SEARCH FOR HIGH MOLECULAR WEIGHT POLYCYCLIC AROMATIC HYDROCARBONS AND FULLERENES IN CARBONACEOUS METEORITES; M. S. de Vries, H.R. Wendt and H. Hunziker, IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099; E. Peterson and S. Chang, Space Science Division, NASA-Ames Research Center, Moffett Field, CA 94035

The chemistry of aromatic carbonaceous material in meteorites lies at the intersection of lines of investigation coming from two other research areas: the role of polycyclic aromatic hydrocarbons (PAHs) in interstellar chemistry [1] and the laboratory synthesis and characterization of closed cage "fullerenes" (e.g., C_{60}, "Buckey ball", and C_{70} [2,3]. Although sizes of interstellar PAHs have been estimated to range from C_{20} [4] to $>C_{50}$ [4,5], the higher molecular weight fullerenes have also been suggested as interstellar species. [6] Insofar as evidence already exists for organic matter of interstellar origin in meteorites [7,8], the nature and origin of meteoritic PAHs and the occurrence of fullerenes in meteorites are of considerable interest.

Typical wet chemical analyses of discrete PAHs in carbonaceous meteorites show the presence of species up to C_{20} (e.g., benzopyrene, $C_{20}H_{12}$), but mostly of species $\leq C_{16}$ [9]; and PAH moieties as large as C_{150} could be components of the kerogen-like material. [10] Molecules containing C_{26} have been detected by two-step laser desorption-photon ionization mass spectrometric (LD-PIMS) analysis of Allende [11], but molecular identifications were limited to species $<C_{20}$. We describe below the detection and preliminary identification of high molecular weight PAHs in acid residues obtained by acid demineralization of Murchison and Allende samples. We also note an intriguing correlation between the meteoritic products with those obtained by laser ablation of graphite in the presence of various amounts of H_2.

Samples derived from Murchison and Allende acid residues were analyzed by LD-PIMS [12]. Vacuum sublimates of the residues were collected on a gold plated sampling bar. Sublimination was performed successively at three different temperatures (300, 450 and 600°C) resulting in three separate spots on the bar, each about three mm in diameter. The bar was then transferred to the LD-PIMS apparatus in which the sublimed material was desorbed by pulses from a KrF laser. The desorbed molecules were entrained in a supersonic expansion which was intersected downstream by light from an ArF laser for ionization. The ions were detected with a time-of-flight mass spectrometer. Analysis of the sampling bar between the sublimate spots gave no evidence of PAHs.

Figure 1 shows the mass spectra from sublimates at the three different temperatures from a Murchison sample. The most prominent peaks strongly suggest the presence of PAHs such as anthracene and penanthrene (mass 178), pyrene (202), perylene (252), benzoperylene (276) and coronene (300). The spectra also show numerous higher mass peaks differing by multiples of 14 mass units from the unsubstituted PAHs. Ions from these alkylated derivatives may contribute to the envelope of masses on which the more prominant ions are superimposed. This is the first time that PAHs of such high mass and carbon number have been observed in meteorites. The presence of coronene ($C_{24}H_{12}$) and its alkyl derivatives is particularly interesting because the main IR emission bands of coronene appear to "give an impressive fit to the observed" unidentified IR interstellar emission bands. [5] Figure 2 shows the results from an Allende sample. Generally, when analyzed under identical conditions, the Allende samples yielded less sublimate than did Murchison. PAHs are evident in the spectra, but they are less abundant; they exhibit a somewhat different PAH composition (with as yet unidentified masses); and they appear to be relatively depleted in the more volatile species relative to Murchison PAHs. Fullerenes have not been detected thus far. Further analysis is in progress starting from fresh meteorite samples.

Results in Figures 1 and 2 can be compared with analyses of material synthesized in the laboratory by laser ablation of graphite in 500 torr of Ar. Ablation products collected on a sample bar and analyzed in the LD-PIMS apparatus yielded the results shown in Figure 3: a wide range of fullerene clusters with C_{60} and C_{70} most prominent. The other panels of Figure 3 show the effect of adding hydrogen to the Ar buffer gas. With increasing concentration of H_2, the production of fullerenes decreases, while synthesis of PAHs increases. At 10% H_2, fullerenes are no longer produced. Remarkably, graphite ablation yields PAH distributions similar to those found in the meteorite samples. These results suggest that cosmic abundances of H_2 in circumstellar or interstellar environments may preclude the synthesis of fullerenes, but not the production of other PAHs.[13] Other factors influencing the (cosmic) synthesis of fullerenes are under investigation.

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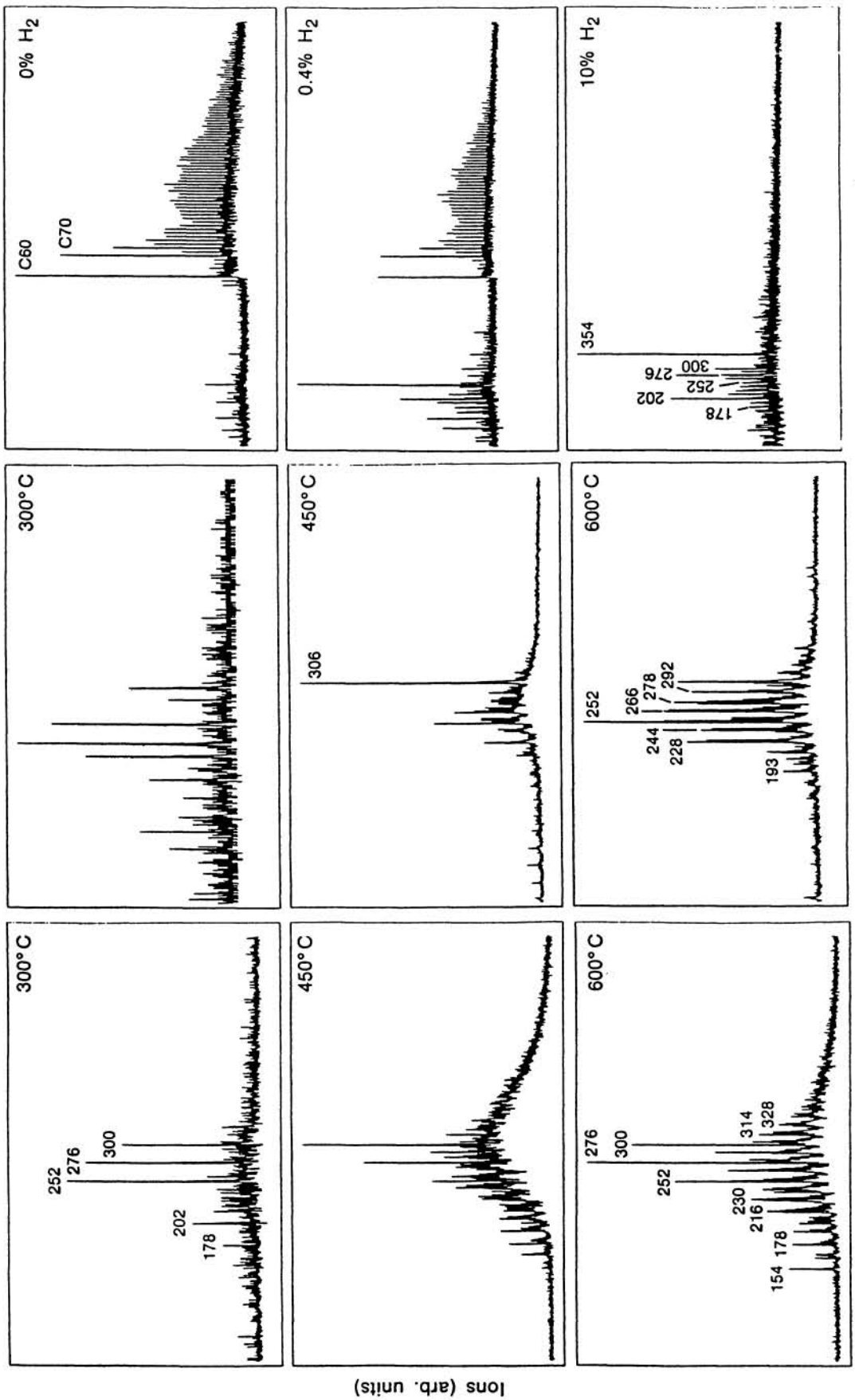

Fig. 3. TOF mass spectra of products of graphite ablation in Ar with different concentrations of H_2. Peaks above C70 in top pannel are 24 amu apart.

Figs. 1 & 2. Time of flight mass spectra obtained from samples collected at different temperatures by sublimation of Murchison (left) and Allende (right) acid residue samples.