Organic compound alteration during hypervelocity collection of carbonaceous materials in aerogel

M. K. SPENCER[1], S. J. CLEMETT[2], S. A. SANDFORD[3], D. S. McKAY[2], and R. N. ZARE[1]*

[1]Department of Chemistry, Stanford University, Stanford, California 94305, USA
[2]NASA Johnson Space Center, Houston, Texas 77058, USA
[3]Astrophysics Branch, NASA Ames Research Center, Moffett Field, California 94035, USA
*Corresponding author. E-mail: zare@stanford.edu

Abstract–The NASA Stardust mission brought to Earth micron-size particles from the coma of comet 81P/Wild 2 using aerogel, a porous silica material, as the capture medium. A major challenge in understanding the organic inventory of the returned comet dust is identifying, unambiguously, which organic molecules are indigenous to the cometary particles, which are produced from carbon contamination in the Stardust aerogel, and which are cometary organics that have been modified by heating during the particle capture process. Here it is shown that 1) alteration of cometary organic molecules along impact tracks in aerogel is highly dependent on the original particle morphology, and 2) organic molecules on test-shot terminal particles are mostly preserved. These conclusions are based on two-step laser mass spectrometry (L^2MS) examinations of test shots with organic-laden particles (both tracks in aerogel and the terminal particles themselves).

INTRODUCTION

Low-density aerogel, a transparent porous silica material, is uniquely suited for the capture of micron-size particles traveling at high velocities (Tsou et al. 1990; Barrett et al. 1992). Recent success of the NASA Stardust mission emphasizes the appeal of aerogel as a capture medium as well as the need for a more thorough understanding of the physical and chemical processes that occur during capture (Brownlee et al. 2006). Specifically, inherent residual organic impurities in Stardust aerogel cause concern, especially as they may be thermally altered in regions close to a captured particle and thus could be erroneously attributed to it (Spencer and Zare 2007). The possibility also exists that particle capture in aerogel can alter organics contained within the impactor, obscuring the original composition. Identifying how organic molecules can be modified by heating during the capture process presents a major challenge in interpreting cometary organic compounds returned by the Stardust mission.

Hypervelocity capture of a particle in aerogel causes thermal pulse generation, owing to non-adiabatic propagation of the impact shock. This extreme stress has the potential to alter organic compounds indigenous to the impacting particle. Hypervelocity impact in the velocity regime relevant to Stardust cometary particle capture (6.1 km/s in vacuum) deposits energy into aerogel faster than it can be dissipated at the impact site, resulting in steep temperature gradients (Burchell et al. 1999). For example, capture of a 10 μm particle at a typical interplanetary dust particle (IDP) density of 1.1 g/cc (Joswiak et al. 2000) traveling at 6.1 km/s releases approximately 10.7 μJ of kinetic energy along the length of its track in aerogel. For comparison, a single phenanthrene molecule would release 34.4 eV (5.5×10^{-18} J) of kinetic energy in such an impact, which is far above the C = C bond energy of approximately 6 eV. The rapidity of the energy release produces extreme thermal gradients along the track wall resulting in particle ablation as well as vaporization and melting of aerogel in the impact vicinity. The extent of particle ablation varies depending on many factors, including particle size, composition, and the density of aerogel used, typically reducing particles to 20–95% of their original size (Burchell et al. 1998; Hörz et al. 1998). Materials that have been investigated include a variety of mineral grains and glasses, meteoritic samples, coal, pure organic materials, and even cocoa powder. The impact process has also been modeled theoretically (see Anderson and Ahrens [1994] for a general model for capture of hypervelocity particles in low-porosity foams and Dominguez et al. [2004] for a recent model of capture specific to aerogel). Such models describe the general deceleration process but fail to describe fully the apparent stochastic survival and destruction of impactor

components in the case of complex aggregate impactors like those derived from comet 81P/Wild 2.

In test shots, submicrometer-size particle residue can be found embedded in molten aerogel along the track walls, particularly in the entry region; similar regions of mixed particle and molten aerogel were seen in the samples returned from comet 81P/Wild 2 (Zolensky et al. 2006). Some portion of the particle material embedded in molten aerogel would have been "cooked", owing to the poor heat conductivity of aerogel (<10 mW/m·K in vacuum; Kistler [1931]). Thermal processing of organic compounds in this embedded particle residue along impact tracks may be significant because of this heating in the vicinity of the particle impact track.

To complicate further this issue, it is clear that the extent of abrasion and heating in these impactor components will be sensitive to details in the composition and structure of each individual impactor. For example, whereas the fine-grained materials in 81P/Wild 2 particles appear to be particularly susceptible to abrasion and heating in the top portions of tracks, such materials can survive to the bottom of a track virtually unchanged if they are protected by larger surrounding grains or the accumulation of a molten silica "cap." An example of this can be found in the "Febo" terminal particle (track 57, 8 µm diameter), which contains a large iron-sulfide grain that apparently protected a clump of adhering fine-grained, organic-containing material by leading the way through the aerogel (Matrajt et al. 2008). Thus, the degree of thermal processing likely has a stochastic component within individual tracks, at least for complex aggregate impactors.

Significant differences in organic molecular identity and abundance have been observed along tracks produced by captured comet 81P/Wild 2 particles, even along impact tracks that lie in close proximity to each other on the same aerogel tile (Sandford et al. 2006). It is still unclear whether these differences belong to the impacting particle or if they are a result of variable organic alterations during impact. Most likely, a combination of these two effects is occurring during hypervelocity particle collection in Stardust aerogel. The uniform impact speed (6.12 km/s) and entry angle of these particles suggest that any differences are introduced by the impactor. Initial data from the Stardust preliminary examination period has revealed that captured 81P/Wild 2 particles are very heterogeneous in morphology and mineral composition. This is evidenced by the significant variety of minerals and fine-grained chondritic composition material detected in the particles as well as the many different track shapes produced by particles impacting at the same velocity and angle (Brownlee et al. 2006; Flynn et al. 2006; McKeegan et al. 2006; Sandford et al. 2006; Zolensky et al. 2006). A variety of different impactors have been used previously as test materials for hypervelocity impact shots into Stardust-type aerogel; however, it is very difficult to mimic the fine-grained aggregate structures of anhydrous interplanetary dust particles (IDP)s and cometary particles at these speeds (Hörz et al. 1998). At this time, the extent to which such differences in particle morphology might affect the degree of organic compound alteration in indigenous cometary organic matter on hypervelocity impact with aerogel remains unknown.

Different impactors have been employed in this study to probe the effect of particle morphology on organic compound alteration in the impacting particle. Two-step laser mass spectrometry (L^2MS) was used to determine the distribution of polycyclic aromatic hydrocarbons (PAHs) along test-shot impact tracks in aerogel and on selected terminal particles. This study focused specifically on the analysis of aromatic hydrocarbons owing to the sensitivity and specificity of L^2MS for this class of compounds. These compounds are astrophysically relevant and are expected to represent at least a component of the collected cometary organic matter. Results from these experiments can potentially be extended to act as a good indicator for overall organic alteration on hypervelocity particle impact into Stardust aerogel.

EXPERIMENTAL

Two-step laser-desorption laser-ionization mass spectrometry (L^2MS) is a highly sensitive analytical technique capable of resolving the spatial distribution (at 10 or 40 µm spatial resolution at the sample surface, depending on the desorption laser utilized) of organic molecules on complex surfaces and particulates (Clemett et al. 1993, 1994; Thomas et al. 1995; McKay et al. 1996). Two different L^2MS instruments were used in this study, enabling both redundancy and increased sample analysis ability. These were the µ-L^2MS instrument in the Stanford University laboratory of Richard Zare and the *ultra*-L^2MS instrument in the NASA Johnson Space Center laboratory of Simon Clemett. In collaboration with the Stardust Organics Preliminary Examination Team (PET), a number of µ- and *ultra*-L^2MS analyses have been performed on contamination control samples (e.g., Stardust aerogel flight spares and aerogel witness coupon), giving us a thorough understanding of aromatic organic contaminants innate to Stardust aerogel (Spencer and Zare 2006). L^2MS, being exceptionally suited for the analysis of particles in an aerogel substrate, has the ability to create spatially resolved intensity profiles of aromatic compounds along particle impact tracks in aerogel.

A detailed description of the L^2MS technique has been presented elsewhere (Kovalenko et al. 1992; Clemett and Zare 1997), and is summarized here. Constituent neutral molecules of the sample are first desorbed with a pulsed infrared laser beam focused to a spot, adjustable to 10 or 40 µm in diameter for the µ-L^2MS setup, using Er:YAG (2.94 µm) and CO_2 (10.6 µm) lasers, respectively. Beam spot size for the *ultra*-L^2MS system is about 10 µm, which is achieved using a line-tuned CO_2 laser with a spatial filter. A selected class of molecules in the desorbed plume is

subsequently preferentially ionized by a single-frequency pulsed ultraviolet (UV) laser (Nd:YAG; 4th harmonic; 266 nm) beam that passes through the plume. The resultant ions are then extracted, injected into a reflectron time-of-flight mass spectrometer, and analyzed according to mass. A complete mass spectrum is obtained for each shot. Soft, species-selective ionization, that is, ionization of molecules containing a characteristic functional group with minimal accompanying fragmentation, is achieved through (1 + 1) resonance enhanced multiphoton ionization (REMPI) (Winograd et al. 1982; Shibanov 1985). The L^2MS system is designed to ionize molecules containing π-conjugated bonds, such as the phenyl moiety, and provides a selective ionization window for PAHs.

Key attributes of L^2MS instruments are (i) high spatial resolution and mapping capabilities allowing complete mass spectral analysis of regions as small as 10 μm in diameter; (ii) desorption with little decomposition and ionization, resulting in spectra consisting of primarily parent ions; (iii) selective ionization of molecules containing π-conjugated bonds, which simplifies the spectra of complex mixtures; (iv) high sensitivity, allowing detection of PAHs at the subattomole level; and (v) in situ analysis, requiring little sample handling and minimizing the possibility of contamination and chemical alteration. This technique enables the sampling of material in surface layers of a sample, with a sampling depth profile that varies based on the optical transparency of a material at the desorption laser wavelength used. Sampling depth is likely in the several micrometer range for experiments reported here.

Relevant previous work has included examinations of organic synthesis from carbon impurities in Stardust aerogel (Spencer and Zare 2007; Spencer et al. 2008), which serve as "blank" studies for the experiments reported here. In this previous work we found that a low-mass envelope of aromatic compounds can be released/synthesized from Stardust aerogel during various hypervelocity particle impact simulations. These impurities could be easily misidentified as cometary, when in fact they are artifacts of the collection process. Aromatic compounds detected on the impact tracks of samples analyzed in the present study were compared with these known artifacts to validate their source (i.e., either as an artifact or as coming from the captured particle).

In the present examination we performed several experiments designed to assess the potential modification of organic compounds from their original form in the impacting particle. Several types of impactors were utilized in this study, including Allende meteorite, Illinois coal, and compressed cocoa powder. Preparation and hypervelocity test shots of these materials were performed by Andrew Westphal and Fred Hörz at the NASA Ames Research Center and NASA Johnson Space Center (JSC) two-stage light-gas gun facilities, respectively (Hörz et al. 1998). Allende meteorite and Illinois coal particle sizes were approximately 50 μm in diameter. Impact speed for all shots was 6 km/s, which is

comparable to the speed at which 81P/Wild 2 particles were collected in aerogel by the Stardust spacecraft. Stardust flight spare aerogel, which is representative of the actual aerogel material that was installed on the Stardust spacecraft, was used in these studies to mimic actual collection of Stardust 81P/Wild 2 particles as closely as possible. Allende meteorite and Illinois coal impact tracks were removed from the aerogel cells by Andrew Westphal and Christopher Snead at the UC-Berkeley Space Sciences Laboratory (SSL) laboratory using their borosilicate glass needle micro-extraction technique, otherwise known as the "keystone" technique (Westphal et al. 2004). Removed tracks were then split in half lengthwise to expose their inner surfaces for analysis. Cocoa powder tracks were obtained from Michael Zolensky (NASA JSC) and dissected by Clemett using a stainless steel type 11 surgical scalpel. Terminal Allende meteorite particles were removed from several tracks by Clemett using a surgical scalpel, as above, and were then pressed into Au foil for subsequent *ultra*-L^2MS analysis.

RESULTS

Allende Meteorite Particles

Using L^2MS, it is straightforward to correlate PAHs with a track in aerogel if they were introduced during impact. The difficulty lies in determining whether these compounds were synthesized during the impact process from material indigenous to the aerogel collector medium, deposited by a fragmenting, organics-laden impactor, or modified from their original form in the impactor. In a previous study we examined the effect of a non-organic (i.e., "blank") particle impact into aerogel (Spencer et al. 2008). For the present study, a series of organics-laden particles were used as hypervelocity impactors into aerogel to reveal the effects, if any, of particle structure and composition (i.e., morphology) on post-impact organic signatures. These included particles of the Allende meteorite (CV3), Illinois coal, and compressed cocoa powder. Impact track, terminal particle (when possible), and standard substrate PAH distributions were compared to determine the potential for organic alteration during hypervelocity particle capture in aerogel.

The Allende meteorite (CV3) is known to contain a number of complex organic compounds including an extended envelope of low-mass PAHs (Zenobi et al. 1989; Elsila et al. 2005). Several Allende matrix particles were shot into Stardust flight spare aerogel and their hypervelocity impact tracks were subsequently dissected lengthwise for spatially resolved surface analyses along their length. Shots were at approximately 6 km/s to provide a realistic comparison to the shock effects experienced by Stardust particles.

Examination with μ-L^2MS along the bulbous entry portion of Allende particle tracks revealed aromatic organic compounds that are somewhat modified in comparison with
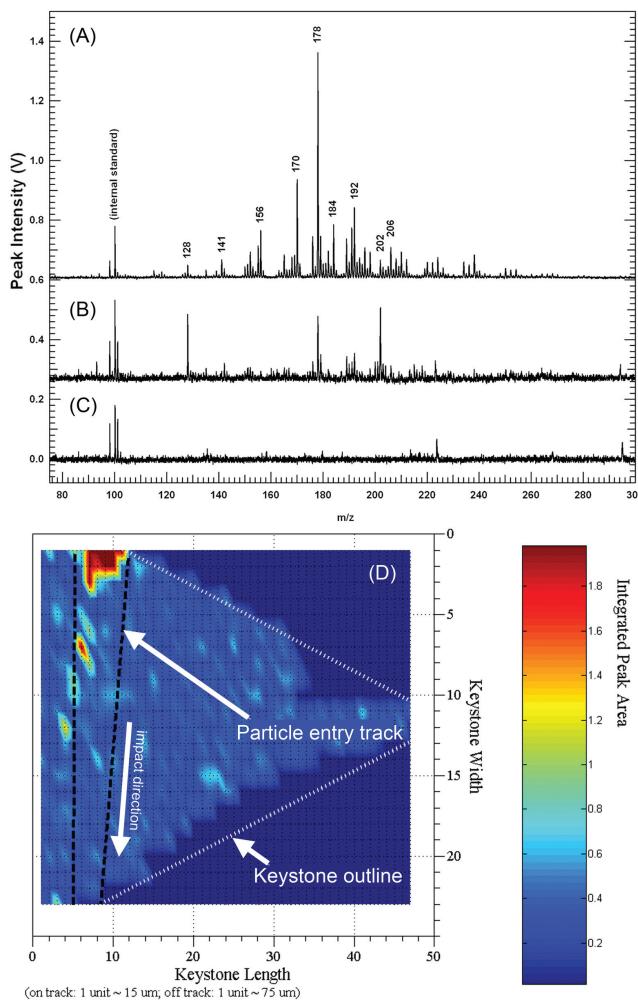
Fig. 1. μ-L²MS mass spectra. a) Mass spectrum consisting of 50 averaged mass spectra taken on unshot bulk Allende (CV3) meteorite. b) Mass spectrum taken with a single laser shot on the bulb portion of keystone dissected Allende particle impact track in aerogel. This spectrum is representative of the "hot spots" as indicated in (d). c) Mass spectrum taken with a single laser shot approximately 5 track widths away from the impact track. (b) and (c) are scaled up by a factor of 2 for ease of comparison. Peaks centered at 100 amu correspond to D_8-toluene, an internal calibration standard. d) Intensity map of phenanthrene from a split Allende particle impact track in aerogel. The impact track was oversampled to enable confidence in detected signals when characterizing ablated particle material. Phenanthrene abundance is representative of Allende meteorite PAHs, as shown in (b).

the unshot bulk Allende (CV3) aromatic signature (Fig. 1). Prominent PAHs in the μ-L²MS mass spectrum of unshot bulk Allende include mass 128 (naphthalene) and its alkylated derivatives (i.e., $C_{10}H_7$-$(CH_2)_n$-H; n = 1,2,3,4): 156 (n = 1), 170 (n = 2), 184 (n = 3), and 198 amu (n = 4). Mass 178 (phenanthrene) is the most dominant PAH and its alkylated components can be observed as well at: 192 (n = 1), 206 (n = 2), and 220 amu (n = 3). Mass 202 (pyrene) is also present in lower concentrations (Fig. 1A). These compounds are higher in mass

than those detected during blank impact test shots into Stardust-type aerogel (Spencer and Zare 2007; Spencer et al. 2008), indicating that they were introduced by the captured particle itself and are not artifacts of the collection process. While these PAHs can be observed along the impact track in aerogel, they differ greatly in relative abundance compared with unshot bulk Allende. In comparison with mass 178 (phenanthrene), mass 128 (naphthalene) and 202 (pyrene) are much greater in intensity than in unshot Allende. Alkylated derivatives of mass 128 (naphthalene) are also strikingly low in relative abundance (Fig. 1b). The absence of some PAHs in the aerogel track, which are present in unshot Allende (CV3), could be caused by several factors, including that the PAHs were (i) destroyed by pyrolysis during impact shock heating, (ii) thermally modified during capture into a compound not detectable by this technique (i.e., a non-aromatic compound), or (iii) volatilized and redeposited into the surrounding aerogel matrix at local concentrations lower than the detection limits of μ-L²MS.

Because the extent to which one or more of these processes might occur would differ for different PAHs this could result in fractionation of the original distribution of PAH components.

Compounds observed in Allende particle track mass spectra, i.e., from material distributed along the inner surfaces of tracks, are distinguishable from innate aerogel components that appear in μ-L²MS as shown in Figs. 1b and 1c. Aerogel background spectra were taken more than 5 track widths away from the impact track to avoid sampling of submicron-size Allende grains and volatiles surrounding the track that may have been redistributed during impact. Very little signal was found from organic compounds more than 500 μm down the impact track in both μ- and *ultra*-L²MS analyses (Fig. 1d). Several processes can cause this behavior, including: (i) maximum particle ablation at the initial impact site, as well as (ii) the rapid accretion of a "protective" compressed silica overshell, which is known to form on the leading edge of particles impacting at high velocity into aerogel, preventing further particle ablation (Tsou 1995; Brownlee et al. 2006).

Ultra-L²MS was used to investigate multiple Allende terminal particles that were removed from hypervelocity impacts in aerogel. Shots were also performed at approximately 6 km/s to provide a realistic comparison to Stardust particle capture. PAH distributions broadly similar to unshot bulk Allende were retained in these particles. While the overall abundance was reduced, PAH mass distribution and ratios were mostly preserved (Fig. 2). Hypervelocity impact produces a strong impact shock of several GPa; yet, the PAHs in the Allende matrix were able to survive this initial shock and the resulting thermal pulse. These results are in stark contrast to the distorted PAH envelope found diffusely distributed along Allende particle impact track walls.

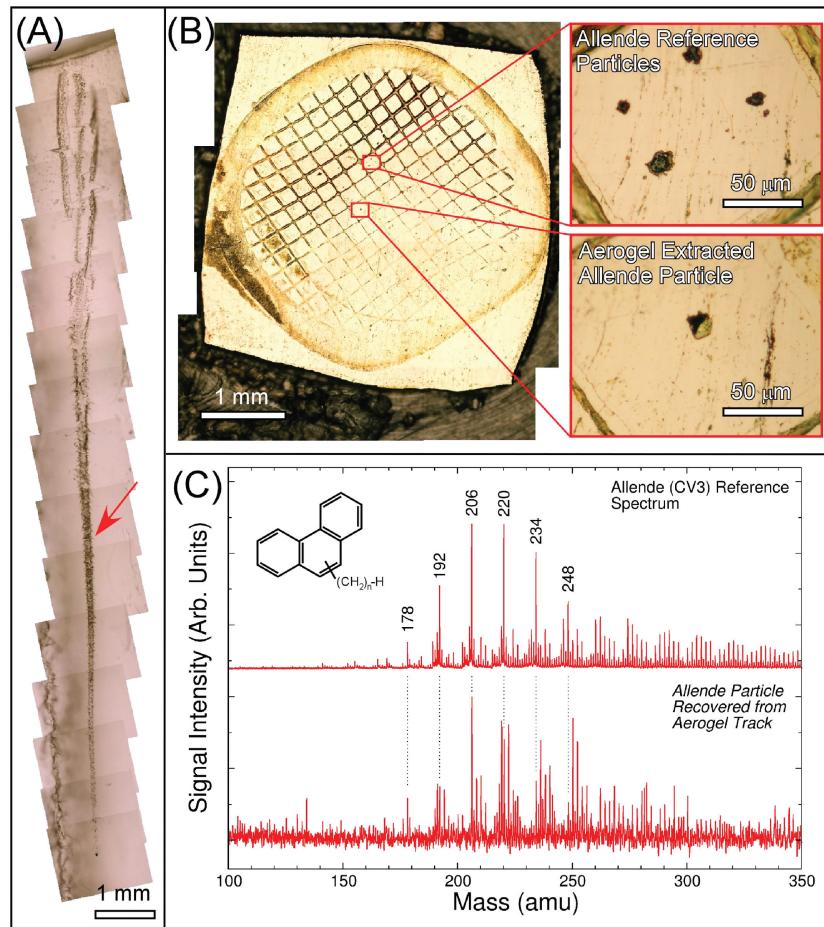It should be noted that mass spectra taken with *ultra*-

Fig. 2. a) Optical mosaic of a track made by the hypervelocity impact of a micron-size Allende particle into a low-density silica aerogel. A single sub-fragment (Red Arrow) was extracted and pressed into a small section of Au Foil (b), along with several pristine Allende reference particles. c) *ultra*-L^{2}MS spectra of the extracted sub-fragment and reference particle spectra.

L^{2}MS differ slightly from those taken using μ-L^{2}MS, owing to their different detection sensitivities for different PAHs. This is based on differing instrumental parameters and desorption laser wavelengths. This results in a PAH envelope centered at 178 amu for μL^{2}MS and an envelope centered at 220 amu for *ultra*-L^{2}MS when considering unshot bulk Allende meteorite (see Fig. 1a and Fig. 2c). Thus, the mass spectra from these two techniques should only be compared with others taken with the same instrument.

Several models indicate that an impacting particle experiences significantly lower temperatures than the surrounding shocked aerogel (Stratton and Szydlik 1997; Dominguez et al. 2004), suggesting that organics contained within the impactor would incur less thermal alteration than those along the track. From modeling studies it is thought that material deposited along the impact track will encounter temperatures of several thousand degrees Kelvin; however, the terminal particle may be heated only to several hundred Kelvin (Stratton and Szydlik 1997). Coupled Thermodynamic and Hydrodynamic code (CTH), developed by Sandia National Laboratories, has been used to model this highly

heterogeneous distribution of temperature along hypervelocity particle impacts in low-density aerogel (Stratton and Szydlik 1997). Using Carnelian (quartz) particles of 0.92 mm impacting at 3.58 km/s into 64.8 mg/cm^3 silica aerogel, this model shows that aerogel in front of and surrounding the impactor reaches greater than 2000 K and up to 6000 K immediately in front of the decelerating particle during impact. The particle, however, remains below 600 K.

This model, developed by Stratton and Szydlik, uses a lower impact velocity and higher density aerogel in comparison with cometary particle capture on the Stardust spacecraft (Stratton and Szydlik 1997). Other models suggest that low density aerogels generate higher temperatures than their higher density counterparts during hypervelocity particle capture (Dominguez et al. 2004). This is evidence that our test shots, which used a slightly lower density aerogel in comparison with the Stratton and Szydlik model, would have potentially experienced greater heating than that found in this model. However, the lower impact velocity that was used in their model would have had a separate effect on the amount of heating present, most likely yielding a lower amount of
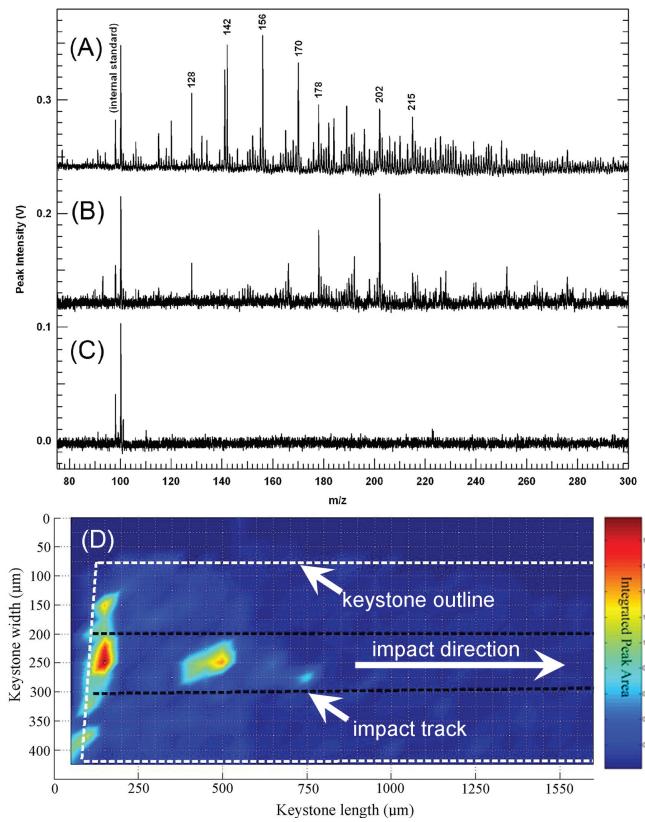
Fig. 3. The μ-L^{2}MS mass spectra taken in the bulb portion of a split Illinois coal particle impact track in aerogel compared to bulk unshot Illinois coal. a) Mass spectrum consisting of 50 averaged mass spectra taken on unshot bulk Illinois coal. b) Single mass spectrum taken on the Illinois coal particle impact track in aerogel. c) Single mass spectrum taken on aerogel approximately 5 track widths away from the impact track. The plot in (a) is scaled up by a factor of 2 for ease of comparison. Peaks centered at 100 amu correspond to D$_8$-toluene, an internal calibration standard. d) Spatial map constructed using the integrated peak area of mass 178 (phenanthrene) from a single μL^{2}MS mass spectra taken over the keystone surface. Rough outlines of the particle entry track and aerogel keystone edges are shown as dashed lines.

heating in comparison with our test shots. It is impossible at this time to determine the extent of these effects as they have opposite influences on the resulting temperatures produced along the aerogel impact track. We expect that, while these conditions do not specifically match the Stardust mission parameters, results presented in this work support the general idea that terminal particles remain cooler than materials deposited near the entry-portion of the impact track. This is consistent with both μ-L^{2}MS and *ultra*-L^{2}MS results presented here.

Illinois Coal Particles

Illinois coal contains a range of 1- to 6-ring PAHs that are similar to Allende (CV3) although the relative abundances vary (Figs. 3a and 1a, respectively). Comparison of these two

particle types enables determination of the extent to which similar materials can be distinguished from each other by analyzing organic compounds along their hypervelocity impact tracks in aerogel. Main peaks in the μ-L^{2}MS mass spectrum of unshot Illinois coal include mass 128 (naphthalene) and its alkylated derivatives out to the addition of 5 CH$_2$ units, with mass 128 + 2 CH$_2$ being the most abundant. Mass 178 (phenanthrene) and its alkylated derivatives up to the addition of 3 CH$_2$ units are also observed. Mass 202 (pyrene) is also observed and is comparable in intensity to mass 178 (phenanthrene) (Fig. 3a). μ-L^{2}MS analysis of dissected Illinois coal particle tracks revealed a PAH distribution that is modified in comparison (Fig. 3B). PAHs found along the walls of the impact tracks are comparable to those found for the Allende meteorite impact track study, although noticeable differences can be observed. Again, alkylated components of mass 128 (naphthalene) are significantly depleted along the track, despite their prominence in the original Illinois coal particle. As was the case for the shot Allende meteorite particles, PAHs localized on the impact track are distinguishable from aerogel components seen far from the track, as shown in Figs. 3b and 3c. Also, these compounds are higher in mass than those detected during blank impact test shots into Stardust-type aerogel (Spencer and Zare 2007; Spencer et al. 2008), indicating that they were introduced by the captured Illinois coal particle itself and are not artifacts of the collection process. Spatially resolved analysis of the PAH intensity distribution along Illinois coal impact tracks in aerogel reveals the deposition of organic material only in the first 500 μm of the track (Fig. 3d). This spatial distribution is very similar to that found for Allende meteorite particles. No *ultra*-L^{2}MS analysis of Illinois coal terminal particles has been performed at this time owing to the availability of samples.

Compressed Cocoa Powder Impactors

As an approximate analog to aggregate IDP-type particles, cocoa powder was compressed with soda-lime glass spheres and used as an impactor into 0.02 g/cm^3 aerogel [Figs. 4a and 4b; (Hörz et al. 1998)]. Unshot cocoa powder gives a very simple L^{2}MS mass spectrum, as shown in Fig. 4c. *Ultra*-L^{2}MS analysis of compressed cocoa powder/soda-lime glass sphere impact tracks found no aromatic compounds associated with the terminal soda-lime glass spheres. All organic matter was volatilized along the bulb-shaped track and was found more than 3 track widths into the surrounding aerogel matrix. Prominent peaks in the mass spectrum of cocoa powder, those most easily tracked with the *ultra*-L^{2}MS system, are the two methylxanthines 3,7,-dihydro-1,3-dimethyl-1H-purine-2,6-dione (theobromine) and 3,7,-dihydro-1,3,7-timethyl-1H-purine-2,6-dione (caffeine) at masses of 180 and 194 amu, respectively. Mass spectra of unshot cocoa powder show these as well-defined, prominent
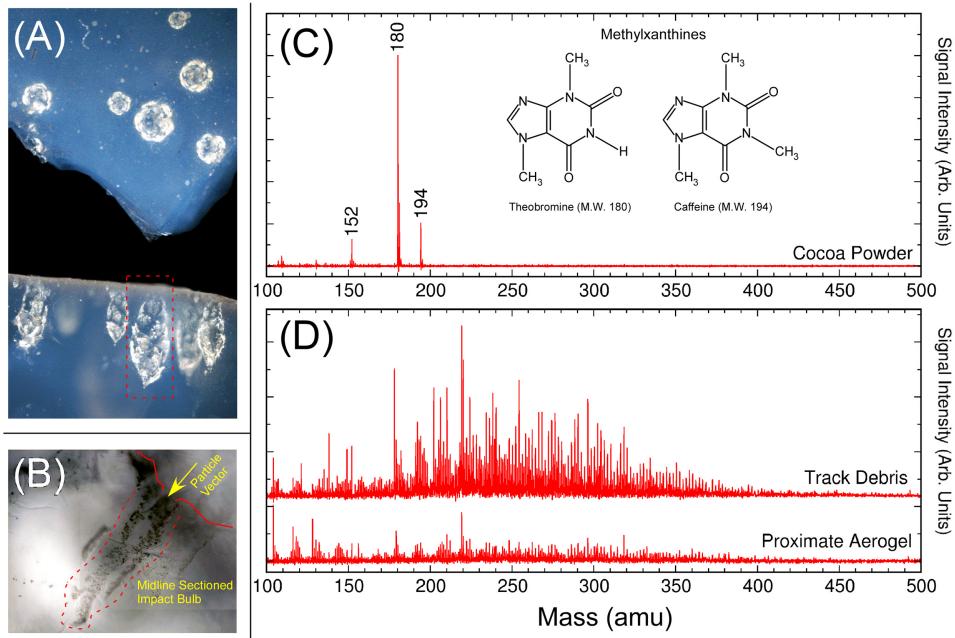
Fig. 4. a) Optical images of aerogel block, from above and from the side, after a shot with soda-lime glass beads coated in cocoa powder. The track with the red dashed rectangle was selected for analysis by *ultra*-L2MS. b) Optical image of one side of the track bulb after midline sectioning along the track axis using a #11 surgical steel scalpel. c) *ultra*-L^{2}MS spectrum of unshot cocoa powder showing the characteristic peaks of the aromatic methylxanthines theobromine and caffeine. d) *ultra*-L^{2}MS spectrum of fine grained debris dispersed along the bulbous track (upper trace) and volatilized material approximately 1 track width perpendicular to the long axis of the track. (Note track sectioned from top-to-bottom, not side-to-side, to avoid potential for dispersion of organic material by the sectioning procedure.

peaks (Fig. 4c). However, the track deposited residues show no evidence of these main cocoa powder-associated PAHs. Instead, a diverse mixture of species too varied to differentiate were detected, including masses ranging from below 100 amu to beyond 400 amu (i.e., synthesis of organics with mass both below and above that of the two methylxanthines originally present; Fig. 4d). This implies significant thermal alteration in the bulbous upper track region after impact into aerogel, much more-so than organic compounds associated with Allende meteorite and Illinois coal particles, as discussed previously.

DISCUSSION

Results from the analysis of Allende and Illinois coal particle test shots into silica aerogel demonstrate that organic components embedded in the aerogel impact track wall do not faithfully represent the organic composition of an impactor. Alkylated naphthalene and phenanthrene components are selectively lost in both cases, skewing the original mass envelopes. Also, lower mass PAHs are reduced in relative intensity in comparison with those of higher mass. This supports the hypothesis that selective volatilization of low-mass PAHs can occur during particle capture. Spatial analysis with µL^{2}MS shows a preferential deposition of organic material in the first 500 µm of Allende and Illinois coal particle impact tracks. Unfortunately, Allende meteorite and Illinois coal particles do not precisely mimic the structure or

composition of the cometary particles that struck the Stardust collector. Cometary particles are thought to have a low-density aggregate structure similar to that found in stratospherically collected particles. Returned Stardust samples are largely consistent with this view (Brownlee et al. 2006). Laboratory simulation of an aggregate impact is limited by the forces necessary to accelerate micron-size particles to velocities on the order of 6 km/s. These aggregated particles do not typically survive accelerations of this magnitude intact.

From the experimental work presented here we suggest that great caution needs to be taken in connecting the organic material present in aerogel impact tracks to pristine cometary organic compounds. Shock heating associated with hypervelocity impact will likely alter or cause the volatilization of organic components in impacting particles. The extent to which this occurs will vary from particle to particle, as evidenced by the disparity in organic alteration observed for different particles in this study, and is particularly apparent in the top (approximately 500 µm) of the impact track. Alteration of impacting particles has been reported on previously for various test shots into aerogel (Hörz et al. 1998; Brownlee et al. 2006; Sandford et al. 2006). It is likely that these processes are occurring to varying degrees and are the result of impact thermal alteration or volatilization. Extension of PAH masses both below and above the mass of innate cocoa powder xanthines indicates that bond-breaking and bond-forming reactions are

simultaneously occurring during the impact process. This is in contrast to the preservation of prominent PAHs along Allende meteorite impact tracks. These laboratory simulations indicate that the retention of aromatic compound signatures is dependent on particle structure and makeup (i.e., morphology and composition) and can vary from track to track, even when parameters other than morphology are held constant.

Recently, it has been shown that organic molecules can be associated with 81P/Wild 2 cometary particles and their impact tracks in Stardust samples (Sandford et al. 2006). Track-to-track variation in organic compound abundance observed in 81P/Wild 2 impact tracks is indicative of the heterogeneity of captured cometary particles. Morphological differences in these highly heterogeneous impactors have the potential to bring about variable degrees of organic compound alteration along their impact tracks, as shown in this study.

The hypervelocity impact test shot studies detailed above indicate that, depending on particle morphology, the detected aromatic hydrocarbons could be similar to those in the impactor. One possibility for the source of compounds discovered along the 81P/Wild 2 particle impact track reported on previously [C2115,26,22; (Sandford et al. 2006)] is macromolecular kerogen material, similar to that found in carbonaceous chondrite meteorites. It has been shown that the types of compounds observed, small 1- to 3-cycle alkylated aromatics, can be generated by anhydrous or hydrous pyrolysis of meteoritic macromolecular material (Bandurski and Nagy 1976; Sephton et al. 2000). Most of the organic material in carbonaceous chondrites exists in this highly cross-linked aromatic material. Detection of these kerogen pyrolysis-like products in the interior of a cometary impact track suggests that the original particle may have contained a macromolecular organic component that pyrolyzed during impact with aerogel. Most models of particle impact in aerogel, although still in their early stages, indicate that temperatures generated during micron-sized particle impact in aerogel are high enough to cause pyrolysis of kerogen (Stratton and Szydlik 1997). The heating time scale, however, may be too brief to allow pyrolysis products to diffuse away from one another before recondensing. It has also been shown that these types of low-mass aromatic compounds can be generated from carbon impurities in Stardust aerogel during hypervelocity particle impact (Spencer and Zare 2007; Spencer et al. 2008). Thus, caution must be exercised in interpreting the origin of organic compounds detected along impact tracks in Stardust aerogel.

Laboratory impact simulations detailed in this paper have shown that aromatic organic compounds can be deposited and thermally processed during hypervelocity capture with aerogel. From these and previous studies (Spencer and Zare 2007; Spencer et al. 2008) we conclude that we cannot definitively determine the original makeup of aromatic compounds found along one hypervelocity 81P/Wild 2

particle impact track (Track C2115,26,22) in aerogel, which was analyzed previously in this laboratory and reported as either cometary or contaminants in the literature (Sandford et al. 2006). Retention of organic signatures on the terminal particle, as shown for the Allende meteorite impact here and in previous studies, provides a promising venue for the determination of organic compounds introduced by an impacting particle (Burchell et al. 2004; Matrajt et al. 2008). Using Raman spectroscopy it has been shown that poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) terminal particle composition is unaltered after acceleration into aerogel at approximately 5 km/s (Burchell et al. 2004). This research was focused on the analysis of terminal particles, which are known to experience significantly lower temperatures than ablated particle material that is left along the impact track in aerogel, as previously discussed. For this reason, their survival should not be correlated to the survival of shed material along the impact track. This previous PMMA/PEMA work and the results presented here highlight the importance of analyzing both impact tracks and terminal particles to determine the origin of any organic material along hypervelocity impact tracks in Stardust aerogel.

SUMMARY

Laboratory impact simulations reported here and in the literature (Spencer and Zare 2007; Spencer et al. 2008) show that, during the particle capture event, chemical processes that might alter, destroy, or volatilize indigenous particle PAHs in ablated material present a significant challenge for highly sensitive analyses such as laser mass spectrometry. Organic compounds indigenous to an impactor are found to change in relative abundance and identity, when detected in ablated material, masking the true chemical composition of the impactor. Compounds on the surviving terminal particle are found to retain their original form.

Correct interpretation of organic signatures detected along hypervelocity particle impact tracks in aerogel is a difficult challenge that must be thoroughly addressed for each analytical technique applied to the analysis of Stardust samples. For direct analysis techniques, such as L^2MS, comparison of impact track aromatic organic signatures with those from the terminal particle is the most informative way to determine the degree of chemical alteration induced by impact and to characterize innate aromatic hydrocarbons in a captured particle. Chemical information relevant to the original particle may be retrievable via the analysis of the material that it sheds while tunneling through aerogel. However, the processing of organic compounds in this material may be extreme, as shown in this study. Analysis of this material is important to gain an unbiased view of the original 81P/Wild 2 particle composition. This work addresses the significance of chemical processes that might occur during the capture of a hypervelocity particle in aerogel

and directly impacts the analysis of all organic compounds in the collected 81P/Wild 2 cometary particles.

REFERENCES

Anderson W. W. and Ahrens T. J. 1994. Physics of interplanetary dust capture via impact into organic polymer foams. *Journal of Geophysical Research* 99(E1):2063–2071.

Bandurski E. L. and Nagy B. 1976. The polymer-like organic material in the Orgueil meteorite. *Geochimica et Cosmochimica Acta* 40:1397–1406.

Barrett R. A., Zolensky M. E., Hörz F., Lindstrom D. J., and Gibson E. K. 1992. Suitability of silica aerogel as a capture medium for interplanetary dust. Proceedings, 22nd Lunar and Planetary Science Conference. pp. 203–212.

Brownlee D., Tsou P., Aléon J., Alexander C. M. O'D., Araki T., Bajt S., Baratta G. A., Bastien R., Bland P., Bleuet P., Borg J., Bradley J. P., Brearley A., Brenker F., Brennan S., Bridges J. C., Browning N., Brucato J. R., Brucato H., Bullock E., Burchell M. J., Busemann H., Butterworth A., Chaussidon M., Cheuvront A., Chi M., Cintala M. J., Clark B. C., Clemett S. J., Cody G., Colangeli L., Cooper G., Cordier P. G., Daghlian C., Dai Z., D'Hendecourt L., Djouadi Z., Dominguez G., Duxbury T., Dworkin J. P., Ebel D., Economou T. E., Fairey S. A. J., Fallon S., Ferrini G., Ferroir T., Fleckenstein H., Floss C., Flynn G., Franchi I. A., Fries M., Gainsforth Z., Gallien J.-P., Genge M., Gilles M. K., Gillet P., Gilmour J., Glavin D. P., Gounelle M., Grady M. M., Graham G. A., Grant P. G., Green S. F., Grossemy F., Grossman L., Grossman J., Guan Y., Hagiya K., Harvey R., Heck P., Herzog G. F., Hoppe P., Hörz F., Huth J., Hutcheon I. D., Ishii H., Ito M., Jacob D., Jacobsen C., Jacobsen S., Joswiak D., Kearsley A. T., Keller L., Khodja H., Kilcoyne A. L. D., Kissel J., Krot A., Langenhorst F., Lanzirotti A., Le L., Leshin L., Leitner J., Lemelle L., Leroux H., Liu M.-C., Luening K., Lyon I., MacPherson G., Marcus M. A., Marhas K., Matrajt G., Meibom A., Mennella V., Messenger K., Mikouchi T., Mostefaoui S., Nakamura T., Nakano T., Newville M., Nittler L. R., Ohnishi I., Ohsumi K., Okudaira K., Papanastassiou D. A., Palma R., Palumbo M. O., Pepin R. E., Perkins D., Perronnet M., Pianetta P., Rao W., Rietmeijer F., Robert F., Rost D., Rotundi A., Ryan R., Sandford S. A., Schwandt C. S., See T. H., Schlutter D., Sheffield-Parker J. A., Simionovici S., Sitnitsky S. I., Snead C. J., Spencer M. K., Stadermann F. J., Steele A., Stephan T., Stroud R., Susini J., Sutton S. R., Taheri M., Taylor S., Teslich N., Tomeoka K., Tomioka N., Toppani A., Trigo-Rodríguez J. M., Troadec D., Tsuchiyama A., Tuzolino A. J., Tyliszczak T., Uesugi K., Velbel M., Vellenga J., Vicenzi E., Vincze L., Warren J., Weber I., Weisberg M., Westphal A. J., Wirick S., Wooden D., Wopenka B., Wozniakiewicz P. A., Wright I., Yabuta H., Yano H., Young E. D., Zare R. N., Zega T., Ziegler K., Zimmerman L., Zinner E., and Zolensky M. 2006. Comet Wild 2 under a microscope. *Science* 314:1711−1716.

Burchell M. J., Cole M. J., McDonnell J. A. M., and Zarnecki J. C. 1999. Hypervelocity impact studies using the 2MV Van de Graaff accelerator and two-stage light gas gun of the University of Kent at Canterbury. *Measurement Science and Technology* 10:41–50.

Burchell M. J., Creighton J. A., and Kearsley A. T. 2004. Identification of organic particles via Raman techniques after capture in hypervelocity impacts on aerogel. *Journal of Raman Spectroscopy* 35:249–253.

Burchell M. J., Thomson R., and Yano H. 1998. Capture of hypervelocity particles in aerogel. *Planetary and Space Science* 47:189–204.

Clemett S. J., Maechling C. R., Zare R. N., Messenger S., Alexander C. M. O. O. D., Gao X., Swan P. D., and Walker R. M. 1994. Measurements of aromatic hydrocarbons in interstellar graphite grains: II. Molecular measurements (abstract). *Meteoritics* 29: 457–458.

Clemett S. J., Maechling C. R., Zare R. N., Swan P. D., and Walker R. M. 1993. Identification of complex aromatic molecules in individual interplanetary dust particles. *Science* 262:721–725.

Clemett S. J. and Zare R. N. 1997. Microprobe two-step laser mass spectrometry as an analytical tool for meteoritic samples. *In Molecules in astrophysics: Probes and processes*, edited by Dishoeck E. F., von. Leiden, The Netherlands: Kluwer Academic Publishers. pp. 305–320.

Dominguez G., Westphal A. J., Jones S. M., and Phillips M. L. F. 2004. Energy loss and impact cratering in aerogels: Theory and experiment. *Icarus*: 613–624.

Elsila J. E., De Leon N. P., Buseck P. R., and Zare R. N. 2005. Alkylation of polycyclic aromatic hydrocarbons in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 69:1349–1357.

Flynn G. J., Bleuet P., Borg J., Bradley J., Brenker F., Brennan S., Bridges J., Brownlee D. E., Bullock E., Clark B. C., Dai Z. R., Daghlian C., Djouadi Z., Fakra S., Ferroir T., Floss C., Franchi I., Gainsforth Z., Gallien J.-P., Gillet Ph., Grant P. G., Graham G. A., Green S., Grossemy F., Heck P., Herzog G. F., Hoppe P., Hörz F., Huth J., Ignatyev K., Ishii H., Joswiak D., Kearsley A. T., Khodja H., Lanzirotti A., Leitner J., Lemelle L., Leroux H., Luening K., MacPherson G., Marhas K., Marcus M., Matrajt G., Nakamura T., Nakano T., Newville M., Papanastassiou D., Pianetta P., Rao W., Rietmeijer F., Rost D., Schwandt C., See T., Sheffield-Parker J., Simionovici A., Sitnitsky I., Snead C., Stadermann F., Stephan T., Stroud R., Susini J., Suzuki Y., Sutton S., Taylor S. R., Teslich N., Troadec D., Tsou P., Tsuchiyama A., Uesugi K., Westphal A., Wozniakiewicz P., Vicenzi E., Vincze L., and Zolensky M. E. 2006. Elemental compositions of comet 81P/Wild 2 samples collected by Stardust. *Science* 314:1731−1735.

Hörz F., Cintala M. J., Zolensky M. E., Bernhard R. B., Davidson W. E., Haynes G., Thomas H. S., Tsou P., and Brownlee D. E. 1998. Capture of hypervelocity particles with low-density aerogel. NASA Technical Memorandum 98-201792.

Joswiak D. J., Brownlee D. E., Pepin R. O., and Schlutter D. J. 2000. Characteristics of asteroidal and cometary IDPs obtained from stratospheric collectors: Summary of measured He release temperatures, velocities, and descriptive mineralogy (abstract #1500). 31st Lunar and Planetary Science Conference. CD-ROM.

Kistler S. S. 1931. Coherent expanded aerogels and jellies. *Nature* 127:741.

Kovalenko L. J., Maechling C. R., Clemett S. J., Phillipoz J.-M., Zare R. N., and Alexander C. M. O. D. 1992. Microscopic organic analysis using two-step laser mass spectrometry: Application to meteoritic acid residues. *Analytical Chemistry* 64:682–690.

Matrajt G., Ito M., Wirick S., Messenger S., Brownlee D. E., Joswiak D. J., Flynn G. J., Sandford S. A., Snead C., and Westphal A. J. 2008. Carbon investigation of Stardust particles: A TEM, NanoSIMS and XANES study. *Meteoritics & Planetary Science* 43:315–334.

McKay D. S., Gibson E. K., Thomas-Keprta K. L., Vali H., Romanek C. S., Clemett S. J., Chillier X. D. F., Maechling C. R., and Zare R. N. 1996. Search for past life on Mars; Possible relic biogenic activity in Martian meteorite ALH 84001. *Science* 273:924–930.

McKeegan K. D., Aléon J., Bradley J., Brownlee D., Busemann H., Butterworth A., Chaussidon M., Fallon S., Floss C., Gilmour J., Gounelle M., Graham G., Guan Y., Heck P. R., Hoppe P., Hutcheon I. D., Huth J., Ishii H., Ito M., Jacobsen S. B., Kearsley A., Leshin L. A., Liu M.-C., Lyon I., Marhas K., Marty B., Matrajt G., Meibom A., Messenger S., Mostefaoui S., Mukhopadhyay S., Nakamura-Messenger K., Nittler L., Palma R., Pepin R. O., Papanastassiou D. A., Robert F., Schlutter D., Snead S. J., Stadermann F. J., Stroud R., Tsou P., Westphal A., Young E. D., Ziegler K., Zimmermann L., and Zinner E. 2006. Isotopic compositions of cometary matter returned by Stardust. *Science* 314:1724–1728.

Sandford S. A., Aléon J., Alexander C., Araki T., Bajt S., Baratta G., Borg J., Brucato J., Burchell M., Busemann H., Butterworth A., Clemett S., Cody G., Colangeli L., Cooper G., D'Hendecourt L., Djouadi Z., Dworkin J., Ferrini G., Fleckenstein H., Flynn G., Franchi I., Fries M., Gilles M., Glavin D., Gounelle M., Grossemy F., Jacobsen C., Keller L., Kilcoyne A., Leitner J., Matrajt G., Meibom A., Mennella V., Mostefaoui S., Nittler L., Palumbo M., Robert F., Rotundi A., Snead C., Spencer M., Steele A., Stephan T., Tyliszczak T., Westphal A., Wirick S., Wopenka B., Yabuta H., Zare R., and Zolensky M. 2006. Organics captured from comet 81P/Wild 2 by the Stardust spacecraft. *Science* 314:1720–1724.

Sephton M. A., Pillinger C. T., and Gilmour I. 2000. Aromatic moieties in meteoritic macromolecular materials: Analyses by hydrous pyrolysis and del13C of individual compounds. *Geochimica et Cosmochimica Acta* 64:321–328.

Shibanov A. N. 1985. *Laser analytical spectrochemistry.* Bristol: Adam Hilger.

Spencer M. K. and Zare R. N. 2006. uL2MS Analysis of standards in preparation for the return of NASA Stardust (abstract). 37th Lunar and Planetary Science Conference. CD-ROM.

Spencer M. K. and Zare R. N. 2007. Comment on "Organics Captured from Comet Wild 2 by the Stardust Spacecraft." *Science* 317:1680.

Spencer M. K., Hammond M. R., and Zare R. N. 2008. Laser mass spectrometric detection of extraterrestrial aromatic molecules: Mini-review and examination of pulsed heating effects. *Proceedings of the National Academy of Sciences* 105:18,096–18,101.

Stratton D. and Szydlik P. 1997. Modeling the capture of cosmic dust particles in aerogel (abstract). 28th Lunar and Planetary Science Conference. p. 1389.

Thomas K. L., Blanford G. E., Clemett S. J., Flynn G. J., Keller L. P., Klock W., Maechling C. R., Mckay D. S., Messenger S., Nier A. O., Schlutter D. J., Sutton S. R., Warren J. L., and Zare R. N. 1995. An asteroidal breccia: The anatomy of a cluster IDP. *Geochimica et Cosmochimica Acta* 59:2797–2815.

Tsou P. 1995. Silica aerogel captures cosmic dust intact. *Journal of Non-Crystalline Solids* 186:415–427.

Tsou P., Bradley J. P., Brownlee D. E., Fechtig H., Hrubesh F. L., Keaton P. W., Laurance M., Simon C. G., Stradling G. L., Teetsov A., and Albee A. L. 1990. Intact capture of cosmic dust analogs in aerogel (abstract). 21st Lunar and Planetary Science Conference. pp. 1264–1265.

Westphal A. J., Snead C., Butterworth A., Graham G. A., Bradley J. P., Bajt S., Grant P. G., Bench G., Brennan S., and Pianetta P. 2004. Aerogel keystones: Extraction of complete hypervelocity impact events from aerogel collectors. *Meteoritics & Planetary Science* 39:1375–1386.

Winograd N., Baxter J. P., and Kimock F. M. 1982. Multiphoton resonance ionization of sputtered neutrals: A novel approach to materials characterization. *Chemical Physics Letters* 88:581–584.

Zenobi R., Philippoz J. M., Buseck P. R., and Zare R. N. 1989. Spatially resolved organic analysis of the Allende meteorite. *Science* 246:1026–1029.

Zolensky M. E., Zega T., Yano H., Wirick S., Westphal A., Weisberg M. K., Weber I., Warren J. L., Velbel M., Tsuchiyama A., Tsou P., Toppani A., Tomioka N., Tomeoka K., Teslich N., Taheri M., Susini J., Stroud R., Stephan T., Stadermann F., Snead C., Simon S., Simionovici A., See T., Robert F., Rietmeijer F., Rao W., Perronnet M., Papanastassiou D., Okudaira K., Ohsumi K., Ohnishi I., Nakamura-Messenger K., Nakamura T., Mostefaoui S., Mikouchi T., Meibom A., Matrajt G., Marcus M., Leroux H., Lemelle L., Le L., Lanzirotti A., Langenhorst F., Krot A., Keller L., Kearsley A., Joswiak D., Jacob D., Ishii H., Harvey R., Hagiya K., Grossman L., Grossman J., Graham G., Gounelle M., Gillet P., Genge M., Flynn G., Ferroir T., Fallon S., Ebel D., Dai Z.-R., Cordier P., Clark B., Chi M., Butterworth A., Brownlee D., Bridges J., Brennan S., Brearley A., Bradley J., Bleuet P., and Bland P., and Bastien R. 2006. Mineralogy and petrology of comet 81P/Wild 2 nucleus samples. *Science* 314:1735–1739.