs is similar to the material that produces the intense interstellar emission feature at about 1610 cm^{-1}. The exact position of the Raman peak near 1600 Δcm^{-1} depends on the degree of disorder of the sample and varies in laboratory-produced carbonaceous material. However, even in glassy carbon this band usually peaks below 1600 Δcm^{-1} (*18*). In contrast, in the Raman spectra of IDPs the band maximum falls between 1602 and 1605 Δcm^{-1}. The closer match of the IDP Raman band to the interstellar feature, both in profile and position, is presumably due to the presence of smaller aromatic domains than those found in laboratory-produced graphitic and amorphous carbon materials.

Raman scattering from aromatic systems is far more sensitive to C–C vibrations than it is to C–H vibrations (*19*). Thus it is not surprising that the prominent interstellar bands assigned to C–H vibrations at about 3050 and 1200 cm^{-1} and in the region from 900 to 600 cm^{-1} are not evident in the Raman spectra of IDPs, meteorites, and amorphous carbon.

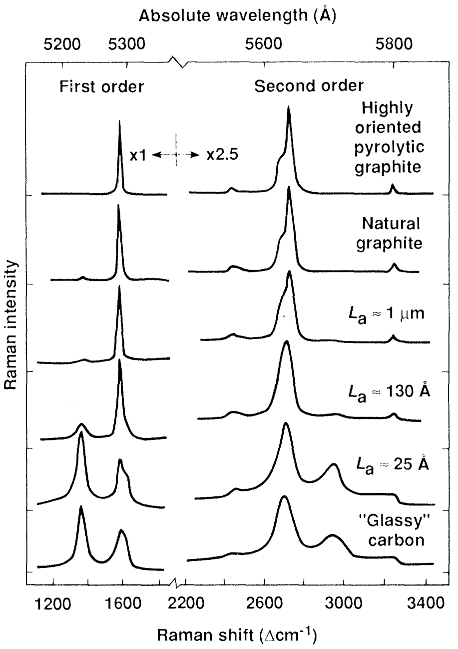

Fig. 1. First- and second-order Raman spectra of several different forms of carbon [adapted from figure 3 in (*12*)]. "Glassy carbon" can be considered to be a form of amorphous carbon; L_a is the mean size of the ordered domains within the sample. The relative heights of the two major first-order Raman bands depend on the degree of disorder of the sample. The second-order Raman features, which correspond to combinations and overtones of the fundamental vibrations, are always substantially weaker than the first-order bands.

In addition to vibrational spectroscopic information, Raman spectra can also show luminescence that arises from electronic transitions. The Raman spectra of some IDPs clearly show such broad visible photoluminescence (Fig. 2). The dominance of the amorphous carbon features and the lack of silicate features in the Raman spectra indicate that the incident 5145 Å laser photons interact mainly with the carbonaceous material that coats the IDP mineral grains. Thus the luminescence is produced not by the minerals in the IDPs but rather by the carbonaceous coatings.

In the IDPs Lea and Calrissian the short wavelength limit of the luminescence band is at ~5400 Å; the feature peaks between 5900 and 6400 Å (Fig. 2). The apparent variability in the peak position among the spectra may be due to superposition of the weak second-order Raman bands on the broader, more intense luminescence feature or an inherent variation in the position of the luminescence peak itself. The low-frequency limit and the width of the luminescence are not yet known. This emission is similar to that from HAC, where the peak position depends somewhat on the carbon to hydrogen (C/H) ratio (*20*). Thus the electronic transitions in some IDPs are similar to those expected for PAH-related materials.

Several celestial objects show a similar broad red emission. For example, Witt, Schild, and Kraiman (*21*) have detected such emission in several reflection nebulae, objects that have the infrared emission features that are assigned to PAHs and PAH-related species. The "Red Rectangle," HD 44179, also shows broad red emission that starts near 5500 Å and peaks between 6300 and 6400 Å. Convincing evidence also exists for a weak, broad emission feature centered at ~5800 Å with a width of over 1000 Å in the general, diffuse interstellar medium (*22*). The red emission from these objects has been attributed by some to HAC on the basis of band shape and position comparisons (*23*). Free PAHs and PAH clusters have also been suggested as a source of this luminescence (*24*).

The chemical properties of the carbonaceous phase in IDPs and meteorites also are indicative of an interstellar component. Many IDPs have D/H ratios that are significantly larger than the terrestrial value (*2*). These deuterium enrichments correlate with hydrogen and carbon concentrations, which suggests the presence of a hydrogenated organic carrier phase. This deuterium-rich phase constitutes only a minor fraction of the total material in the particles (*7*) and may be similar to the deuterium-rich material that is found in the bulk samples and acid residues of certain meteorites. The meteoritic acid residues contain a polymer with a C/H ratio of ~1.4 and consist of aromatic molecular units of various sizes that are interconnected by short linear bridges (*25*).

The large deuterium enrichments in carbonaceous meteoritic material have been attributed to a carrier formed through gas-phase, ion-molecule reactions at temperatures below 120 K (*26*). The high D/H phase in IDPs and meteorites is thought to represent material formed outside the solar nebula because the low temperatures required to produce the observed level of fractionation may not have existed in the early solar system. Even if temperatures were low enough, the chemical equilibrium necessary for the production of the high D/H phase probably could not have been reached in the relatively short time available during solar system formation (*27*). The interstellar enrichment process is thought to occur in cold, dense molecular clouds where simple species such as HCN and HCO$^+$ are enriched in deuterium by large factors (*28*). These deuterium enrichments may then be "frozen" into interstellar grains by the accretion of these simple species onto icy mantles (*29*). Presumably the more complex, high D/H organic material in IDPs and meteorites could then be formed in an interstellar phase, or during solar system formation, or both, through unspecified reactions that processed these simpler, deuterium-rich molecules.

However, the existence of PAHs in the general interstellar medium offers an additional path by which deuterium-rich hydrocarbons may be formed. Small PAHs are expected to become deuterium enriched in space through the selective loss of hydrogen during photodissociation events (*30*). This process is temperature independent and should occur in all small PAHs exposed to ultraviolet (UV) photons. The interstellar UV radiation field cuts off at a wavelength of ~936 Å (13.6 eV), so that 106,000 cm^{-1} is the maximum energy likely to be deposited into an interstellar molecule by a UV photon. Large PAHs can accommodate this energy without dissociation by distributing it statistically over the available internal vibrational modes ($3N - 6$ modes for an N-atom PAH). Such vibrationally excited PAHs relax in about 0.1 second through infrared fluorescence (*30*). Smaller PAHs may have an insufficient number of internal vibrational modes in which to distribute the energy, so that there is enough energy to break one or more bonds within the PAH before radiative relaxation is significant. The weakest and most likely bond to be broken in PAHs is the C–H bond, which has a strength of about 36,000 to 40,000 cm^{-1}. The C–D bond zero-point energy is about 30% lower than that of the C–H bond, so that hydrogen loss is favored over deuterium loss. The rupture rate is expected to be two to four times larger for C–H than for C–D (*30*). The aromatic C–C bonds are stronger still and are less likely to be broken than either the C–H or C–D bonds.

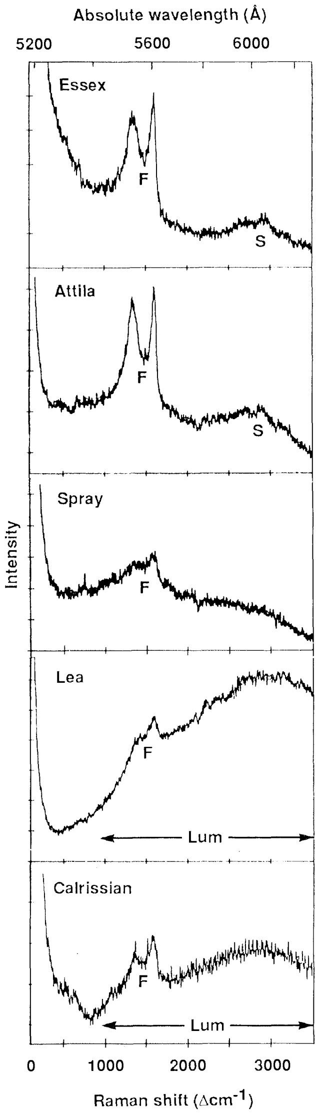

Fig. 2. Examples of IDP Raman spectra. Some of the spectra are dominated by the Raman bands of disordered carbonaceous material (Essex, for example) while others are dominated by red luminescence (Lea, for example). The relative strength of these effects varies from particle to particle. The designations F, S, and Lum label the first- and second-order Raman bands and visible luminescence, respectively. The large increase in count rate near 0 Δcm^{-1} is due to Rayleigh-scattered incident laser light. All the spectra shown were taken at a resolution of 5 cm^{-1} with a RAMANOR U-1000 laser Raman microprobe by exciting the sample with the 5145 Å Ar^+ laser line. The upper axis indicates the absolute wavelength of the emission; the lower axis indicates the Raman shift (Stokes lines) with respect to the exciting-laser frequency.

The radical site that results after loss of a hydrogen atom can then bond to a new atom or functional group. Hydrogen, which is the most abundant, is most likely to replace the lost atom. Functional groups, such as methyl and amino groups, generally have lower bond strengths to aromatic rings than hydrogen, and if they become attached to the site they will be the first to be lost in subsequent dissociation events. Thus small, free, molecular PAHs in interstellar space would be expected to scavenge hydrogen with D/H ratios characteristic of local interstellar conditions while surrendering back hydrogen preferentially over deuterium. Calculations suggest that photodissociation events occur in small PAHs on the order of once per year (*31*), so that at a cosmic D/H ratio of $\sim 10^{-5}$ small molecular PAHs would be expected to replace one hydrogen atom with deuterium on time scales on the order of 10^5 years.

Deuterium enrichment by this process depends crucially on the size of the molecule. The photoenrichment of deuterium in PAHs is expected to be most significant for molecules in the range of sizes spanned by naphthalene ($C_{10}H_8$, C/H = 1.25) and hexabenzocoronene ($C_{42}H_{18}$, C/H = 2.33) (see Table 1). Deuterium enrichments are not expected in benzene because this aromatic molecule is not stable in the interstellar radiation field (*32*). Deuterium enrichments in PAHs that contain more than about 40 carbon atoms are not expected because these molecules have large numbers of vibrational modes and are stable against photolytic bond rupture. Similar enrichment by this process is not expected for the known nonaromatic interstellar molecules because they are not stable against photolysis.

The D/H ratios of acid-soluble hydrocarbon phases in meteorites increase as the C/H ratio increases from 0.2 to 1.5 [see figure 6 in (*26*)]. Conversely, the D/H ratios in meteorite acid residues decrease slightly as the C/H ratio of the material increases from 2.3 to 3.0 [see figure 8 in (*33*)]. If we assume that the soluble and insoluble phases represent different degrees of molecular complexity of related materials, then the deuterium enrichment peaks at a measured C/H ratio of about 2. In general, for any mixture of pure hydrocarbons, as the C/H ratio increases from 0.2 to 1.0, the contribution of aromatics relative to nonaromatics increases. Ratios of C/H greater than 2 imply the dominance of larger aromatic molecules. If we assume that all of the measured carbon and hydrogen is from the high D/H carrier phase, then the peak in the D/H ratio at a C/H ratio of ~2 corresponds to PAHs that contain about 20 to 50 carbon atoms. This is the same size range inferred

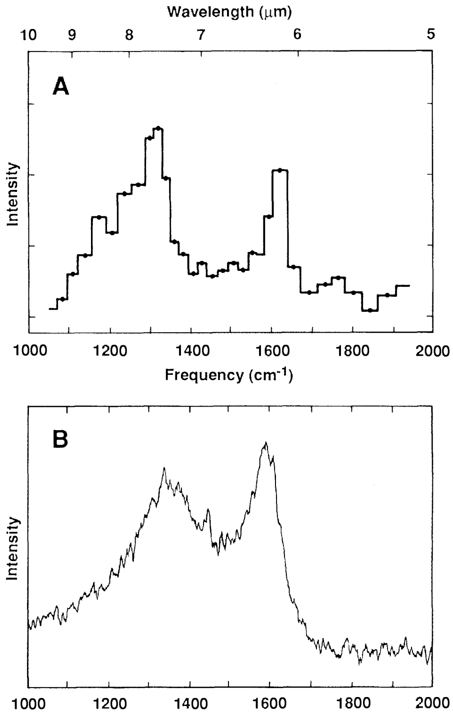

Fig. 3. Comparison between (**A**) the infrared emission spectrum from the Orion Bar [Orion Bar data from (*35*)] and (**B**) the Raman spectrum of the IDP Essex.

for the most abundant interstellar molecular PAHs from astronomical infrared emission spectra (*11*). Thus the observations are consistent with partial production of the observed deuterium enrichments by photoprocessing of free PAH molecules. Caution is warranted, however, since it is not clear how much significance to ascribe to this comparison because it is not certain that all of the carbon and hydrogen measured in IDPs and meteorite acid residues is part of the deuterium-rich carrier phase. As an example, the hydrogen content measured in these materials may include a contribution from water of hydration.

The D/H ratio in meteoritic acid residues roughly correlates with total hydrogen concentration [see figure 4 in (*26*)]. This is consistent with interstellar photolytic enrichment since larger PAHs have lower relative hydrogen concentrations and will produce smaller deuterium enrichments. The high D/H ratios in IDPs and meteorite acid residues do not correlate with the $^{13}C/^{12}C$ ratios in the same material (*2, 26, 34*). This is consistent with deuterium enrichments that originate from both photoprocessed interstellar PAHs and ion-molecule reactions.

Although the observed characteristics of the deuterium carrier in meteorites and IDPs are consistent with an interstellar PAH interpretation, the relation is not proven. The deuterium enrichment of the insoluble polymer seen in meteorites could also be explained by ion-molecule reactions combined with subsequent chemical processing. There are observational tests that can potentially separate the possibilities. The ion-molecule reaction scheme would predict that both the aromatic structures (regardless of size) and their cross-linking bridges should have related D/H ratios since both structures would presumably be made from the same deuterium-rich parent molecules. The PAH photodissociation model, however, does not necessarily predict that the D/H ratios in the aromatic structures will be related to the D/H ratios of their associated inter-ring links. In addition, the photoprocessing scenario would predict that above a C/H ratio of about 2 the deuterium enrichments within the aromatic structures would decrease with increasing molecular size.

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Fossil Mycorrhizae: A Case for Symbiosis

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Vesicular-arbuscular mycorrhizae are significant in the physiology and ecology of extant vascular plants, and they may also have played a major role in the origin of the vascular land flora. The case for fossil vesicular-arbuscular mycorrhizae rests upon hyphae and chlamydospore-like bodies in several Paleozoic taxa, but fossil arbuscles are unknown to date. Specimens from the Triassic of Antarctica represent the first known occurrence of arbuscles in the fossil record.

ALTHOUGH IT WAS ASSUMED FOR many years that fungi would not be significantly represented in the fossil record because of their delicacy, it is now known that fossil fungi parallel modern forms in diversity, complexity, and function. Although the development of fungal diversity early in geological time has been relatively well demonstrated, with all of the major groups of fungi being present by the Paleozoic (*1*), the biological relations between fungi and land plants have been more difficult to investigate. This difficulty has been particularly obvious when researchers have attempted to document the physiological relation in mycorrhizal associations.

Vascular plants are believed to have originated in the Late Silurian. Pirozynski and Malloch (*2*) speculated that the appearance of vascular plants was facilitated by the evolution of mycorrhizal associations. In their view, the increased efficiency in nitrogen and phosphorus uptake that resulted from a symbiotic association was necessary for the exploitation of new habitats and the development of more complex tissue systems. In support of these arguments Piro-

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