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Response to Comment on "Organics Captured from Comet 81P/Wild 2 by the Stardust Spacecraft"

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Caution must be taken in interpreting measurements of organics in Stardust samples. In particular, as noted in Sandford *et al*. and reinforced in the comment by Spencer and Zare, one component of Stardust organics, the low-mass polycyclic aromatic hydrocarbons seen diffusely along track surfaces, should be treated cautiously because they may be due to impact conversion of aerogel carbon.

In Sandford *et al*. (*1*), we reported that organics found in samples returned by the Stardust spacecraft to Earth from Comet 81P/Wild 2 show a heterogeneous and unequilibrated distribution in both abundance and composition. Portions of the organics show similarities to those in meteorites and interplanetary dust particles (IDPs), but the entire suite of returned organics is more diverse and varied than those seen in either meteorites or IDPs. Unique to the cometary materials is a class of aromatic-poor organic material. Stardust organics are generally richer in O and N than meteoritic organics but show O/C and N/C ratios similar to those in IDPs. Aromatic compounds are present, but overall the samples tend to be relatively poorer in aromatics than are meteorites and IDPs. The extraterrestrial origin of many of these organics is evidenced by their intimate association with captured mineral grains and the presence of enrichments of D and ^{15}N (*2*, *3*). Thus, a remarkably diverse suite of organic compounds is present and identifiable within the returned samples, and substantial portions of them are demonstrably of cometary origin.

However, as noted in (*1*), caution must be taken in interpreting measurements made of organics in the Stardust samples. As with the study of meteoritic organics, one must be wary of the potential for sample contamination. There is nothing unique about the Stardust samples in this regard, although the small size of the samples makes this especially important. Several issues must be constantly considered. There is the possibility of external organic contaminants introduced during the manufacture, flight, and recovery of the spacecraft, or during subsequent processing of the samples. Organic contamination control and assessment activities done throughout the Stardust mission indicate that contaminants of this sort do not represent a major problem. More problematic, however, are the issues of alteration of the original cometary organics and production of new molecular species during the impact collection process.

The cometary samples were collected at an encounter velocity of ~6.1 km/sec into aerogel containing a few weight percent carbon, the majority of which is in the form of methyl groups. As noted by Spencer and Zare (*4*), and in (*1*), deceleration of particles from these velocities liberates sufficient energy to break chemical bonds and raises the possibility that (i) some of the incoming cometary material will be altered and (ii) some of the carbon originally in the aerogel may be converted into new forms. The variable extent of these two types of modification during impact is not yet fully constrained. However, examination of materials along aerogel tracks shows that the degree of modification can vary across the entire range from total destruction to near pristine capture within an individual track. Clearly, all Stardust samples must be examined carefully with this in mind. Fortunately, the highly heterogeneous nature of the samples, the presence of isotopic anomalies, and the presence of labile materials (*1*–*3*, *5*, *6*) clearly indicate that substantial portions of the incoming particles were not completely thermally processed.

The impact creation of new organic materials from the carbon present in the original aerogel is most problematic for a subset of aromatic organics seen diffusely spread along the walls of impact tracks. Microprobe laser desorption laser ionization mass spectrometry (μL^2MS) analysis of track interior surfaces showed the presence of a population of low-mass polycyclic aromatic hydrocarbons (PAHs) not seen on aerogel surfaces outside the track (*1*). However, as we noted in the Supporting Online Material in (*1*), and as is presented in more detail in (*4*), this population of low-mass PAHs can be essentially reproduced during high-power laser shots into aerogel. Furthermore, Spencer and Zare show that these low-mass PAHs can subsequently be detected near the high-power laser shot locations using the lower laser powers used for normal measurements. Thus, insofar as high energy laser pulses simulate hypervelocity impacts, these results reinforce our earlier admonishment that investigators should exercise extreme caution when considering the population of low-mass PAHs seen diffusely spread on the interior surfaces of Stardust impact tracks.

While the efficiency of the conversion of C indigenous to the aerogel into low-mass PAHs during impact is unknown, it cannot be very high. If a substantial fraction of the indigenous C were converted in this manner, infrared spectral maps of Stardust impact tracks would show track-associated production of new aromatic C-H stretching bands correlated with an appropriate depletion of the aliphatic CH_3 stretching mode band of the original aerogel. This effect is not seen within the sensitivity of the infrared mapping technique (*1*). Given the extremely high sensitivity of the μL^2MS technique (typically in the attomole range), the low-mass PAH populations seen in the high-power laser shots reported by Spencer and Zare could presumably be explained by quite low conversion efficiencies.

It is also worth noting what is not seen in the new work of Spencer and Zare. Their high-power laser shots do not produce the more complex distribution of higher mass PAHs seen associated with whole particles (*1*), nor do they generate PAHs with appreciable O or N contents. Thus, the majority of the organics seen in the Stardust samples are clearly not generated by this process. Instead, this issue is largely associated with the population of low-mass PAHs seen diffusely distributed along track surfaces. Nonetheless, the cautions expressed in our original paper (*1*), and reinforced by the new work of Spencer and Zare, should serve investigators of Stardust samples (organics or otherwise) as a reminder that constant and continued attention needs to be paid to issues associated with contamination and alteration of these samples.

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