
Space Sciences Laboratory, University of California at Berkeley, Berkeley, CA 94720, USA (westphal@ssl.berkeley.edu), Lawrence Livermore National Laboratory, 7000 East Avenue, L-395, Livermore, CA 94550, USA, Department of Geological Sciences and Center for Meteorite Studies, Arizona State University, P. O. Box 871404, Tempe, AZ 85287-1404, ELORET, NASA Ames Research Center, MS 229-1, Moffett Field, CA 94035-1000, Institute for Geophysics and Planetary Physics, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA.

Introduction: Extraction of fine residues of hypervelocity impacts in aerogel collectors is a major challenge. The problem is likely to be especially severe for the Stardust mission. If cometary dust particles are similar to IDPs, they are unlikely to survive as structurally intact particles, but will instead break up into their fine-grained (micron to sub-micron) constituents. Large, refractory grains (e.g., olivines) that can be extracted relatively easily are likely to survive completely intact. But recovery of fine-grained material, distributed along the impact tracks[1,2], is required for comprehensive analysis of cometary material. The recovery and analysis of organics and carbonaceous material is a particular priority for Stardust.

Etching in HF liquid has been used for many years to remove silicates and to isolate organics and carbon from chondritic materials[3-6]. Etching of aerogel collectors to remove silicate aerogel has been suggested previously[7], but the large background of contaminants and inclusions in the aerogel collectors has discouraged this approach. Here we describe our first steps in the development of a technique for isolating certain types of non-silicate chondritic grains, and, potentially, partially etched larger silicate grains from aerogel collectors. This technique may be a useful addition to the analytical toolbox available to the Stardust community. Specifically, we describe two key innovations. First, the use of HF vapor instead of liquid for removing the aerogel matrix takes advantage of the enormous contrast (at least two orders of magnitude) in surface area, and thus etch-rate, between aerogel and ordinary silicates, and the rate can be readily controlled and monitored. Second, etching extracted aerogel keystones minimizes the volume of aerogel matrix and therefore the background of terrestrial organics and particulates.

Technique: For this development effort, we used particle impacts from the “chondritic swarm” population from the ODCE aerogel collector, which was deployed externally on the Russian space station Mir for 18 months in 1996-1997[8]. First, we extracted complete particle impact tracks in aerogel keystones with total volume ~0.01 mm³. We describe this technique in detail elsewhere [1]. We placed the aerogel keystone on a graphite disk, then placed the disk in a small (~25 cm³) closed polystyrene box with a optically clear and flat CR-39 plastic window so that the keystone could be optically imaged.

Fig. 1 Frames from time-lapse movie of HF vapor etching of an aerogel keystone. a) keystone before etching. b) beginning of homologous collapse. c) end of first phase. d) final residue.

We imaged the keystone through the window using a Digital Blue QX3+ microscope. We chose this microscope because of its good imaging capability and its plastic optics (to avoid frosting of optics due to accidental exposure to HF vapor). We then injected a few drops of HF, with concentrations varying from 49% to ~5%, into a small plastic dish inside the box using a syringe and a teflon tube threaded through a hole in the wall of the vapor-etch cell. In one test, we included powdered forsterite in the vapor-etch cell to understand the effect of HF vapor on a silicate common in meteoritic materials; in another, we included soda lime glass beads, whose size can be measured very precisely using the automated scanning microscope at Berkeley.

Results: Time-lapse movies of the etching process show the aerogel keystones collapse nearly homologously, with some distortion in shape, to approximately 1% of their initial volumes (Fig. 1 shows selected frames a recent test.) In our early tests, with relatively rapid etch rates, a small liquid drop forms near the end of the process, which then spreads to wet the surface of the graphite disk and eventually evapo-
rates. In later tests with slower etch rates, the liquid droplet did not form. The residue of the process is a “rubble field” surrounded by a roughly circular thin film of unknown evaporate residue.

We find that the etch rate is a very strong function of the concentration of the HF solution, and that the volume of the liquid drop increases dramatically with increased etch-rate. For our slowest etch, using ~5% HF, no discernable liquid drop was formed. This sample has not yet been analyzed.

In our simultaneous etches of aerogel keystone forsterite, and glass beads we saw no discernable change in the forsterite or glass when imaged optically, even after the ~200 µm aerogel keystone had completely evaporated. We were able to set an upper limit on the change in size of forsterite of ~1 µm and for spherical glass beads of ~0.1µm (see [9] for review of technique). This raises the hope that micron-sized chondritic silicates will survive the etching process, although this possibility must be evaluated qualitatively and with better chondritic analogs.

Discussion: This approach was partly motivated by the fact that SiF₄ is a gas, and that most other fluorides are refractory. We suspect that the liquid drop that we observed is condensed water from the reaction 4HF + SiO₂ → SiF₄ + 2H₂O. This hypothesis is consistent with observation that the liquid drop volume is correlated with the etch-rate, since slower production of water may discourage condensation.

We analyzed one of the rubble fields in three instruments. Both SEM/EDX and EMPA analyses showed nearly universal presence of S and Si, with some particles high in Mg. We also imaged the rubble pile in C, CN⁺, O, Si⁺ and S using the Cameca NanoSIMS at LLNL, using Cs⁺ as the primary beam. The nanoSIMS maps show ubiquitous Si and S in the rubble fields. We hypothesize that a soluble evaporate residue has coated the residual particles uniformly. The survival of some silicates is consistent with our observation that the HF-vapor etch-rate for aerogel is orders of magnitude faster than that of ordinary silicates. Such a large contrast is not surprising since aerogel is highly porous, consists of nanometer-sized structures, and has a very large effective surface area for chemical reactions (hundreds of m² per gram). We stress that it is not yet clear whether the surviving silicates are associated with the projectile or are simply melted and compressed aerogel associated with the particle impact.

One potential advantage of this technique is that particles resistant against HF etching are concentrated into a small area by the homologous collapse of the keystones. The physical mechanism that causes the aerogel to collapse homologically is not clear. This concentration of particles into a compact rubble field can facilitate the efficient analysis of residual particles without the necessity of scanning a very large area.

It is clearly desirable to etch without the formation of a liquid drop, particularly since SiF₄ decomposes into silicic acid and HF in water. This decomposition reaction may explain the ubiquity of Si in the elemental maps. We plan to do carefully-controlled experiments using artificially-implanted standards to evaluate the effect of HF vapor etching on typical chondritic materials, particularly organics, and to determine the effective etch rate for a variety of silicates, thus determining a lower size limit for survival of silicate fine particles. We also plan to evaluate backgrounds from the vapor-etched aerogel capture medium by analyzing blank aerogel keystones.


Additional Information: Time-lapse movies of HF-vapor etched keystone may be viewed at http://ultraman.berkeley.edu/~westphal/vapormovies

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