MEASUREMENT OF POLYCYCLIC AROMATIC HYDROCARBON (PAHs) IN INTERPLANETARY DUST PARTICLES; S. J. Clemett, C. R. Maechling, and R. N. Zare, Department of Chemistry, Stanford University, Stanford, CA 94305-5080.
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We report here the first definitive measurements of specific organic molecules (PAHs) in interplanetary dust particles (IDPs). An improved version of the microbeam-two-step laser mass spectrometer (μL^2MS) described previously [1,2] was used for the analysis. Two IDPs gave similar mass spectra showing an abundance of PAHs. Control samples, including particles of probable terrestrial origin from the same stratospheric collector, gave either null results or quite different spectra. We conclude that the PAHs are probably indigenous to the IDPs and are not terrestrial contaminants.

The instrument used to study the particles is a two-step laser mass spectrometer. Constituent neutral molecules of the sample are first desorbed with a pulsed infrared laser beam focussed to 40 μm. In the second step, PAHs in the desorbed plume are preferentially ionized by a pulsed UV laser beam. Resulting ions produced by resonant absorption are extracted into a reflectron time-of-flight mass spectrometer. This instrument has high spatial resolution, high ion transmission, unlimited mass range and multichannel detection of all ion masses from a single laser shot.

IDPs studied at WU are analyzed by several techniques [3]. Following EDS measurements, IDPs are crushed between quartz plates and adhering material is transferred to a KBr crystal for micro-FTIR absorption measurements [4] and/or micro-Raman [5] studies. Material on the other quartz plate is transferred to Au foils and isotopic measurements are made using a modified Cameca IMS-3F ion probe [6]. The KBr mounts proved satisfactory for analysis by μL^2MS. The molecular data were obtained on particles originally studied by F. Stadermann [7].

Positive results were obtained on two IDPs, Aurelian and Florianus. Both particles are certainly extraterrestrial; each has a chondritic elemental spectrum and both have large deuterium enrichments (up to δD = 771± 85‰ for Aurelian and δD =1120 ±100‰ for Florianus). In addition, Florianus has a large ^{15}N enrichment ($\delta^{15}N$ = 411 ± 20) [8]. Florianus has a typical pyroxene type IR spectrum while Aurelian has an IR spectrum characteristic of layer-lattice silicate IDPs [4]. Prior to shipping to Stanford the relevant dust fragments were relocated on the KBr mounts and remeasured by FTIR spectroscopy. A mark was then scribed on the KBr to locate the particles. Laser shots made at various locations on the KBr mount away from the marked IDPs gave negative results.

The μL^2MS results for Aurelian and Florianus are shown in Fig. 1. With the exception of the peaks in the Florianus spectrum at 155-165 amu, which we attribute to isotopomers of dipotassium bromide cation, the spectra are qualitatively similar although different in detail. Both show three major mass envelopes, one near 60 amu, one at moderate mass peaking at 250 amu, and one at high mass peaking at 370 amu. The moderate mass envelope has the largest intensity, followed in decreasing order by the high and low mass envelopes. The low mass envelope is dominated by inorganic species such as Na, K, and Fe. In contrast, the moderate and high mass envelopes contain clear signatures of PAHs and their alkylated derivates, indicated by clusters of peaks separated by 14 amu as a consequence of the successive addition of methylene ($-CH_2$) groups to the PAH skeletons. This identification is based on extensive experience with standard samples and the fact that the UV laser is tuned to selectively photoionize such molecules. The virtual absence of low mass PAHs (between 78-192 amu) such as alkyl-benzenes, alkyl-naphthalenes, and alkyl-phenanthrenes on these IDP spectra should be noted. This is consistent with the evaporation of these more volatile, lower mass organic components from an IDP during prolonged exposure in space, as well as loss by heating during atmospheric entry.

The zeptomole (10^{-21} mole) sensitivity of μL^2MS coupled with the wide scale distribution of PAHs in the terrestrial environment makes it difficult to prove that the observed molecules are not terrestrial contaminants. To examine this question samples of the silicone oil from collector U-47 were put on a fine-grained silica substrate (Cabosil) and looked at with μL^2MS. The xylene used to clean the IDPs and the Fomblin oil used in the SEM diffusion pumps were similarly studied. None of these samples gave spectra similar to those seen in Aurelian or Florianus. As a final test, we studied two particles that we had previously identified as "probable terrestrial contaminants" from collector U-47. One particle was dominated by Si, O, and Al, and the second by Ca, O, and Si. Both particles were measured in the ion probe and neither had measurable isotopic anomalies in H, N, C, or Mg. The total integrated yield of masses measured by μL^2MS was $\leq 5\%$ that measured in Aurelian; the mass spectrum showed no evidence of PAHs within the detection limits. The fact that control particles which had been exposed to the same environment as Aurelian and Florianus did not show abundant PAHs lends strong support to the indigenous origin of the PAHs in the IDPs.

The results reported here are perhaps not surprising in view of prior indirect evidence for the presence of complex organic molecules in IDPs [5,6,8,9]. PAHs have also been previously measured using μL^2MS in various meteorites and their acid residues [1,10,11,12]. It is interesting to note however that the mass patterns seen by us in Aurelian and Florianus are different than those previously found in other extraterrestrial materials. Much work remains to be done to elucidate the nature of the organic molecules and their relationship to other properties of IDPs. The effects of heating during entry also need to be studied. To the extent that certain IDPs may represent the most primitive materials available, continued studies of the type described here can be expected to better elucidate the nature of the original organic materials in the solar system. These issues are now amenable to study thanks to the unprecedented sensitivity and specificity of μL^2MS .

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FIG. 1