TOF-SIMS ANALYSIS OF RESIDUES OF PROJECTILES SHOT ONTO STARDUST ALUMINUM FOIL. J. Leitner\textsuperscript{1}, T. Stephan\textsuperscript{1}, and F. Hörz\textsuperscript{2}, \textsuperscript{1}Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany (leitner@uni-muenster.de), \textsuperscript{2}NASA Johnson Space Center, Houston, Texas 77058, USA.

Introduction: The samples from the \textit{Stardust} space probe will offer the first opportunity for analyzing cometary matter collected under controlled conditions together with contemporary interstellar dust particles [1, 2]. Moreover, \textit{Stardust} is the first sample return mission ever that provides material from a known solar system object other than the moon. The primary goal after sample arrival is to determine the elemental, isotopic, mineralogical, and organic composition of the dust and thus the properties of the comet’s nucleus.

\textit{Stardust} provides two different types of capture media containing cometary samples [2]. Besides aerogel, about 153 cm\textsuperscript{2} of aluminum foils (Al 1100; >99\% pure) were exposed to the comet. These foils were mainly used for fixing and facilitating the removal of the aerogel blocks from the collector trays.

Although even small cometary grains are not expected to survive impacts on metal foils unaltered at 6.12 km/s, Al foil might be the primary target material for small (sub-\(\mu\)m) or fluffy particles that disintegrate by penetrating the aerogel and thus cannot be extracted easily from the highly porous and friable capture material.

In this ongoing study [3, 4], time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used for the analysis of crater residues on Al foil from impact experiments using material from the Allende meteorite, a hornblende standard, and coal from the Illinois basin.

The major goal of this investigation is to evaluate how well the chemical composition of the projectile materials can be reproduced by TOF-SIMS analysis.

Samples and Experimental Procedures: Powdered bulk material of the CV3 chondrite Allende, powdered hornblende (Kakanui, USNM 143965), and powdered coal (Illinois) were shot onto Al foil using a 5 mm caliber Light Gas Gun at NASA Johnson Space Center. The following table summarizes grain size ranges and impact velocities of the different projectiles.

<table>
<thead>
<tr>
<th>material</th>
<th>grain size</th>
<th>impact velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allende</td>
<td>38–43 (\mu)m</td>
<td>5.9 km/s</td>
</tr>
<tr>
<td>hornblende</td>
<td>53–63 (\mu)m</td>
<td>4.2 km/s</td>
</tr>
<tr>
<td>Illinois coal</td>
<td>43–53 (\mu)m</td>
<td>4.2 km/s</td>
</tr>
</tbody>
</table>

Based upon the nominal projectile sizes, crater diameters up to 180 \(\mu\)m for Allende material and up to 215 \(\mu\)m for hornblende impactors were expected [5]. Due to the differing material parameters and the lack of appropriate calibration measurements, no estimation could be made for the coal projectiles. However, many of the grains fragmented during the launch process, thus producing craters in a wide range of sizes.

In this study, a set of 18 impact features from Allende material was selected. Furthermore, two hornblende craters and one crater from a coal projectile have been analyzed so far.

Craditer diameters for the Allende samples range from 4 \(\mu\)m to 190 \(\mu\)m, while the Hornblende residue craters display sizes of 130 \(\mu\)m and 180 \(\mu\)m, respectively, and the coal crater is about 200 \(\mu\)m in diameter.

All sample regions were analyzed after sputter cleaning by Ar ion bombardment. This procedure was necessary because all three Al foils were covered with a thin layer of mostly organic contaminants from the vaporized projectile sabot, which initially inhibited a proper analysis. Additional analyses were carried out prior to the sputter process for selected craters in order to monitor changes, especially fragmentation of hydrocarbons, caused by the sputtering process.

During the actual TOF-SIMS analysis, the sample was rastered with a \textasciitilde 0.2 \(\mu\)m \(^{60}\text{Ga}\) primary ion beam. From the resulting distribution of Mg, Si, Ca, and Fe secondary ions, regions of interest were selected, for which complete mass spectra were generated. After Al foil blank correction, element ratios were calculated using relative SIMS sensitivity factors gained from glass standards. Further details are given in the literature [4, 6].

Results: 

\textit{Allende}. Besides one crater that does not contain enough residual material for a proper impactor characterization and two residues that are clearly non-chondritic, geometric mean values of most element ratios for all other examined residues are close to CV element ratios and fit well within the range of ratios observed for Allende chondrules [7]. More detailed information on the TOF-SIMS results of Allende residues on Al foil are given in [3] and [4].

\textit{Hornblende}. Two craters from hornblende projectiles were analyzed in this study so far, both showing enough residual material for a proper quantitative analysis. Element ratios normalized to Si show significantly less deviations from reference data [8] than the Allende data. Most major element ratios are within a factor of 1.5 identical to literature values (yellow area in Fig. 1). Na/Si- and K/Si-ratios are more than a fac-
tor of 2 higher than in the reference data, probably due to contamination with these elements. Quantitative analysis of Li, Be, B, C, and O is prevented by contamination of the Al foils, since secondary ion signals for these elements predominately stem from the blank. Presently, it is unknown if this contamination is imminent in the Al foil or a result of the conditions during the impact experiments. However, Ar sputter cleaning could not remove this contamination completely.

Fig. 1: Element ratios relative to Si for two hornblende crater residues normalized to literature values

Illinois coal. Since sputtering was necessary prior to TOF-SIMS analysis of Allende and hornblende residues, similar conditions for the coal sample foil had to be expected. In contrast to the previous two sample materials, coal has a different structure and composition, so that the relative sensitivity factors used for silicates cannot be applied here. Thus, a quantitative analysis is not possible for this set of samples. Furthermore, the main constituents of the coal projectiles, C, O, and hydrocarbons, are strongly affected by both, the sputter cleaning and the contamination of the foils, regardless if the latter is due to the impact process or inherent in the sample foils.

Consequently, in this case, analyses have to be performed before and after sputtering of sample areas. Ion intensities relative to carbon were calculated for the non-sputtered sample as well as for the same region after Ar bombardment. Intensity ratios of most elements are increased by factors of 2.5–10 after sputtering. Only H/C, V/C, and Zn/C are in the same order of magnitude as before sputtering, and Si/C as well as Sc/C is decreased by a factor of ~2. Hydrocarbons relative to C show a general decrease, as can be seen in the following table (ion ratios relative to C and relative to ratios before sputtering).

<table>
<thead>
<tr>
<th>Compound</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>C₄H₁₀</th>
<th>C₅H₁₂</th>
<th>C₇H₁₄</th>
<th>C₈H₁₆</th>
<th>PAHs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion ratio</td>
<td>0.077</td>
<td>0.044</td>
<td>0.024</td>
<td>0.030</td>
<td>0.052</td>
<td>0.026</td>
<td>0.019</td>
<td>0.026</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.014</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

For nitrogen-bearing ions, increased intensity ratios are observed after sputtering; values are up to 800 times larger than for the non-sputtered material.

Discussion: Despite rather large variations in element ratios from individual craters, the geometrical mean value of all analyzed Allende residues resembles very well the expected element pattern from literature data. Especially if compared with Allende chondrule data, the TOF-SIMS data yield a correlation coefficient of 0.97 [4].

The element ratios of the hornblende samples display significantly smaller variations than the Allende data. This was expected because the hornblende from Kakanui, New Zealand, is used as a microbeam mineral standard (USNM 143965) and therefore much more homogeneous in composition than Allende bulk material. Comparison of the geometrical mean value of the element ratios of the examined samples with the literature [8] yields a correlation coefficient of about 0.98, even despite the relative large deviations of the Na/Si- and K/Si-ratios.

Although the main work on the coal sample foil is still in progress, these first results show certain tendencies: Ar ion bombardment removes the contamination layer, but ion images and the increasing element-to-carbon-ratios of the major elements show that residual material is not only still present in the crater rim after sputtering but even more accessible to analysis.

Intensities especially for large hydrocarbons relative to C are decreased after the sputter process. This can be explained by fragmentation of complex molecules by impinging Ar⁺ ions, generating a certain amount of low-mass hydrocarbon fragments. The same effect may lead to increased intensities of low-mass nitrogen species, but here further analysis is needed.

The results of this study clearly show that projectiles of chondritic composition or silicates impinging on aluminum foil at ~6 km/s can be identified by TOF-SIMS analysis of their residual matter. Moreover, as the coal data indicate, even for complex molecules, it is possible to survive the impact on Al foil at the given velocities.