GENERATION OF COMPLEX AROMATIC HYDROCARBONS DURING ATMOSPHERIC ENTRY OF AN ARTIFICIAL METEOR.

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Introduction: Exogenous organic carbon continually enters the atmosphere and may have made a significant contribution to the inventory of prebiotic organic compounds on early Earth [1]. In the heavy bombardment period, from 4.5-3.8 Gyr ago, as much as $1x10^9$ kg/yr organic carbon was delivered, assuming it survived the harsh conditions of entry [2]. More likely, however, the original composition was altered on entry, reducing the surviving organic carbon to ~ 10^6 to 10^7 kg/yr [3].

To gain a comprehensive view of organic destruction and/or alteration during the atmospheric entry of exogenous organic material we treated the NASA Stardust Mission Sample Return Capsule (SRC) as an artificial meteor. At 12.6 km/s, the SRC return was the first scheduled entry of a known material at a meteor-relevant speed [4]. The SRC heat shield has a simple and astrochemically relevant organic composition. This heat shield is a phenolic-impregnated carbon ablator (PICA), containing fibrous carbon and low-mass aromatic hydrocarbons [5]. Similar aromatic compounds have been identified as one of the organic components of carbonaceous chondrite meteorites. Ejection of surface material from PICA is comparable to the ablation process occurring in natural meteor events and evidence has been found for an analogous process occurring on infall of extraterrestrial material [6]. Investigating organic alteration in outer layers of the Stardust SRC heat shield enables, for the first time, a direct analysis of meteor effects on exogenous organic carbon.

Samples and Methods: Two-step laser mass spectrometry (μL^2MS) was used in this study to perform depth-resolved characterization of aromatic hydrocarbons in ablated PICA samples. μL^2MS combines focused laser-assisted thermal desorption with ultrasensitive laser ionization methods to produce an exceptional combination of sensitivity, selectivity, and spatial resolution [7]. This technique is also used for analysis of Wild2 cometary particles returned by NASA Stardust [8]. Laser desorption was performed using a CO_2 laser (10.6μm; ~$2.5x10^6$ W/cm^2) with spot size of 40 μm. An ionization wavelength of 266 nm (Nd:YAG; 4th harmonic) was used. A complete mass spectrum is obtained for each laser desorption shot.

Two different types of Stardust PICA samples were chosen for this study [9]. These included a post-entry SRC PICA depth core and a PICA lab simulation depth core.

Full depth cores of the post-entry Stardust SRC heat shield were obtained from the stagnation point (location of highest heat flux; 900 W/cm^2) and from the SRC flank (550 W/cm^2). Stardust SRC depth cores were ~6cm deep and 2" diameter. Arc jet laboratory simulations of PICA atmospheric entry were also performed using Stardust-analog PICA material. A 21 mm deep, 1" diameter depth core of arc jet exposed PICA was obtained [9]. Depth cores were sectioned into ~1mm thick slices. Samples were homogenized by crushing a ~1x1 mm piece between two Al foil sheets and missing the resulting powder. Powders were mounted onto individual brass μL^2MS sample platters using tape adhesive. Four averages of fifty mass spectra each were taken randomly across the surface of each sample.

Results: ***Stardust SRC Depth Core Analysis.*** Analysis of individual slices from the SRC PICA stagnation point and flank cores reveals a fairly constant PAH signature for PICA at depths > 7 mm. This signature has been attributed to "pristine" Stardust PICA and ranges from 78 amu (e.g., benzene) to 220 amu (e.g., phenanthrene+3CH_2). Charred material contains a considerably larger abundance of PAHs with broader range of masses, including significant intensities beyond 278 amu (e.g., pentaphene). Mass distributions in both the stagnation point and flank cores are almost identical. Comparison of PAH identities in pristine PICA (15 mm depth) to those found in charred PICA (1mm depth) reveals shows a dramatic increase in molecular complexity for charred PICA (**Fig. 1**). Depth analysis of the first 7mm of both SRC cores reveals a fluctuating intensity and relative abundance of PAHs (**Fig. 2**). A significant amount of mass 106 (e.g., benzene+2CH_2)

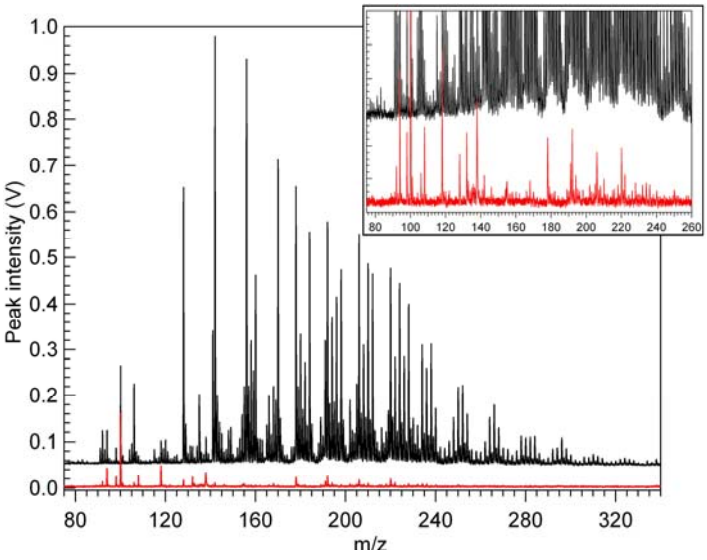

Figure 1. Upper mass spectrum (black) is 0-1 mm depth of stagnation point core. Lower spectrum (red) is 15 mm depth of same core. Spectra offset for comparison. Inset is a magnification for ease of comparison. Peaks centered at m/z 100 are for internal calibration(D_8-toluene).

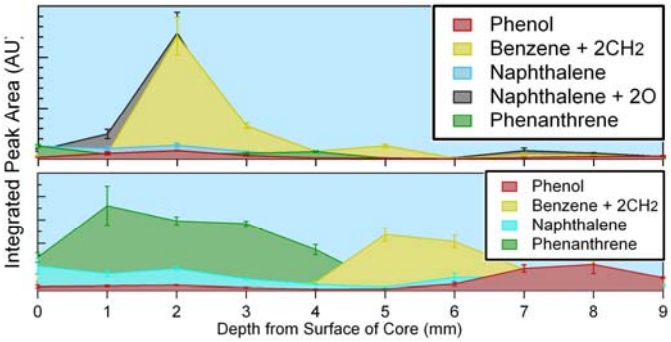

Figure 2. Integrated peak area of main PAHs for shallow core depths in the the SRC stagnation point core (upper graph) and the arc jet PICA core (lower graph). At depths >9mm the PAH abundances are constant at pristine PICA levels and are not shown here. Tentative mass assignments shown. Error bars indicate 1 standard deviation based on quadruplicate analyses.

and mass 160 (e.g., naphthalene+2O) is observed at a depth of 2-3 mm in both SRC cores.

Arc Jet Exposed PICA Depth Core Analysis. PICA arc jet core analysis also reveals a constant PAH signature for pristine PICA at depths >10 mm. This distribution ranges from 78 amu (e.g., benzene) to 178 amu (e.g., phenanthrene). Charred material also contains PAHs with increased abundance and broader mass range compared to pristine PICA, including significant intensities up to 268 amu (e.g., phenylanthracene+CH_2). Mass spectra from pristine PICA (17mm depth) compared with charred PICA (4mm depth) again shows drastic differences. Full core analysis reveals depth trends that were not observed in the Stardust SRC cores (**Fig. 2**). These results indicate the presence of three different "zones" in the arc jet lab simulation sample, in stark contrast to the relatively simple depth profile of SRC cores.

Discussion: This work shows that atmospheric entry of Stardust PICA results in formation of higher order PAHs from initial low-mass aromatic and carbon precursors, and potentially from atmospheric components as well. PAH chemistry has been observed with μL^2MS at depths up to 10mm in ablated PICA depth cores. Thermal and shock processing experienced by an object during entry is known to cause ablation of up to 99.4% of the original entering mass for carbonaceous chondrites [1, 10]. Thus, highly abundant complex aromatic compounds, such as those found in Stardust SRC heat shield surface material, would likely be distributed into the surrounding atmosphere during an actual meteor event. For all PICA samples analyzed, relative abundance of PAHs in comparison with pristine PICA shows a greater than four times increase in PAH peak intensity. This result implies that PAHs are being created during the PICA ablation process and survive the thermal stresses of entry.

Laboratory simulation of PICA atmospheric entry is found to not accurately reproduce depth trends of aromatic organic compounds. No evidence of oxidized PAHs was found at any depth in the arc jet PICA ablation models. This model also fails to accurately reproduce the abundance depth profile of PAHs, showing several depth-dependent peaks in PAH abundance in stark contrast to the SRC's one peak in PAH abundance. The main difference between arc jet exposed and post-entry Stardust PICA is the period of time allotted for sample cool-down after exposure to maximum heat flux conditions. This suggests that the fast quenching of arc jet exposed PICA after heating produces different reaction conditions, thus resulting in different depth profiles and PAH identities, in comparison with the ~120 s cool-down period for the Stardust SRC.

Conclusions: We find that aromatic compounds can become structurally altered and react to form higher molecular weight compounds during an artificial meteor event. Data suggests that complex compounds are generated during the cool-down stage of atmospheric entry. Further testing is underway to pursue the effect of cooling rates on compounds generated during arc jet PICA ablation simulations.

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