DEVELOPMENT OF A TECHNIQUE TO PREPARE ~100 NM PRESOLAR SIC FOR ATOM-PROBE TOMOGRAPHY.
J. B. Lewis, P. Bhadharla, and C. Floss, Laboratory for Space Sciences, Physics Department, Washington University, St. Louis, MO 63130. USA. Email: jblewis@go.wustl.edu

Introduction: Presolar silicon carbide (SiC) grains have been studied extensively [1,2], including studies of their morphologies, crystallographies [e.g., 3], isotopic and trace element compositions [e.g., 4], and subgrains [e.g., 5]. Most SiCs are less than half a µm in diameter [2], but the smaller the size, the more difficult it is to achieve the isotopic and elemental efficiency and precision, as well as spatial and mass resolving power, to determine which extrasolar source produced a particular grain. Studies of a 0.2–0.5 µm fraction of SiC grains from Murchison CM suggest the distribution of grains from various stellar sources may be different for grains from smaller size fractions compared to grains from larger fractions [6]. Atom-probe tomography (APT) has been a successful technique for isotopic studies of very small (~3 nm) meteoritic nanodiamonds [7–9]. APT has also been used to reproduce nanoscale secondary ion mass spectrometry (NanoSIMS) isotopic and elemental data from 1–2 µm presolar SiC grains, while also yielding insight on elemental distributions and grain boundaries on the nm-scale [10–12]. We are conducting APT studies of small (100–200 nm) presolar SiC grains to investigate their elemental and isotopic distributions, trace element concentrations, subgrains, grain boundaries, surface features, and radial heterogeneities. These features will provide insights into the formation environments of these grains and their subsequent alteration in the interstellar medium and on their asteroidal parent bodies. We hope to evaluate if these small presolar SiC grains have experienced unique formation and/or alteration conditions compared to larger size fractions, and also to determine whether these small grains also accommodate subgrains.

Development of a sample preparation technique for APT of nanodiamonds was a multi-year process [7]. While 100–200 nm diameter SiC grains are almost two orders of magnitude larger than the 3 nm diameter average size of meteoritic nanodiamonds, they are still small enough to make preparation for APT analysis a challenge. We report here on our development of a procedure to prepare these grains for APT analysis.

Method: We selected 100–200 nm diameter SiC grains from polished sections of the meteorites MET 00426 CR, QUE 99177 CR [13], and Adelaide C-ung [14], which were previously characterized by Auger spectroscopy and NanoSIMS analysis.

We developed an electropolishing cell and procedure for in-house preparation of Cu half-grid sample holders for atom-probe sample mounting. This will allow for transmission electron microscopy (TEM) analysis of potential grain boundaries and subgrains prior to APT analysis.

The meteoritic polished sections were introduced into a focused ion beam (FIB) microscope. The grains we selected for APT analysis were relocated by secondary electron microscopy, a difficult task, as some of the surface was altered or covered by focused ion beam (FIB) liftout of nearby grains. After identifying a grain *in situ* in its host section (Figure 1a), we used a gas injection system and the ebeam to deposit a 'X'-shaped fiduciary marker, constructed of two 100 nm wide by 4 µm long by 150 nm or more deep rectangular patterns deposited simultaneously (Figure 1b). We found this fiduciary to be optimal for keeping the location of the grain centered later during the sharpening process. Fiduciaries over smaller areas allowed for too much Pt growth on adjacent surface features (Figure 2), while structures with a larger coverage made it impossible to target the grain later with sufficient precision. This fiduciary also serves as a sacrificial layer to protect the grain from the 30 kV Ga ions used to mill on top of the grain. An additional 150 nm-deep strap of Pt was also deposited using the Ga ion beam (Figure 2).

We conducted a standard FIB liftout procedure of an, optimally, 4.5 µm-long, 2.5 µm wide liftout with a 27 degree undercut angle (Figure 2). We placed the lifted-out slice with the SiC grain on a 2 µm-base atop a micropost, and attached it to the post with Pt deposition (Figure 1b). Annular rather than tetrahedral milling [8] was found to be optimal for sharpening the meteoritic thin section material while preserving a broad connection between the lift-out and the post.

Results: Our electropolishing cell is standardized for speedy and reproducible use and is cheaper and more optimized for our application than commercial units [15]. A number of half-grids are prepared for a finishing pass of FIB milling and deposition of grains onto the polished posts.

The FIB sample preparation procedure we have developed for 100–200 nm grains identified *in situ* in a polished section is straightforward and should take an experienced user about four hours per grain.

During development and testing of our procedure we prepared three APT samples, one from QUE 99177 and two from Adelaide (Figure 3). APT of these samples is still necessary to confirm proper positioning of the SiC in the sharp microtip and sample survivability.

Small voids, visible in the meteorite matrix, may be failure points under the stress from the high electric field utilized by APT.

Outlook: The top surface of each SiC grain was sputtered away during NanoSIMS analysis, so while APT analysis of the prepared microtips should preserve the interface between the current top surface of the grain with any contamination lying on top and the deposited Pt, it is the bottom surface of the grain that will be of most interest, in order to look for surface coatings and trace element depth profiles, as it has not been damaged by prior analyses.

Some SiC grains will be lifted out onto half-grids so that high-resolution elemental identification by electron energy loss spectroscopy (EELS) or energy-dispersive x-ray spectroscopy (EDXS) can be conducted by TEM. These samples will then be mounted for APT analysis, using a sample holder adapter.

Nanoscale studies of small presolar SiC grains using APT and TEM are methodologically viable as well as high in potential.

References: [1] Hynes K. M. and Gyngard F. (2009) *LPS XL*, Abstract #1198. [2] Zinner E. (2014) *Treatise on Geochemistry v1*, Elsevier, 181–213. [3] Daulton T. L. et al. (2003) *GCA, 67*, 4743–4767. [4] Amari S. et al. (1995) *Meteoritics, 30*, 679–693. [5] Hynes K. M. et al. (2010) *Meteoritics & Planet. Sci., 45*, 596–614. [6] Hoppe P. et al. (2010) *ApJ, 719*, 1370–1384. [7] Heck P. R. et al. (2014) *Meteorit. & Planet. Sci., 49*, 453–467. [8] Lewis J. B. et al. (2015) *Ultramicroscopy, 159*, 248–254. [9] Isheim D. et al. (2013) *M&M, 19, Suppl 2*, 974–975. [10] Lewis J. B. et al. (2014) *77th Meteoritical Society Meeting*, Abstract #5367. [11] Stadermann F. J. et al. (2010) *LPS XLI*, Abstract #2134. [12] Heck P. R. et al. (2010) *LPS XLI*, Abstract #2112. [13] Floss C. and Stadermann F. J. (2009) *ApJ 697*, 1242–1255. [14] Floss C. and Stadermann F. J. (2012) *Meteorit. & Planet. Sci. 47*, 992–1009. [15] Bhadharla P. and Lewis J. B. (2018) *LPS XLIX*, Abstract #2345.

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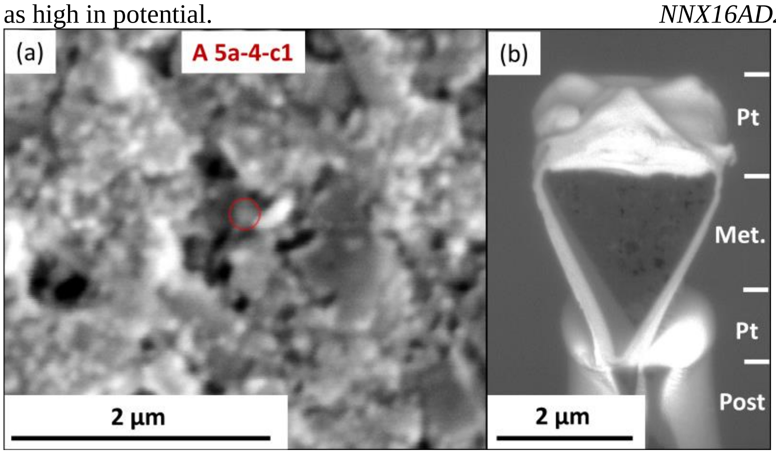

Figure 1: (a) Secondary electron image of Adelaide section with grain 5a-4-c1 circled. (b) Backscatter electron image of the lifted-out region (dark, low z-contrast "Met.") covered with Pt strap and fiduciary 'x' (bright, high z-contrast, top “Pt”); attached to a micropost ("post") using a Pt deposit (lower "Pt").

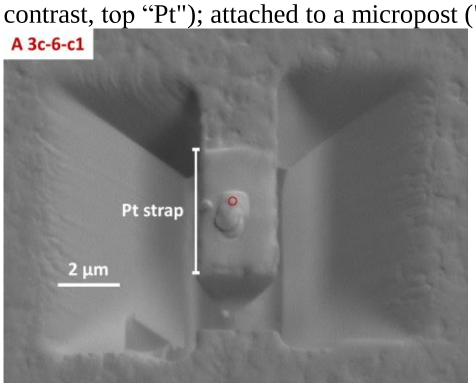

Figure 2: Topographic backscatter electron image of Adelaide grain 3c-6-c1 (red circle) covered with a Pt strap and a sub-optimal "button" fiduciary that deposited over too large an area and grew Pt on adjacent features.

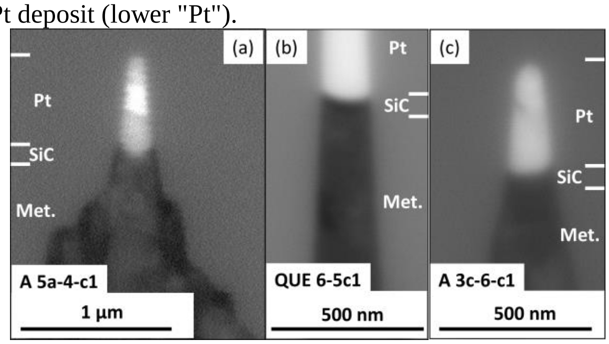

Figure 3: Backscatter electron images of three microtips containing presolar SiC grains lifted out in preparation for atom-probe analysis. “SiC” is the region where the grains are putatively located. The bright material is layers of protective Pt. Darker material is meteoritic. (a) Adelaide 5a-4-c1, (b) QUE 99177 6-5c1, and (c) Adelaide 3c-6-c1.