

Laser mass spectrometric detection of extraterrestrial aromatic molecules: Mini-review and examination of pulsed heating effects

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Laser mass spectrometry is a powerful tool for the sensitive, selective, and spatially resolved analysis of organic compounds in extraterrestrial materials. Using microprobe two-step laser mass spectrometry ($\mu\text{L}^2\text{MS}$), we have explored the organic composition of many different exogenous materials, including meteorites, interplanetary dust particles, and interstellar ice analogs, gaining significant insight into the nature of extraterrestrial materials. Recently, we applied $\mu\text{L}^2\text{MS}$ to analyze the effect of heating caused by hypervelocity particle capture in aerogel, which was used on the NASA Stardust Mission to capture comet particles. We show that this material exhibits complex organic molecules upon sudden heating. Similar pulsed heating of carbonaceous materials is shown to produce an artifactual fullerene signal. We review the use of $\mu\text{L}^2\text{MS}$ to investigate extraterrestrial materials, and we discuss its recent application to characterize the effect of pulsed heating on samples of interest.

astrochemistry | interplanetary dust particles | mass spectrometry | meteorites | polycyclic aromatic hydrocarbons

Determining the chemical composition of exogenous material (not from Earth), including meteorites, interplanetary dust particles (IDPs), and cometary coma dust, is a fascinating endeavor, and its pursuit can significantly increase our knowledge of planetary formation and interstellar chemistry. Several factors make this task challenging, including sample acquisition in a manner that does not alter compounds and analysis of micrometer-scale samples. Mass spectrometry (MS) offers one means of meeting these criteria. In the past, MS instruments have flown on missions to outer space and the surrounding planets. Notably, the NASA Viking Landers, which touched down on Mars in 1976, used gas chromatography followed by MS to gain the first analysis of the Martian atmosphere (1). MS investigations in space have enabled the understanding that planets exchange material and, in particular, that Earth has received meteorites from the moon and Mars. Much information about our surroundings has been gained by the MS analysis of extraterrestrial materials.

Laser MS techniques have particular utility when analyzing low concentrations of organic compounds on complex surfaces and particulates, which are often encountered with extraterrestrial materials. In general, these techniques are able to perform spatially resolved, micrometer-scale surface analyses and have achieved sensitivities in the subattomole regime (2). Most commercial laser MS instrumentation uses one laser pulse, to both thermally desorb surface material and ionize resulting gaseous compounds. A matrix is often added to the sample to facilitate desorption, such as in matrix-assisted laser desorption/ionization (MALDI) (3, 4). Less widespread, because of an increased complexity and specificity, are laser MS techniques that use two lasers, one for sample desorption and one for ionization (2). This two-step laser MS can be used to selectively detect specific organic compound classes with high sensitivity and does not require matrix addition. Only femtograms of surface material are

removed during desorption, minimally altering the sample and permitting subsequent analyses with other techniques. For extraterrestrial materials, which are rare and tend to have low organic concentrations, this technique is quite advantageous.

We have applied two-step laser MS to detect extraterrestrial polycyclic aromatic hydrocarbons (PAHs) using a microprobe laser-desorption laser-ionization MS ($\mu\text{L}^2\text{MS}$). These aromatic compounds likely represent a considerable portion of interstellar organic carbon (5, 6) and have been identified in many exogenous samples (7). In this article we first present a minireview of previous $\mu\text{L}^2\text{MS}$ studies of extraterrestrial samples, including meteorites, IDPs, and interstellar ice analogs, in this laboratory. Subsequently, we present the recent application of $\mu\text{L}^2\text{MS}$ to determine pulsed heating effects, via hypervelocity particle capture in aerogel and laser desorption heating, on the analysis of extraterrestrial samples. This work highlights the challenges associated with studying extraterrestrial materials.

Review of $\mu\text{L}^2\text{MS}$ for the Study of Extraterrestrial Materials

Carbonaceous Chondrite Meteorites. Meteorites are the most available type of exogenous material on Earth and are representative of the early Solar System. Organic carbon comprises up to 3% by weight of carbonaceous chondrite meteorites (8). Their interiors exhibit highly heterogeneous morphologies, with different regions containing information about their individual histories before incorporation in the meteorite parent body. These components have the unparalleled potential to increase our knowledge of environments present in the early Solar System.

Many meteorite experiments have been carried out, revealing an amazing variety of compounds and minerals, some of which are highly localized (9). Evidence of melting for some components is apparent, such as for chondrules (10), whereas other minerals show no sign of ever exceeding their low decomposition temperatures (11). This implies that meteorites have not experienced extreme heating since their initial formation. For carbonaceous meteorites, organic molecules can also be effective indicators to assess past thermal and aqueous exposure. These effects are known to influence the degree of hydroxyl or alkyl substitution on aromatic compounds in meteorites (12).

$\mu\text{L}^2\text{MS}$ studies of carbonaceous chondrite meteorites have been carried out in this laboratory. Several of these analyses exemplify the spatial resolving power of $\mu\text{L}^2\text{MS}$. For Murchison

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(CM2; moderate aqueous exposure) and Allende (CV3; little thermal or aqueous exposure) meteorites, fine-grained macromolecular material was found to exhibit consistent PAH abundances, with mass ranges extending from 128 amu (naphthalene) to beyond 202 amu (pyrene) [supporting information (SI) Fig. S1] (13, 14). A striking contrast in PAH intensity was seen when comparing the mass spectrum taken on matrix material versus embedded chondrules (Fig. S2). The latter were conspicuously lacking in PAHs. Localization of PAH gradients to specific features implies that these compounds are original to the time of meteorite parent-body formation, if not earlier (13). A similar analysis of PAHs in the Allan Hills (ALH) Martian meteorite 84001 uncovered PAHs localized in and around carbonate globules (15, 16). This was perhaps the most controversial observation made using $\mu\text{L}^2\text{MS}$, because interpretation of how these PAHs were generated is a matter of continuing debate and has stimulated a significant amount of work (17, 18). PAHs were not detected in ALH84001 fusion crust, nor were they found to be depth-dependent, as would be expected for terrestrial contaminants. Debates on the origin of PAHs, like those found in ALH84001, continue to catalyze experiments that further the body of knowledge on organic compound formation in the interstellar medium (ISM).

The sensitivity and selectivity of $\mu\text{L}^2\text{MS}$ was exemplified in a set of experiments aimed at correlating PAH distributions to meteorite alteration histories. The degree of PAH alkylation [$\text{PAH}-(\text{CH}_2)_n$], in particular, was characterized in carbonaceous chondrites (15, 19, 20) and Antarctic micrometeorites (AMMs) (21), which represent a range of thermal and aqueous alteration histories. Increasing PAH alkylation was found to associate with increasing aqueous exposure of carbonaceous chondrite parent bodies (19). This trend can be explained by the higher relative solubility and vapor pressure of simple PAHs versus their alkylated counterparts (22). Thus, PAHs with less alkylation migrate more effectively, causing their preferential chromatographic separation and removal (23). AMMs, which have experienced more heating than carbonaceous chondrites, exhibited a more diverse suite of PAHs, showing a greater degree of alkylation as well as partially dehydrogenated alkyl substituents (21). For AMMs, a smooth increase in alkylation degree was correlated with increasing thermal exposure. In a similar study, thermally altered meteorites exhibited relatively low PAH abundances, implying their volatilization from a parent body (19). The greater PAH structural complexity, higher alkylation degree, and decrease in PAH abundance for thermally exposed bodies supports the theory that alteration events may have significantly changed the composition of organic compounds in exogenous material, either during its atmospheric entry on Earth (for AMMs) or at the time of meteorite formation in the developing Solar System (for carbonaceous chondrites).

Large deuterium (D) enrichments and highly variable carbon isotope ratios ($^{12}\text{C}/^{13}\text{C}$) detected in these grains from primitive meteorites clearly demonstrate that some of these molecules originated from other stars, predating Solar System formation (24). The $^{12}\text{C}/^{13}\text{C}$ ratio for solar system materials is ≈ 89 whereas the reported (25) carbon isotope ratios for PAH molecules detected by $\mu\text{L}^2\text{MS}$ in these carbon grains ranged from 2.4 to 1,700. This work represents a unique detection of presolar organic molecules from beyond our Solar System.

Interplanetary Dust Particles (IDPs). Micrometer-size IDPs, which likely formed from primitive materials during Solar System birth (26), have displayed very high carbon contents as well as potential PAH signatures (27, 28). A number of stratospherically collected particles (2–50 μm in diameter) have been analyzed with $\mu\text{L}^2\text{MS}$ in this laboratory. In one research project, two such particles exhibited broad PAH envelopes (29), as well as other signatures (28, 30, 31), which confirmed their identification as

IDPs. PAHs were found to cluster in three mass envelopes (with peaks at 60, 250, and 370 amu) and exhibited more extensive alkylation and nitrogen addition (i.e., $-\text{NH}_2$, $-\text{CN}$, or $-\text{NC}$) than those observed in carbonaceous chondrites (14, 19, 20). Relative to carbonaceous chondrites, a strikingly low abundance of PAHs < 192 amu was found. Exposure of IDPs to the vacuum of space and atmospheric entry heating may have played an important role in removing these more volatile compounds.

In another project, four cluster IDP fragments (32) were analyzed by using $\mu\text{L}^2\text{MS}$. These particles showed a high variability, with PAHs that were dissimilar, lower in mass range, and less structurally complex than those found in our previous work (29). These $\mu\text{L}^2\text{MS}$ analyses reveal a high heterogeneity among IDPs, supporting the widely held belief that Solar System organics can be quite complex in nature and distribution.

Laboratory Analogs. Investigation of laboratory analogs, in combination with optical spectroscopy observations (33), can provide an invaluable tool for characterizing organic compounds in space. PAHs, in particular, are of interest as carriers for several diffuse interstellar bands (DIBs) (34) and are likely frozen in interstellar molecular cloud ices (35). Despite their relatively low chemical reactivity, these PAHs can absorb radiation, resulting in their structural alteration (36).

Taking advantage of the selectivity and sensitivity of $\mu\text{L}^2\text{MS}$ toward PAHs, we have investigated this process by characterizing nonvolatile aromatic photo-products in irradiated interstellar ice analogs (37–41). This work was performed in collaboration with the NASA Ames Research Center Astrochemistry group and researchers at the University of Leiden. In an initial study, photolysis products from interstellar ice analogs comprised only of small molecules (no PAHs) were studied. Various ice analog mixtures containing H_2O , CO , NH_3 , CH_3OH , CH_4 , and C_2H_2 were exposed to both UV and solar radiation (41). Using $\mu\text{L}^2\text{MS}$, we detected a complex mixture of PAH photoproducts that contained evidence of alkylation, hydrogenation, and in some cases the addition of nitrogen (i.e., $-\text{NH}_2$, $-\text{CN}$, or $-\text{NC}$). PAHs were more complex than those observed in chondritic meteorites and resembled those found in IDPs.

In more extensive experiments, UV photo-products of PAHs (i.e., pyrene, benzo[ghi]perylene, and coronene) in interstellar water ice analogs were characterized by using $\mu\text{L}^2\text{MS}$ (37, 39). Oxygenated and hydrogenated photolysis products were detected. Unexpectedly, intramolecular bridging ethers were also observed. UV radiation effects on alkanes [methane (CH_4) and octane (C_8H_{18})] in phenanthrene-containing interstellar ice analogs were also investigated, revealing alkylated phenanthrene photo-products (42). These alkylation processes likely compete with oxidation reactions in interstellar ices. Interstellar ice analogs containing coronene and other astrochemically relevant compounds (i.e., NH_3 , CH_4 , CH_3OH , HCN , CO , and CO_2) were also UV and proton irradiated (39, 40, 43). A number of photoproducts were detected (Fig. S3). Isotopic substitution experiments were also carried out (37, 38). Surprisingly, PAHs were found to exchange hydrogen easily with available deuterium in surrounding ice. This work revealed that D-enrichment, similar to that found in extraterrestrial materials (29, 44), can occur by UV photolysis of PAHs in D-rich interstellar ices. The ability of ice irradiation to generate complex PAHs indicates its great potential to contribute to the ISM organic inventory. Detected aromatic photolysis products, briefly summarized here, are similar to those detected in meteorites and other exogenous materials. A greater understanding of the fundamental molecular processes occurring in space can be gained through the analysis of analog systems such as these.

The chemistry of global organic haze in the nitrogen- and methane-rich atmosphere of Titan, the largest moon of Saturn, was explored in a separate set of experiments (45). Application

of $\mu\text{L}^2\text{MS}$ to analyze Titan haze laboratory analogues, known as Titan “tholins,” enabled the assessment of aromatic compounds in this material. Methane/nitrogen gas mixtures (10/90 premixed ratio) at various pressures (13–2,300 Pa) were exposed to cold plasma inductively coupled to an RF source to simulate the radiation exposure of Titan’s atmosphere. The resulting tholins were analyzed with several techniques, including $\mu\text{L}^2\text{MS}$. We discovered a complex range of aromatic compounds mainly in low-pressure tholins (13–26 Pa) that consisted of highly alkylated and nitrogenated one- and two-ring aromatic structures. This was the first confirmation of nitrogen-containing PAHs, which are efficient UV absorbers and charge exchange intermediaries, in Titan tholins, resulting in a better understanding of both the optical properties and chemical reactivity of the Titan atmosphere.

Study of Pulsed Heating Effects on Extraterrestrial PAHs

As with any study of organic compounds in exogenous samples, such as those briefly summarized in the review portion of this article, considerable work must be performed to interpret with confidence the origin of detected compounds. Pulsed heating of samples, in particular, poses a great threat to the original organic composition of a material, sometimes destroying, transforming, or completely obscuring original sample constituents. For laser mass spectrometers, which are used to analyze extraterrestrial materials in several research laboratories, determining the extent of this threat is of timely importance. Here, we present recent results from studies that we have performed to understand better the effects of pulse heating. In particular, we focus on two forms of heating: (i) high-velocity particle impact in silica aerogel, to assess potential contamination for the NASA Stardust Mission capture of cometary particles; and (ii) laser desorption on a carbonaceous substrate, to gauge fullerene modification or synthesis during one-step laser MS analysis.

Particle Collection in Silica Aerogel. Introduction. Development of low-density silica aerogel for hypervelocity particle capture was a great achievement (46). This material enables a relatively soft capture of high-velocity, micrometer-size grains. Aerogel has been used on the exterior of NASA Space Shuttles for IDP capture and was recently used to capture dust from comet 81P/Wild 2 by the NASA Stardust Mission (47).

Low-density silica aerogel can capture these particles without completely destroying the original material (46). Similar impact into a solid target would nearly vaporize a particle, removing original spatial and chemical information. On capture, particle kinetic energy is transferred to aerogel, generating heat and causing it to melt in the immediate impact vicinity. The leading particle surface also heats during capture and can result in the shedding of particle material. This ablative process leaves particle debris along the hollow impact track in aerogel (48). There is great interest in analyzing this shed material, particularly for comet particles captured in aerogel by NASA Stardust (49, 50). Knowledge of its makeup is vital for achieving a comprehensive view of the original particle composition.

Thermal gradients generated during impact complicate the analysis of this shed material. Particle debris likely experiences higher temperatures than the terminal particle itself, with aerogel along the impact track reaching above the silica melting point ($\approx 1,650^\circ\text{C}$) (51). In this temperature regime it is possible to alter or generate organic compounds from carbon impurities in aerogel. Compounds generated in this manner would correlate directly with particle tracks. If they occur, these impact-generated compounds could be easily, and incorrectly, assigned to the captured particle and thus to a cometary origin in the case of Stardust particles. Aerogel used for NASA Stardust is known to contain up to 2% carbon impurities by mass, which is present as trapped organic volatiles and short aliphatic groups bonded to

silicon (52). Even at these low levels, carbon impurities present a unique challenge for sensitive analyses (e.g., $\mu\text{L}^2\text{MS}$) of aerogel-collected particles.

We participated in the Stardust Mission as members of the Organics Preliminary Examination Team (PET) (53). Thus, we performed several tests to determine the effect of impact heating on carbon in aerogel. Two studies were performed: (i) borosilicate glass bead impacts into Stardust-type aerogel at 6 km/s and (ii) IR laser pulse heating of Stardust aerogel (54, 55). Stardust aerogel material, including flight spares and witness aerogel (overall contamination control for the mission), was used to mimic the actual capture environment for cometary particles on Stardust.

Results and discussion. To assess the potential for aerogel carbon impurities to form or release organic compounds during hypervelocity particle capture, glass beads were used as impactors into Stardust flight spare aerogel. Stardust aerogel is known to contain both aliphatic and aromatic compound contaminants. $\mu\text{L}^2\text{MS}$ analysis of unshot glass beads (20 μm in diameter) showed no background PAHs, indicating that these could serve as “blank” impactors. A two-stage light gas gun (NASA Ames Research Center) was used to accelerate these beads, achieving a velocity of 6 km/s at the aerogel substrate. Surface analyses of PAHs on a keystone-dissected (56) bead impact track were performed by using $\mu\text{L}^2\text{MS}$. Unfortunately, a more structurally relevant (i.e., more aggregated or IDP-like) blank impactor was not achievable. Acceleration shocks produced during particle test shots virtually destroy IDP-like particles, making their impact into aerogel difficult to mimic in the laboratory. Glass beads were used here as an approximate analog.

Several distinctive features were apparent during the analysis of this impact track, including (i) a low-intensity distribution of PAHs at the initial bead impact site and (ii) the presence of two high-intensity peaks at 27 and 70 amu along the exposed aerogel edge.

Spatially resolved $\mu\text{L}^2\text{MS}$ analysis of the bead impact track revealed a low-intensity distribution of PAHs at the initial entry portion of the track (Fig. 1A). Almost no PAHs were detected away from the impact track on the keystone (Fig. 1B), indicating that they are associated with the impact event itself. Prominent peaks in the mass spectra are tentatively assigned to toluene (92 amu), styrene (104 amu), naphthalene (128 amu), phenanthrene (178 amu), and pyrene (202 amu). Residual gun material produced during two-stage light gas gun acceleration of the beads was found along the entry portion of the track as well as along the exposed keystone edge (Fig. 1C). The presence of this gun residue has been reported previously and likely originates from Al [detected as Al (27 amu) and Al_2O (70 amu); not shown in Fig. 1C] in the gun muzzle flapper valve (50). Mass spectra taken on gun residue samples show very few PAHs in the area of interest (Fig. 1D), verifying that PAHs detected along the bead impact track are original to the impact event itself and not an artifact of the shooting process.

Impact velocity is at a maximum in the entry region of the aerogel track. At this site a high amount of energy must be absorbed by the aerogel. It is expected that the most chemical alteration, if any, would occur here. Detection of aromatic compounds only at the entry portion of the glass bead impact event implies that these compounds were synthesized or exposed during the hypervelocity impact event. Nearly identical aromatic compounds, including very similar relative PAH abundances, were found at the initial impact site when both Er:YAG and CO_2 desorption lasers were used during $\mu\text{L}^2\text{MS}$ analysis. These detected compounds support initial hypotheses that organic compounds can be generated or exposed, albeit in very low abundances, during hypervelocity particle capture in aerogel (53).

Gun shot residue is unavoidable when shooting particles with a hypervelocity gun, introducing contaminants into the sample

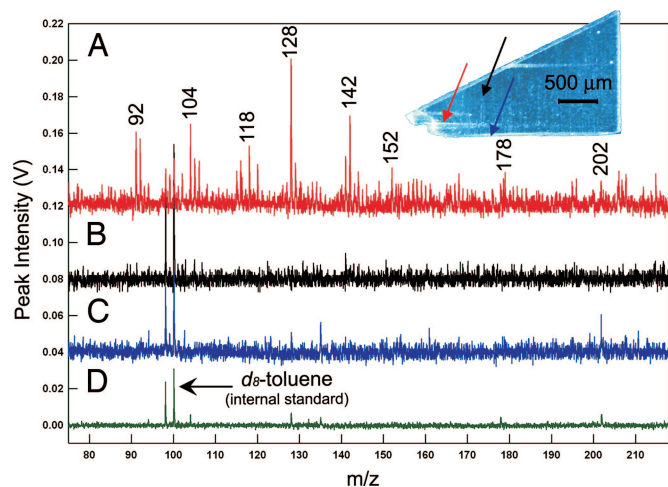


Fig. 1. $\mu\text{L}^2\text{MS}$ mass spectra (offset for clarity). (Inset) Optical image of a keystone dissected glass bead impact track in aerogel (6 km/s impact velocity). Color-coded arrows in Inset indicate positions of mass spectra in A–D. (A) Entry portion of bead track. (B) On aerogel away from the impact track. No peaks in the m/z range of interest. (C) Keystone edge, which was exposed during two-stage light gas gun shots. Small m/z peaks are observed, which correspond to gun shot residue. (D) Gun shot residual powder from a witness plate used during a similar 5.90 km/s test shot of glass beads. Main peaks are at 27 and 70 amu (not shown), from Al (3.9-V signal) and Al_2O_3 (3.7-V signal), respectively. Several low-intensity peaks are also detected in the area of interest; however, no PAHs were detected in significant quantities.

of interest. An additional, cleaner method of simulating a blank hypervelocity impact was also pursued in this laboratory to complement the glass bead impact tests described above. Laser pulses have been shown to approximate the rapid heating associated with hypervelocity impact events (57, 58). This procedure is quite clean, making it highly desirable as a “blank” impact test. Infrared (IR) laser pulses were used on both Stardust flight spare and witness coupon aerogels to achieve further understanding of contaminants that might be generated or released from aerogel during hypervelocity particle capture. As reported in ref. 54, at normal laser operating parameters, $\mu\text{L}^2\text{MS}$ analysis of witness coupon samples (WCARMI1CPN,0,6 and WCARMI1CPN,0,7) revealed the presence of no PAHs. Analyses at increasing laser desorption powers, however, produced a distinctive, low-mass envelope of aromatic compounds. Identical compounds were detected in a similar laser pulse study using Stardust flight spare aerogel. Tentative mass assignments include: benzene (78 amu), toluene (92 amu), and styrene (104 amu), as well as masses beyond chrysene (228 amu).

In comparison with PAHs detected at the glass bead impact site in aerogel, which is described above, the two PAH envelopes are a near perfect match (Fig. 2 B and C). These compounds are very similar to those typically found in carbonaceous chondrite meteorites and potentially make up some part of organic carbon in cometary material as well. A nearly identical envelope of PAHs was detected with $\mu\text{L}^2\text{MS}$ along a Stardust cometary particle impact track in aerogel (Fig. 2A) (53). The origin of these compounds, either contaminants or cometary, is ambiguous, despite their striking correlation with the impact event. Results from this study confirm our initial suspicions that these compounds are likely an artifact of the impact event itself and not original to the cometary particle.

This work shows that hypervelocity particle capture in silica aerogel can give rise to a low-abundance artifactual signature that can obscure the interpretation of low-mass aromatic compounds, and potentially other organic compounds as well (53, 54). Based on these results we believe that the assignment of the

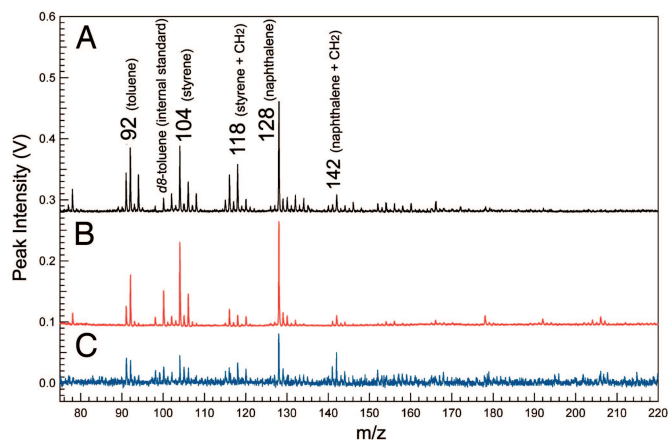


Fig. 2. $\mu\text{L}^2\text{MS}$ mass spectra (offset for clarity). (A) Dissected bulb portion of cometary particle impact track C2115,26,22. The spectrum is scaled down by a factor of 4 for ease of comparison. Tentative peak assignments are given. (B) High-power laser desorption on witness coupon aerogel. Similar m/z peaks and ratios are visible in the spectrum shown in A. (C) Entryway of the glass bead impact track (see Fig. 1). Again, similar m/z peaks and ratios are apparent in comparison with the spectra shown in A and B.

origin of aromatic molecules along particle impact tracks in aerogel is fraught with difficulties. Fortunately, captured terminal grains are thought to experience lower temperatures relative to ablated particle material (51). Preliminary characterization of controls has shown that organic compounds are unaltered in these terminal particles (49, 59), and a wealth of data on the composition of comet 81P/Wild 2 has already been obtained from them (47, 53). Unavoidably, a significant portion of material remains as debris along many of the Stardust impact tracks. With comprehensive preliminary control experiments, however, it may be possible to glean some information from this shed material as well.

Fullerene Detection with Laser Desorption Mass Spectrometry. Introduction. Laser desorption mass spectrometry (LDMS), a one-step technique, can be a particularly valuable tool for detecting fullerenes, which have been reported in various extraterrestrial samples (60, 61). Toluene extracts of acid-digested Allende meteorite powder have revealed the presence of several small fullerenes up to C_{84} (62). Use of high-boiling solvents, however, reveals fullerene envelopes up to C_{250} in Allende (63), Murchison (64), and Tagish Lake meteorite powders (61). Results of fullerene detection in exogenous materials are still considered controversial, because numerous attempts to corroborate fullerene detection in meteorite extracts have been unsuccessful regardless of whether LDMS (65) or other detection techniques were used (66). Formation conditions of extracted fullerenes are also still under debate. Reported smooth fullerene envelope distributions, as well as a lack of particularly stable fullerene structures, indicate that detected fullerenes have not yet reached thermodynamic equilibrium. This conclusion runs counter to the expectation that atmospheric entry heating and impact processing would result in a thermodynamic equilibrium distribution for extant fullerenes (67).

Despite the advantages of LDMS for fullerene detection, one of its major weaknesses is that these compounds can be generated, under certain conditions, by laser desorption during the analysis of carbonaceous materials. This effect depends mainly on laser energy and has been widely observed in various laser ablation studies (68, 69). Efforts have been made to control for this effect in meteorite extracts, where carbonaceous materials are reported to exhibit no high mass fullerenes, even at laser

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