AN IMPROVED HF VAPOR ETCHING APPARATUS FOR STARDUST PARTICLE EXTRACTION. K. A. McCain,[1] T. M. Hahn[1], R. M. G. Armytage[1], W. P. Buckley[1], C. J. Snead[2], and A. N. Nguyen[3] [1]Jacobs JETSII contract, NASA JSC, Mail Code XI3, Houston, TX 77058 (kaitlyn.a.mccain@nasa.gov), [2]ARES, NASA JSC, Mail Code XI2, Houston, TX 77058, [3]ARES, NASA JSC, Mail Code XI3, Houston, TX 77058.

Introduction: The NASA Stardust mission captured thousands of particles from the Jupiter-family comet 81P/Wild 2 in a collector composed of aluminum foil and blocks of silica aerogel [1]. To date, most Wild 2 particles available for study are coherent particles > 1 μm in size, extracted individually from the ends of hollow, carrot-shaped impact tracks produced during sample impact into aerogel. However, >65% of the impacting mass can be found in the 'bulb' of the track, including nearly all of the <1 μm size fraction [2]. This fraction contains organic-rich material and is likely to include presolar grains, representing a critical opportunity to constrain the organic and presolar inventory of primitive outer solar system materials.

Very few presolar grains have been identified in Stardust foils and tracks to date [3, 4 and references therein], which has been interpreted as destruction upon impact into foil and preferential sampling of terminal particles rather than a dearth of presolar material in Wild 2 [4]. Indeed, the initial abundance of presolar O-rich grains in Wild 2 was inferred to be 600-830 ppm [4]. Analysis of bulb material may therefore significantly expand the inventory of presolar materials from the outer solar system. However, the susceptibility of the small size fraction found within the bulb to melting or alteration during capture poses significant analytical challenges.

Previous efforts to extract and concentrate fine-grained material from the bulb of Stardust tracks involved compression or destruction of aerogel while leaving impactor particles relatively unharmed [5-7]. The low density and high porosity of silica aerogel make it more susceptible to attack by etching with hydrofluoric acid (HF) [6] or CF_4 plasma ashing [7] than collected cometary silicates. Previous studies of HF vapor etching used HF solutions varying between 5 to 49% (~3 to 29 M) and noted that at high concentrations and etch rates, a liquid droplet was produced according to the etching reaction $4HF + SiO2 \rightarrow SiF_4 (g) + 2H_2O$ [6]. SiF_4 readily decomposes into HF and silicic acid in water, which has the potential to alter the freed cometary silicates. The plasma ashing technique avoids production of a liquid droplet and minimizes damage to embedded silicates but requires specialized equipment [7].

In this abstract, we present recent improvements to the HF etching procedure with the aim of constructing an etching chamber capable of slowly etching silica aerogel using small quantities of dilute HF, such that liquid droplets will not be produced.

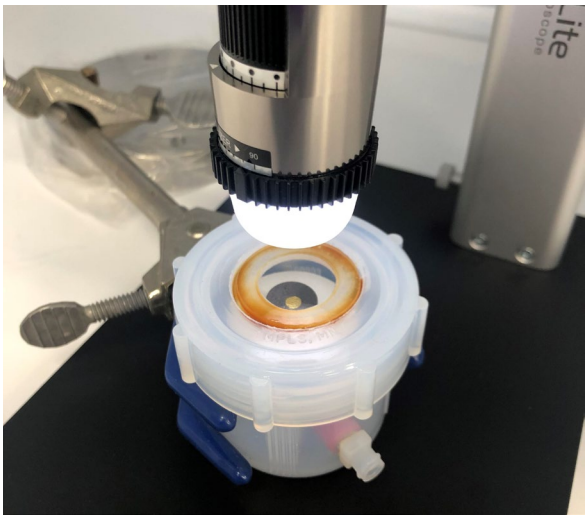

Figure 1. Chamber used for HF etching of Stardust aerogel keystones. Visible through the chamber lid is gold foil suitable for SEM and NanoSIMS analysis on a graphite SEM stub.

Methods: The HF etching chamber was assembled using readily available materials. The chamber consists of a modified Savillex sample jar and lid (Figure 1). A portion of the lid has been milled out and fitted with a HF-compatible clear CR-39 plastic window using HF-resistant epoxy. An HF-compatible inlet port to allow injection of small quantities of acid is installed several mm above the bottom of the jar and affixed using HF-resistant epoxy. A high-density polyethylene sample stand with a removable secondary electron microscope (SEM) stub sample holder is attached to the bottom of the sample chamber using HF-compatible epoxy to raise the sample safely above the acid and allow easy sample loading and unloading.

The HF solution is injected into the sealed jar below the sample stand through the port using an HF-compatible syringe. The reaction progress is monitored in real-time and with time-lapse photography through the viewport in the lid using a Dino-Lite Edge digital microscope. The etching procedure is carried out in a fully exhausting fume hood used for HF digestion, which allows us to open the chamber once the aerogel has been consumed to stop the etching process quickly

and safely, thereby minimizing alteration of embedded particles. After removing the sample holder, all components can be easily cleaned by soaking in ultrapure water (UPW) and readied for another etch process. The sample stub and holder can be left to evaporate in the hood before transferring the Au foil to an Al stub for further SEM and NanoSIMS characterization.

In our initial test, we determined the minimum concentration of HF solution capable of vapor etching aerogel to avoid leaving behind a liquid droplet. We injected HF solutions of 0.01 N, 1.5 N, and 3.0 N into an etching chamber containing a ~2 mm aerogel fragment resting on an HF-compatible graphite SEM stub. Time-lapse photography was used to monitor the etch rate and progression for each concentration.

Results and Discussion: The 0.01 N and 1.5 N solutions did not produce any vapor etching visible to our time-lapse photography setup within 20 minutes after injection of acid into the chamber. Approximately 20 minutes after injection of 1 mL 3.0 N HF, the aerogel increased in opacity, indicating that etching had begun. The 2 mm aerogel fragment slowly decreased in size and was fully consumed after approximately 2 hours and 40 minutes. Therefore, 3.0 N appears to be the most dilute HF capable of destroying aerogel in our setup within a few hours. No liquid droplet was observed during the digestion process, nor was condensation noted inside the chamber or on the chamber window at any of the tested concentrations, suggesting that this apparatus and procedure reduces the risk of producing an HF-rich water droplet capable of etching the cometary particles. Subsequent etching tests will be performed with 3.0 N HF solution.

Benefits of this technique over plasma ashing include the relative ease of setup and cleanup of the apparatus and the ease of which etched samples can be prepared for SEM and NanoSIMS analyses. Compared with compressing aerogel into substrates (e.g., indium, [5]), HF etching removes a significant fraction of insulating Si- and O-rich aerogel from the target which reduces isotopic dilution from the matrix and deleterious charging effects during NanoSIMS analysis.

Future tests: We will investigate the effect of the vapor etching procedure on target particles by pressing a variety of analogue mineral grains into an annealed, HF-cleaned Au foil overlaid with an HF-cleaned Au grid for reference. The pressed minerals will include San Carlos olivine, Eagle Station olivine, Admire olivine, SLP-400 orthopyroxene, calcite, dolomite, Burma spinel, and magnetite. All analogue minerals except SLP-400 have well-established oxygen isotopic compositions, which will allow us to identify any effects of the etching procedure upon the isotopic compositions of target particles. Before exposure to HF vapor, the appearance of these mineral grains will be documented using optical microscopy and SEM imaging.

A 1 mm fragment of aerogel from the bulb of a track produced by firing Allende particles using a light gas gun will be placed on top of the same Au foil away from the mineral grains to serve as an analogue for embedded Stardust particles. This foil will be placed into the etching chamber, which will be injected with ~1 mL 3N HF and monitored using time-lapse photography. After the aerogel fragment etches, the reaction will be stopped by removing the lid from the chamber. The Allende residue and mineral grains will be imaged using SEM and optical microscopy to assess the results of the etching procedure and the collapse behavior of the aerogel. NanoSIMS O isotopic analysis of the minerals will be conducted to ensure that etching does not affect the isotopic compositions.

The etched analogue minerals and Allende particles will also be used to refine the etching procedure. For instance, if the target minerals are significantly affected by the etching process, or the bulb fragment produces a droplet, the concentration of injected HF (and therefore the etch rate) will be further adjusted.

Additional tests include etching of tracks produced by firing Allende particles into silica aerogel to determine the degree to which homologous collapse and aerogel etching affect the spatial distribution of freed cometary particles. Based upon the results of these tests, further refinements to the procedure will be made before we etch full Stardust keystones or bulb fragments.

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