Acrylic embedding of Stardust particles encased in aerogel

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Abstract–Ultramicrotomy of samples embedded in epoxy resin is a standard method for preparing ultra-thin sections for electron microscopy. In this report we describe a new embedding technique that uses acrylic resin instead of epoxy. This method offers several important advantages for sectioning small extraterrestrial samples. One is that the acrylic resin is soluble and can be removed after ultramicrotomy to leave a sample that is free of the mounting media. This is important for studying carbon and insoluble organic components. A second major advantage of acrylic is that, when combined with pre-embedding compression, it provides a very effective method of mounting samples collected in silica aerogel. Acrylic embedding is currently being used to mount comet particles collected by NASA’s Stardust mission. Combined with a flattening process, the acrylic embedding and sectioning preserves all pieces of collected samples in their collection matrix. In addition to Stardust, acrylic may be applied to other samples collected in aerogel such as those from the Russian Mir space station (Hörz et al. 2000) and future missions such as Sample Collection for Investigation of Mars (SCIM) (Leshin 2003), a proposed mission to collect atmospheric dust particles from Mars.

INTRODUCTION

The NASA Stardust mission returned thousands of samples from the Jupiter family comet 81P/Wild-2. The particles were captured by 6 km/s impact into silica aerogel, a microporous material with a graded density ranging from 0.005–0.01 g/cm³ at the entry surface to 0.05 g/cm³ at 3 cm depth. The impacting particles on Stardust as well as other meteoroid capture experiments often form long hollow tracks, which have shapes similar to carrots or turnips (Hörz et al. 2000; Burchell et al. 2001) (Fig. 1). Nonfragmenting particles travel up to 200 projectile diameters and have a single terminal particle at the end of the track. Particles that fragment leave debris along the track and often produce tracks with multiple roots. It is not uncommon for impacts to have over half a dozen side tracks made by grains in the 5–10 μm size range (see Fig. 1).

Preparing thin sections of such samples for electron microscopy is a challenge. The two established methods are ultramicrotomy (Bradley and Brownlee 1986) with a diamond knife and sectioning with a focus ion beam (FIB) (Stroud et al. 2000). Microtomy is a violent process for minerals and success requires that samples be embedded in a suitable medium. Normally this medium is epoxy resin. In most respects, epoxy is an excellent embedding medium but it has a major limitation for meteoritic materials in that it cannot be effectively removed and it interferes with the detection and analysis of carbon or organic components. Epoxy is used for samples in aerogel (Barrett and Zolensky 1991), but the process used to remove air bubbles fractures aerogel and makes it difficult to see and isolate very small fragments. Sulfur embedding has been highly successful for embedding interplanetary dust samples (Bradley et al. 1993) and might be used for samples in aerogel. An advantage of sulfur is that is carbon-free and it can be removed by sublimation. In practice, it has been very difficult to impregnate aerogel with molten sulfur in an effective way. Another disadvantage of sulfur is that it slowly sublimes at room temperature and the potted butt, the remaining particle that was not sectioned, cannot be stored in sulfur for long periods of time and it cannot be examined under vacuum-based instruments such as scanning electron microscopes. In contrast, potted butts in epoxy or acrylic resin are samples that can be examined by a variety of methods and stored for years as a source of future sections.

As an addition to sulfur and epoxy, we now add acrylic as a medium that is effective for sectioning particles in aerogel. Acrylic does not bond to the surfaces of minerals as well as epoxy, but the polymer that we use is removable with chloroform after sectioning and it has several properties that are highly advantageous for mounting samples in silica aerogel. The acrylic infiltrates small pieces of aerogel and typically expels all the void-filling air as a single bubble. This
bubble can easily be removed with the procedure described below. The final impregnated aerogel is remarkable because the refractive index of acrylic is very close to aerogel, and melted or compressed aerogel and all pure silica components are virtually invisible. Before impregnation, tracks are quite visible, partly due to the thousands of small pieces of melted or compressed aerogel. After impregnation and curing, these artifacts become invisible and the only debris seen is projectile material. This is both good and bad. The tracks of typical particles are easily seen, but purely transparent projectile materials sometimes leave tracks that are difficult to distinguish.

We developed a methodology that involves embedding particles and sometimes their entire tracks or selected portions of tracks in acrylic plastic for ultramicrotomy. This preserves the spatial relationship between captured samples and their capture matrix. Retention of samples in their aerogel capture matrix eliminates the possibility of confusing a sample with a contaminant and reduces many possibilities of contamination artifacts. It permits preservation of the sample in its media and provides a means of seeing thermal alteration and aerogel interaction effects around the perimeter of captured particles. In some cases, altered material is in direct contact with melted vesicular aerogel, forming somewhat of a fusion crust.

The acrylic embedding process for particles in aerogel includes the following steps: a) compression of aerogel to reduce porosity; b) subdivision of compressed tracks by a razor blade; c) embedding with acrylic; d) curing under high-pressure argon; e) ultramicrotome sectioning; and f) removal of acrylic using chloroform (CHCl₃) solvent.

**METHODS**

**Aerogel Flattening**

Impregnation and general handling is best done on aerogel that has been compressed to reduce the total void space. The density at the top of Stardust aerogel is about 0.01 g/cm³; after compression this increased by a factor of 10 to 100. Compression and reduction of void space greatly improves the way that acrylic resin impregnates samples. It also improves the optical clarity of aerogel by collapsing voids that scatter light and the optical features (shape, color) of the terminal particle (Fig. 2). Compression of a track is best done on aerogel that is thin (preferably <1.5 mm) and flat. The following method works well with typical wedge-shaped keystones prepared by the method developed by Westphal et al. (2004).

A 100 μm thick flat mylar sheet is placed over a glass slide and the aerogel containing the track is placed on top of it. If needed, the mylar can be held down by tape at its ends. The sample is flattened with a top microscope slide that has a strip of 2.5 μm thick mylar (provided by SPI) held to its bottom side by electrostatic attraction. The compression process is watched with substage illumination in stereo microscope looking down through both slides. We have found that the compression can be done in a very controlled way by placing the bottom slide on a 1.2 cm thick flat plastic base. The sample slide points away from the observer and then the top slide is placed either in parallel orientation (Fig. 3) or in perpendicular orientation to form a cross. The cross orientation method provides the best control. For precise alignment with the cross method and control of the top slide, we used a third glass slide on the left as a spacer and a small strip of open cell foam (weather stripping) on the right. Left to right, resting on the plastic base, are the spacer slide, the slide with the sample, and finally the foam. During flattening, the left edge of the top slide is pressed tightly with a finger against the spacer slide and the right slide of the top slide is moved downward, compressing both the aerogel in the center slide and the open cell foam spacer on the right. This is easily done with considerable control. Strong force with a single finger on the center of the slide will compress a millimeter-size piece of aerogel that was originally 1.5 mm thick to 10–100 μm thick. If such a compression is not reached, then acrylic impregnation may fail. If the compression is too severe, then the acrylic will not fully impregnate the aerogel.
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Moderate compression provides ideal porosity that allows resin to wick in, fill all open space, and displace all air.

The compressed keystone is excellent for final imaging of the track in a compound microscope because all components are on the same plane. Once the aerogel has been compressed, it can be trimmed with a 100 μm thick stainless steel razor blade (Model personna, Electron Microscopy Sciences). For tracks that contain many pieces, it is possible to cut single fragments out, each mounted inside a small square. The trimmed pieces can be removed with a glass or tungsten needle. All of this work is done with ion generators nearby to eliminate charging problems. Before embedding, we sometimes sputter a thin Pd coat over the aerogel so its outline can be more easily observed when mounted in acrylic.

**Acrylic Embedding**

We tried several acrylic resins but only had success with WELD-ON 40 (IPS corporation) acrylic, a commercial two-part glue used for bonding acrylic sheets. After mixing, it hardens in ~20 min to form a water-clear acrylic that is soluble in chloroform. We mount the aerogel on top of an acrylic cylinder 7 mm in diameter and 10 mm long (Fig. 4). This solid acrylic block is prepared by pouring WELD-ON into a cylindrical teflon or delrin mold 25 mm in outside diameter that simply rests on top of a glass slide. The end of the cylinder in contact with the glass comes out smooth and flush with the mold. Embedding of the sample is done with the cylinder still in its mold and with its smooth face facing upward.

WELD-ON 40 develops a crust when exposed to air and the actual mounting must be done within a few minutes time. The embedding process starts with the compressed aerogel sitting on top of a 2 cm square of 100 μm thick mylar located next to a stereo microscope. The acrylic cylinder that the aerogel will be mounted on is located under the stereo microscope. A small drop of acrylic resin is dropped directly onto the aerogel sample and then the mylar is picked up with tweezers, inverted, and placed over the cylinder. Carefully, the mylar with the compressed aerogel square is lowered to the cylinder, while observing the sample in the microscope (Fig. 4). After a minute or two, all of the air is displaced from the aerogel, forming an exterior bubble. The top of the mylar is then pushed on with the end of a rounded 1 mm glass rod or...
similar object. With repeated pushing and movement of the probe, all air bubbles can be moved to the edge of the cylinder and the thickness of the liquid acrylic can be reduced to about the thickness of the compressed aerogel. Capillary forces in the gap between the cylinder and the mylar also assist this process. This stage can be done at a somewhat casual pace with the only time constraint being the actual setting of the two-component acrylic.

Under ambient conditions, aerogel can crack when the acrylic solidifies, probably because the acrylic shrinks when it becomes solid. This possibility is prevented by putting the sample inside a simple chamber pressurized with 100 atmospheres of argon while the acrylic cures. We believe that it is important to purge the chamber to remove oxygen before it is pressurized. Acrylic solidifies in about 20 min and under pressure it needs about 2 h to fully cure. It is best to allow the acrylic to cure for a day before ultramicrotomy, although this can be accelerated by heating to 60 °C.

Chloroform Washing

Once the acrylic is cured, it can be trimmed and ultramicrotomed. The ultramicrotomed sections on a TEM grid can be washed with chloroform to dissolve the acrylic. Because solvents always contain impurities, sub-boiling distillation is recommended before or during the washing process. For this we built a cylindrical stainless steel grid washing device (Fig. 5, left). The sample grid rests on a small square of filter paper that rests on central-air-cooled pedestal cold finger that keeps the grid near room temperature (Fig. 5, right). The surrounding volume is heated to 60 °C and vapor is produced without boiling. Vapor condenses on the grid and dissolves the acrylic. This is usually run 3–5 h to fully remove the acrylic (depending on the thickness of the ultramicrotomed section). Figure 6 shows ultramicrotomed sections of a particle before and after removal of acrylic with chloroform.

Ultramicrotomy

The samples embedded in acrylic microtome very well. The main difference between microtoming acrylic and epoxy is that the level of the water in the knife boat needs to be slightly lower for acrylic, since the sections tend to stick together and may be pulled down with the microtome arm movement. The main difference of microtoming acrylic versus sulfur is that, unlike sulfur, acrylic is hard and does not break apart in pieces while microtoming, minimizing the risk of losing the entire particle by breakage.

Observation in the Electron Microscope

The samples prepared in the manner described above can be analyzed with a transmission electron microscope (TEM) and/or with a scanning electron microscope (SEM). In neither case did we observe any problem of carbon contamination. We have never seen any acrylic remaining in the sections, either optically or in the TEM. In addition, we have systematically searched for carbon contamination deposits that could be left on the film after chloroform washing using electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDXS), and we did not detect any carbon deposition. We used this embedding procedure to study organic material in Murchison, polar micrometeorites, and IDPs (Matrajt et al. 2005) and we did not have any difficulty finding the organic phases. However, as chloroform is a solvent, we cannot rule out the possibility that some organic compounds may be washed away with chloroform. Acrylic embedding did not have any effect on the morphology of the particles examined (Fig. 2).
ADVANTAGES OF THIS METHODOLOGY

Acrylic embedding allows all of a precious sample in aerogel to be preserved. The relationship between the surviving particle core and the severely heated pieces that broke apart during aerogel entry is also preserved because the entire track can be embedded intact. Indeed, with this method, a several mm long track can be embedded and ultramicrotomed to create thin sections for TEM, XANES, nanoSIMS, STXM, and FTIR studies. The fact that the acrylic can be fully removed permits a better detection and analysis of carbonaceous materials that may be otherwise hidden by or confused with the embedding medium. Because the aerogel is compressed prior to embedding, during ultramicrotomy the cutting distance in “z” required to section the entire track is reduced by a factor of up to 100. Acrylic has better optical properties than epoxy and sulfur because it has a similar refractive index to aerogel. Its transparency makes it possible to optically observe a particle during all its processing which is important in ultramicrotomy. The potted butts have long term stability because acrylic, unlike sulfur, does not sublime. Therefore the samples can be stored and preserved for future sectioning. In addition, acrylic, unlike sulfur, microtomes very well and is very stable under the electron beam. The potted butt can also be examined with the scanning electron microscope (SEM) and the electron microprobe for general mineralogy studies, and with the ion microprobe (SIMS) for isotope studies.

CONCLUSIONS

We have developed an embedding technique that can be applied to particles inside aerogel tracks, such as the Stardust samples. We have shown that acrylic is an embedding medium that enables complete removal from ultramicrotomed particles still embedded in their aerogel matrix. With the use of a good compound microscope it is possible to section particles and fragments of particles as small as a micron across. This technique, which is currently being used for the preparation of Stardust samples, may be used in the future for samples collected in aerogel. The overall process may also have other applications to sample analysis when a removable embedding medium is needed.

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