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# Evidence that polycyclic aromatic hydrocarbons in two carbonaceous chondrites predate parent-body formation

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**Abstract**—Organic material in meteorites provides insight into the cosmochemistry of the early solar system. The distribution of polycyclic aromatic hydrocarbons (PAHs) in the Allende and Murchison carbonaceous chondrites was investigated by use of a technique called microprobe laser-desorption laser-ionization mass spectrometry, which permits spatial resolution with approximately a 40-$\mu$m spot size. Sharp chemical gradients of PAHs are associated with specific meteorite features. The ratios of various PAH intensities relative to the smallest PAH, naphthalene, are nearly constant across the sample. These findings suggest a common origin for PAHs dating before or during the formation of the parent body, consistent with proposed interstellar formation mechanisms. *Copyright © 2003 Elsevier Science Ltd*

## 1. INTRODUCTION

All terrestrial rock samples are far younger than the time of formation of Earth. In contrast, the primitive carbonaceous chondritic meteorites are known from isotopic dating to have formed at about the same time as the solar system, some 4.6 billion years ago. These heterogeneous extraterrestrial rocks have never been heated to even close to their melting points since the time of their assembly, although individual components have thermal histories reflecting their formation environments before incorporation into the meteorite body. Hence, carbonaceous chondrites are among the most primitive known solids, holding great potential for understanding conditions during and possibly before solar system formation (McSween, 1979; Wark, 1979). Analyses of carbon-rich meteorites have revealed the presence of organic compounds such as amino acids, alkanes, aromatics, and macromolecular organic material (kerogen) (Han et al., 1969; Levy et al., 1973; Cronin and Chang, 1993; Pizzarello et al., 2001). The extent of parent-body processing of these compounds, however, is not well known, giving rise to great uncertainty as to the original distribution of organic compounds available in the early solar system.

Polycyclic aromatic hydrocarbons (PAHs), molecules whose cores consist of two or more fused benzene rings, are among the most abundant compounds in the universe, comprising ~10 to 20% of all carbon (Allamandola et al., 1989; Puget and Leger, 1989). Their prevalence arises from their stability as well as their relative ease of formation. Proposed formation mechanisms include UV processing of interstellar ice grains, circumstellar synthesis, and mineral-catalyzed shock formation during impacts (Ehrenfreund and Charnley, 2000). PAHs have been identified in interstellar grains, molecular clouds in deep space, interplanetary dust particles, and meteorites (Allamandola et al., 1987; Hahn et al., 1988; Cronin and Chang, 1993; Sellgren et al., 1995; Chiar et al., 2000).

Carbonaceous chondrites originated from planetesimals or asteroids that accreted during the formation of the solar system. They are aggregates of many components including chondrules, calcium–aluminum inclusions (CAIs), dark inclusions, and individual mineral grains, all of which can be surrounded by fine-grained rims and occur within a fine-grained matrix. Some of these components experienced temperatures before parent-body assembly sufficient to cause them to melt, whereas the minerals contained in other components have low decomposition temperatures showing that they never reached high temperatures. CAIs and chondrules were formed from materials

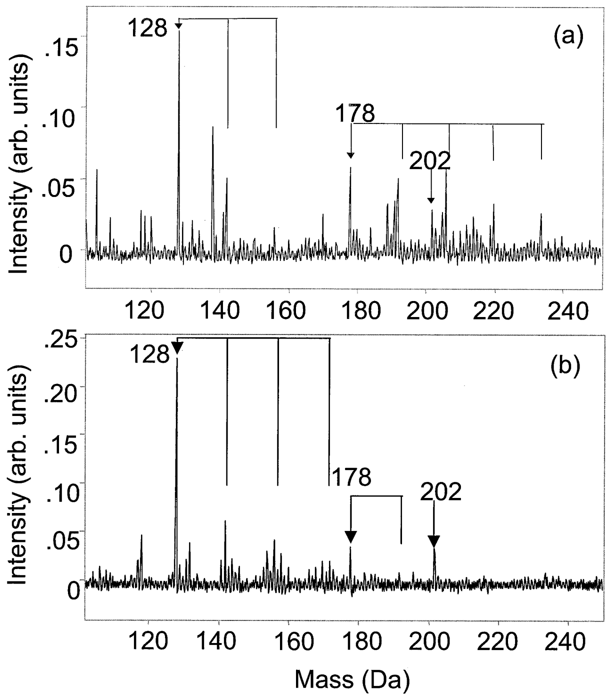

Fig. 1. Representative $\mu L^2MS$ spectra from matrix areas of the (a) Allende and (b) Murchison samples. Parent PAH peaks are labeled with their mass number; peaks belonging to alkylated PAHs are indicated by series of connected vertical lines.

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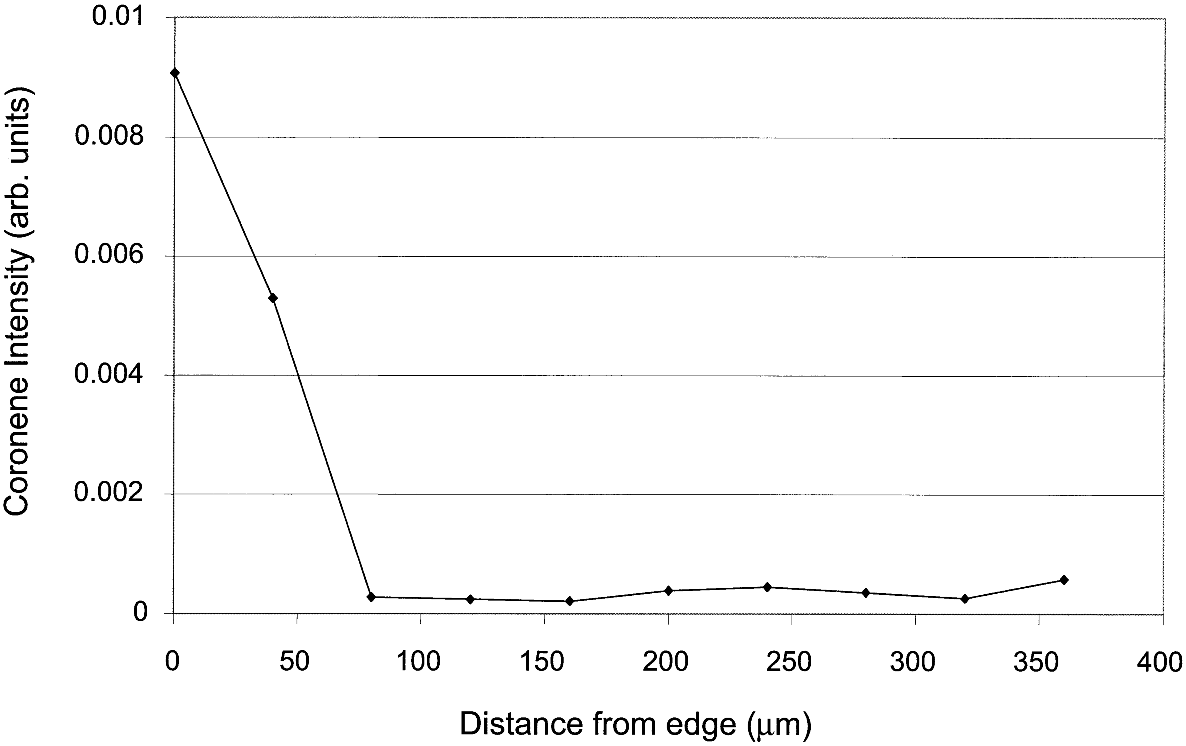

Fig. 2. Control experiment. Intensity of coronene peak along the freshly cut surface of a rock that was externally doped with coronene solution before cutting. The coronene signal falls to background noise levels within 80 $\mu$m of the doped edge. Background noise levels are approximately an order of magnitude less than PAH signals from the interiors of the meteorite samples.

heated to ~1400 to 2400 K (MacPherson and Wark, 1988; Connolly et al., 1998), whereas the matrix material accreted at lower temperatures (Buseck and Hua, 1993). Allende (CV3) and Murchison (CM2) are important examples of carbonaceous chondrites, and their mineralogy and bulk organic composition have been extensively investigated (Han et al., 1969; Levy et al., 1973; McSween, 1979; Grossman, 1980; Kerridge et al., 1987; Cronin and Chang, 1993).

In the work reported here, the spatial distributions of PAHs in samples of these meteorites were examined by use of microprobe laser-desorption laser-ionization mass spectrometry ($\mu L^2MS$). This technique has been used previously to study the low-resolution spatial distribution of PAHs in meteorites, giving mass distributions averaged over each region or mineral type (Zenobi et al., 1989; McKay et al., 1996). The current work, however, provides a higher spatial resolution of this distribution, allowing determination of the variation of total and relative PAH intensities and the correlation with various meteorite components. We find a striking constancy across the sample in the ratios of PAH intensities relative to the smallest PAH, naphthalene. We interpret these results to indicate that PAHs preexisted and were incorporated at the earliest stages of chondrite formation.

## 2. EXPERIMENTAL

### 2.1. Samples

Thick sections (~6 mm diameter, 1 mm thickness) of both the Allende and Murchison meteorites were investigated. The Allende sample was purchased from Michael I. Casper Meteorites Inc. (Ithaca, NY). Two sections were prepared at Burnham Petrographics (Monrovia, CA) by cutting with a water-cooled diamond blade. The Murchison sample was supplied from the U.S. National Meteorite Collection of the Smithsonian Institute. One thick section was dry cut immediately before investigation, with a diamond blade, at Stanford University.

### 2.2. Surface Visualization

Visual characterization of the sample surfaces was accomplished by photographing overlapping sectors with a stereomicroscope (120× magnification) linked to a digitizing unit (Snappy, manufactured by Play Incorporated, Rancho Cordova, CA). The overlapping images were stitched together (by Panavue Image Assembler software; Panavue, Quebec, Canada) to yield a mosaic of the sample surface. This mosaic was then used to match visual features to the on-screen image of the sample within the $\mu L^2MS$ vacuum chamber, ensuring that each $\mu L^2MS$ shot sampled a known area on the meteorite surface.

### 2.3. $\mu L^2MS$ Analysis

Samples were analyzed by $\mu L^2MS$, a sensitive, selective, and spatially resolved technique that has been used to detect PAHs in a variety of ancient terrestrial rocks (Mahajan et al., 2001), contaminated soils and sediments (Gillette et al., 1999; Ghosh et al., 2000), and meteorites (Zenobi et al., 1989; McKay et al., 1996). The samples were placed on a brass sample platter that was introduced into the $\mu L^2MS$ chamber through a vacuum interlock. A detailed description of the instrument has been presented elsewhere (Clemett and Zare, 1997). In the first step, a pulsed infrared laser beam (Alltech AL853 $CO_2$ laser, 10.6 $\mu$m, FWHM =120 ns with a 4-$\mu$s tail, Alltech, Lubeck, Germany) is focused to a 40-$\mu$m spot with a microscope objective and desorbs constituent sample molecules. This process combines thermal desorption of molecular PAHs and pyrolysis of meteoritic kerogen, which

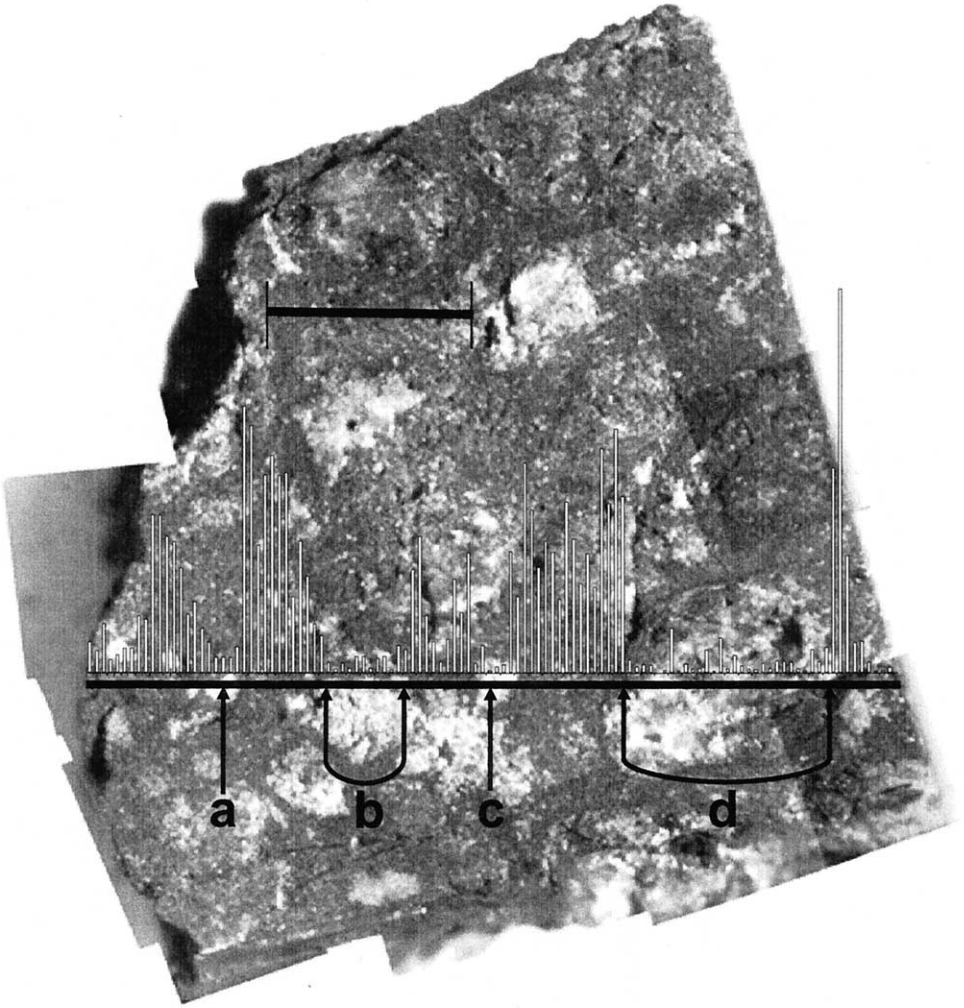

Fig. 3. Allende section. Composite (120× magnification) picture with overlay showing correlation of intensity of mass 128 Da with meteorite features. The thick line denotes the desorption path. Arrows indicate the major features (a, b, c, d) visible along this line and the corresponding changes in peak intensities. This correlation holds for all PAHs investigated (cf. Fig. 3). Scale bar = 1000 $\mu$m.

releases PAHs from the larger macromolecular material (Mahajan et al., 2001). In the second step, a pulsed ultraviolet laser (266 nm) selectively ionizes the desorbed molecules. The resulting ions are analyzed in a reflectron time-of-flight mass spectrometer. The mass spectra consist of the PAHs and their derivatives with little fragmentation. The lack of fragmentation allows identification of the PAH distribution intrinsically present within the sample. Figure 1 shows representative $\mu L^2MS$ spectra from matrix sections of both the Allende and Murchison samples.

Mass spectra were recorded for a series of 40-$\mu$m diameter spots across each sample, one spot per laser shot. These single-shot spectra show the distribution of PAHs, without any averaging effects. This procedure is in contrast to previous work (McKay et al., 1996) that used 20-shot averages to map the spatial distribution of PAHs. The relative intensities of the PAHs within one sample, under the same experimental conditions, may be found by comparing the PAH time-of-flight peak areas. Peak areas were integrated by IGOR software (WaveMetrics, Lake Oswego, OR). Peak intensities depend on several factors, including desorption and photoionization characteristics and the instrument response. The observed desorption characteristics have been found in previous work in this laboratory to depend on the nature of the matrix holding the sample molecules. Within classes of matrix materials (plastics, metals, silicates) with a reasonably flat surface, we find that the desorption characteristics and amount of organics released with each desorption shot are similar.

The peak intensity for each species is a function of the detector and instrument geometry. The photoionization cross section depends on both the ultraviolet absorption cross-section and the efficiency of ionization resulting from absorption; thus, it differs for each molecular species. A direct comparison of two peak intensities will generally not give a directly comparable concentration; a change in *relative* peak intensities, however, is of significance. In addition, to a first approximation alkylation (replacement of -H with -$CH_3$) does not perturb the aromatic $\pi$-bonding. Hence, the peak intensities of a PAH and its alkylated homologs may be directly compared to obtain relative concentrations. This technique does not distinguish between species of identical mass so isomers cannot be distinguished without a study of signal vs. photoionization wavelength.

## 2.4. Extraterrestrial Nature of PAHs within Meteorite

The source of the PAHs is a major concern when analyzing extraterrestrial samples that have been collected after infall to Earth. This concern may be divided into two areas: first, contamination during sample residence on Earth, both before and after collection, and second,

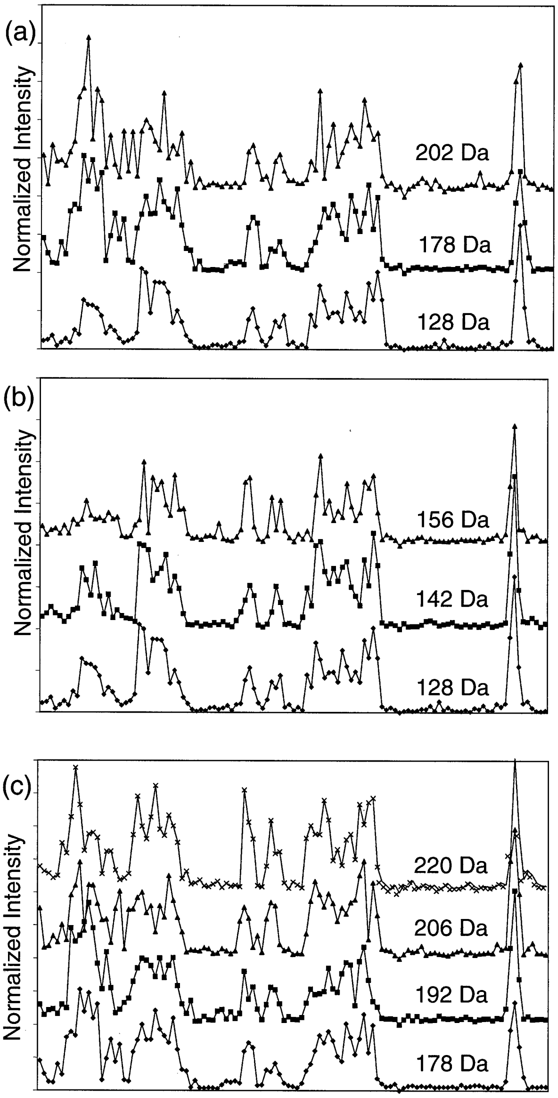

Fig. 4. Normalized integrated intensities along the desorption line in Figure 2 for (a) masses 128 Da (naphthalene, $C_{10}H_8$), 178 Da (phenanthrene, $C_{14}H_{10}$), and 202 Da (pyrene or fluoranthene, $C_{16}H_{10}$), (b) 128 Da (naphthalene), 142 Da (methylnaphthalene, $C_{11}H_{10}$), and 156 Da (dimethylnaphthalene or ethylnaphthalene, $C_{12}H_{12}$), and (c) the alkylation series for phenanthrene. Trends are the same for all PAHs.

contamination during sample preparation. We address these concerns separately.

### 2.4.1. *Possibility of Sample Contamination during Terrestrial Residence*

Both the Allende and Murchison carbonaceous chondrites fell to Earth in 1969, and so the samples studied have been exposed to the terrestrial environment for over three decades, raising concerns about the possibility of contamination from terrestrial PAH sources. Any such contamination would be expected to be concentrated on the surface of the samples, with possible migration of PAHs from the surface into the interior, resulting in concentration gradients (Cronin and Pizzarello, 1990). The samples studied in this work were freshly exposed interior pieces, removed from the exteriors. The observed PAH distributions did not correspond to simple gradients that would indicate migration of PAH contaminants, and PAH levels were not significantly higher at the edges of the samples.

PAHs have very low solubilities in water, and, if released to the environment, do not remain in solution but associate with particulate matter (see http://www.epa.gov/safewater/dwh/t-soc/pahs.html). Contamination of these meteorite samples from contact with PAH-containing water or water vapor is therefore unlikely. Exposure to atmospheric PAHs would be the most likely source of contamination, either in the laboratory or during curation. Atmospheric PAH pollution, much of which is emitted from sources such as internal combustion engines, contains a large proportion of alkylated PAHs (Kawamura and Suzuki, 1994; Gingrich et al., 2001). We do not observe such a pattern for extraterrestrial samples. In combination with the observed concentration pattern, as discussed above, we conclude that the observed PAHs do not result from terrestrial contamination.

### 2.4.2. *Possibility of Sample Contamination during Preparation for $\mu L^2MS$*

Control experiments were performed to test the possibility of sample contamination by terrestrial PAHs during preparation and analysis. Blank glass and rock samples were sectioned and analyzed to examine the effects on the sample of cutting, the only sample preparation used. No PAHs were observed within detection limits, indicating that the sectioning process and the exposure of the sample to the laboratory environment do not introduce PAHs. We discuss both possibilities in more detail.

To investigate the likelihood of the diamond blade smearing carbonaceous matter from the exterior of a sample to the freshly cut interior, a $10^{-4}$ M solution of the PAH coronene ($C_{24}H_{12}$) was evaporated onto the exterior of a small rock (Franciscan graywacke, Palo Alto, CA). The doped piece was dry cut with the diamond blade and analyzed. Figure 2 shows that signal from the coronene dopant was clearly evident at the edge of the sample, dropping to an undetectable level within two shots (80 $\mu$m). The signal was integrated over a set time interval for each mass spectrum, giving a nonzero baseline value arising from noise associated with a single-shot mass spectrum. This baseline value was comparable to the integrated signal from a sample of undoped rock. The experiment was repeated with plain glass samples, obtaining similar results. Even with deliberately introduced exterior PAHs, at levels equal to the highest intensities observed in the meteorite samples, the diamond blade does not contaminate the interior being exposed during the cutting process.

It is possible that the surface of a sample might become contaminated during sample storage or handling. Blank glass and rock samples were exposed to ambient laboratory air for several days, far longer than the exposure times of a few minutes that are needed for cutting. No PAHs were observed within detection limits. Samples were also left within the $\mu L^2MS$ vacuum chamber for a period of five days, much longer than the normal analysis time of a few hours. No changes in PAH intensities were observed over this time period, confirming that routine laboratory exposure of samples in our laboratory during analysis does not cause PAH contamination of these samples.

## 3. RESULTS AND DISCUSSION

Figure 3 shows a section of Allende. Overlaid on it are both a desorption line and a graph illustrating the integrated peak area of mass 128 Da (naphthalene, $C_{10}H_8$) for each shot along this line. Feature d in Figure 3 is rounded, has a dark rim, and is probably a chondrule. It shows an almost total lack of PAH intensity in the interior coupled with high levels of PAHs close to the exterior, dropping off to intermediate levels within the matrix. Other visible features simply show low levels of PAHs. These observations are consistent with previous low-resolution studies from this laboratory (Zenobi et al., 1989, 1992) as well as studies of the total carbon content in these carbonaceous chondrites (Bunch and Chang, 1980; Heymann et al., 1987; Brearley, 2002).

The normalized integrated intensities for several PAHs along

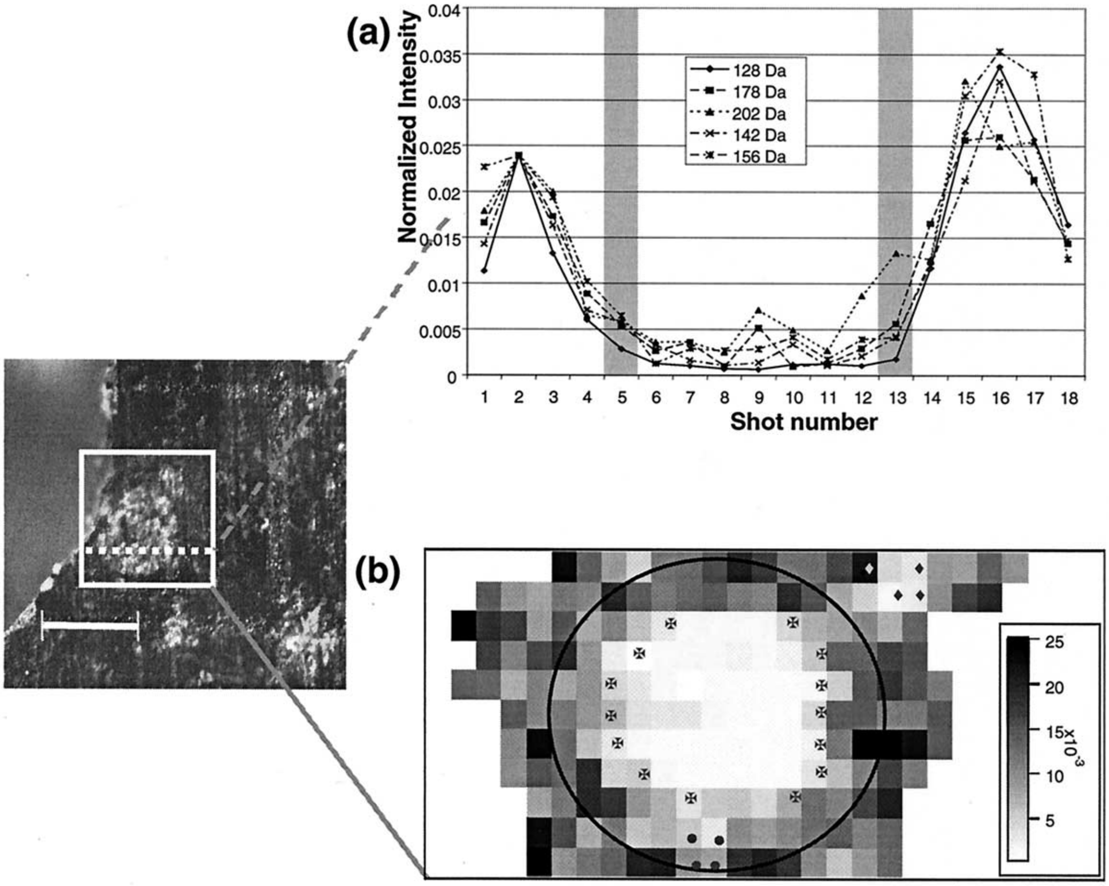

Fig. 5. Murchison chondrule. (a) Normalized PAH intensities across the dashed desorption line. Shot numbers 5 and 13 (shaded) are at the chondrule limits. (b) Naphthalene intensity map for the area denoted by the white box. The marks are the feature limits observed during the experiment: a cross denotes the chondrule; and a circle and a diamond denote smaller features below and to the upper right of the chondrule, respectively. Scale bar = 400 $\mu$m.

the desorption line denoted in Figure 3 show that all PAH intensities follow the same distribution (Fig. 4). Similar results were observed along several desorption lines for both the relatively unaltered Allende (CV3) and the moderately aqueously altered Murchison (CM2). Even though the mineralogy of Murchison shows that it was once exposed to water, PAHs are extremely insoluble in this solvent (Clemett et al., 1998). It is unlikely that in situ migration or alteration of the PAHs would allow the meteorites to retain such sharp chemical gradients and leave some areas free of PAHs while mixing PAHs essentially uniformly with the matrix.

Figure 5 is an enlarged view of a probable chondrule in Murchison. Figure 5a represents the normalized intensities of masses 128 Da (naphthalene, $C_{10}H_8$), 142 Da (methylnaphthalene, $C_{11}H_{10}$), 156 Da (dimethylnaphthalene or ethylnaphthalene, $C_{12}H_{12}$), 178 Da (phenanthrene, $C_{14}H_{10}$), and 202 Da (pyrene or fluoranthene, $C_{16}H_{10}$) for a representative desorption line traversing this chondrule. Again, similar relative intensities are apparent for all PAHs, although the absolute intensities vary. Few, if any, PAHs are present within the chondrule. The PAH signal intensity rapidly rises from zero in the chondrule interior to a peak close to the chondrule edge, and then drops off to an intermediate value in the matrix. Figure 5b presents an intensity map of naphthalene for the chondrule and surrounding region. Maps for the other PAHs have similar appearances. Intensity changes correspond closely with the chondrule outline. Two smaller features associated with the chondrule are also observed to be low in PAHs. A line connecting the spots of high naphthalene intensity around the chondrule has been drawn to guide the eye.

If the material that formed the high-temperature components such as chondrules and CAIs originally had solar chemical abundances, their lack of PAHs might result from heating events associated with their origins. Such heating would have caused volatilization as well as partial or complete breakdown of organic compounds. Even without complete molecular breakdown, heating would have produced simple movement of compounds, possibly with some breakdown of more complex species or some recondensation. In either case, the cooling rate would need to be faster than the diffusion rate to maintain the chemical gradients in the observed PAH spatial distributions.

The presence of PAHs throughout these meteorites implies that the meteorite as a whole has not experienced heating above PAH destruction temperatures (several hundred degrees Celsius) for times on the order of minutes. The PAH destruction temperatures provide upper bounds to the meteorite processing

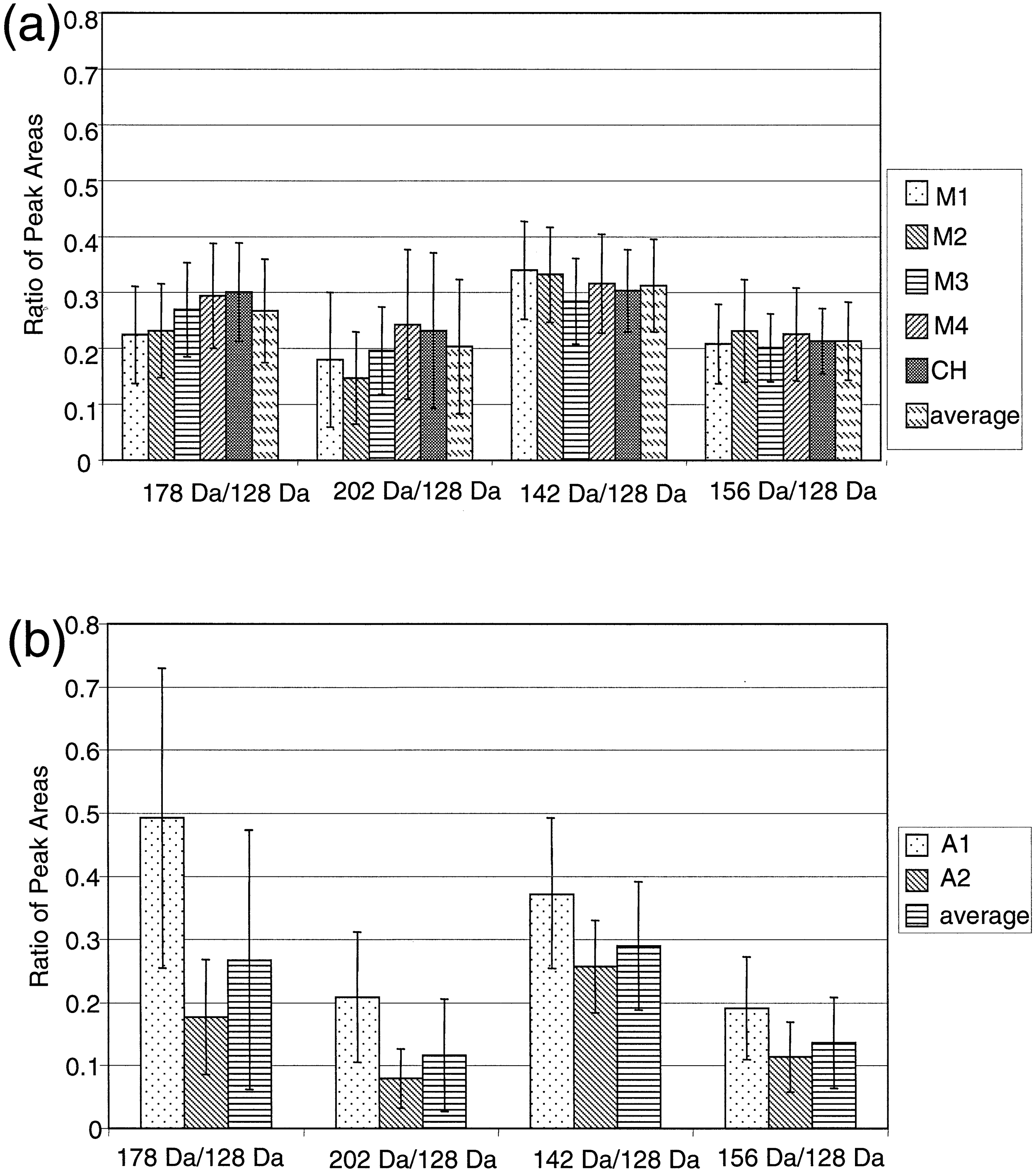

Fig. 6. Intensity ratios of PAHs normalized to naphthalene. Error bars represent 1 standard deviation. Desorption shots that produced spectra with a signal-to-noise ratio less than three for the naphthalene peak are excluded. (a) Murchison: M1, M2, M3, and M4 are desorption lines consisting of 114, 63, 110, and 65 included shots, respectively; CH is the area over the chondrule in Figure 4, consisting of 160 included shots. (b) Allende: A1 and A2 are desorption lines consisting of 46 and 115 included shots, respectively.

temperature, consistent with the presence of low-temperature silicate alteration products (Tomeoka and Buseck, 1985; McSween, 1987; Buseck and Hua, 1993). Recent studies have suggested that the Allende meteorite experienced aqueous alteration followed by a period of heating to 300 to 400°C (Kojima and Tomeoka, 1996; Krot et al., 1997; Brearley, 1999). Preliminary work in our laboratory has shown that although PAHs within meteorite samples can withstand these temperatures for short periods of time, extended exposure to such temperatures (on the order of several hours) causes the

Table 1. Comparison of PAH ratios of Murchison and Allende carbonaceous chondrites.[a]

| Ratio | Murchison | Allende |
|---|---|---|
| 178:128 | 0.27 ± 0.09 | 0.27 ± 0.21 |
| 202:128 | 0.20 ± 0.12 | 0.12 ± 0.09 |
| 142:128 | 0.31 ± 0.08 | 0.29 ± 0.10 |
| 156:128 | 0.21 ± 0.07 | 0.14 ± 0.07 |

[a] Ratios compare PAHs of mass 178 Da (phenanthrene, $C_{14}H_{10}$), 202 Da (pyrene or fluoranthene, $C_{16}H_{10}$), 142 Da (methylnaphthalene, $C_{11}H_{10}$), and 156 Da (dimethylnaphthalene or ethylnaphthalene, $C_{12}H_{12}$) to mass 128 Da (naphthalene, $C_{10}H_8$). Uncertainties represent 1 standard deviation. Data are shown for all spectra with a signal-to-noise ratio >3.

disappearance of PAHs and would be inconsistent with the results reported in our work. PAH disappearance may be caused by volatilization, which occurs at temperatures of a few hundred degrees Celsius, rather than actual thermal alteration, which occurs around 700 to 800°C (Morterra and Low, 1983; Flickinger et al., 1990). Further experiments are planned to investigate the effects of aqueous exposure and thermal metamorphism on PAH distributions.

Given that the carbonaceous chondrites have not experienced extensive exposure to high temperatures since their formation, the correlation of textural features and chemical gradients suggests that the PAHs were in their host materials from the time of meteorite formation. Such a correlation implies that the PAH distribution has not been affected after incorporation into the meteorite parent body by PAH formation events within the meteorite, migration of PAHs caused by aqueous alteration, or differential processing and destruction of PAHs. These observations are consistent with a distribution for the PAHs that has not been significantly altered since the meteorites formed. Hence, our findings suggest an origin for the meteoritic PAHs that is contemporary with or before parent-body formation.

Figure 6a presents the ratios of the main molecular PAHs and their alkylation series relative to naphthalene for the desorption shots taken across Murchison. Although the data are for single laser shots taken in lines across the surface of the sample, the uncertainties shown by the error bars are consistent and modest. The ratios are constant within a factor of two for all spots. We have excluded data corresponding to areas with signal-to-noise ratios of less than three. Similar data exist for Allende and are presented in Figure 6b. Considering that the meteorites are agglomerations of many components, different origins for the PAHs contained within each component is a plausible assumption. It is unlikely, however, that material from unrelated components would give PAH distributions that correlate so closely with one another. The similarity of the PAH ratios for all spots across a sample suggest to us that the PAHs within a meteorite result from a common pool of compounds before incorporation into the meteorite; no evidence exists for localized reactions or postincorporation redistribution. Many different PAH formation mechanisms have been proposed (Ehrenfreund and Charnley, 2000), each of which can be expected to give a different PAH distribution. This common ratio suggests that the PAHs in these two meteorites were either formed by only one of the proposed mechanisms, or that the PAH-containing material formed by several mechanisms had been well mixed to form a homogeneous distribution before parent-body accretion.

The normalized PAH ratios are not only similar within each of the two carbonaceous chondrites, but also the ratios for the two samples match each other within experimental error (Table 1). Nevertheless, more samples need to be studied to give a reasonable evaluation of the statistical significance of these results. With that in mind, however, these observations suggest that the PAHs within a given meteorite have a common origin and, moreover, all the meteoritic PAHs in Allende and Murchison may come from a common origin. It is even possible that the PAHs predate the formation of the solar system. We do know that PAHs in certain meteorites are associated with anomalous deuterium enrichments (Kerridge et al., 1987) that are consistent with low-temperature formation in the gas phase or on grains—that is, conditions that prevail within the interstellar medium (Sandford et al., 2000).

Our results lead us to propose a hypothesis for the origin of the PAHs in meteorites. The similarity of the PAH ratios relative to naphthalene, regardless of location in the samples of meteorite investigated, is consistent with a common origin for the PAH compounds. This observation, along with the preservation of sharp chemical gradients, suggests their origin was before or contemporary with parent-body formation. The closeness of PAH distributions in the samples examined so far is suggestive that PAHs present in the early solar system may have a common origin. Investigation of more meteorites and samples from different points in the solar system, such as those that would be available from planned and proposed cometary return missions, will provide a powerful test of this hypothesis.

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