ATOM-PROBE TOMOGRAPHIC STUDY OF THE THREE-DIMENSIONAL STRUCTURE OF PRESOLAR SILICON CARBIDE AND NANODIAMONDS AT ATOMIC RESOLUTION.

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Introduction: Presolar grains are nanometer- to micrometer-sized particles that are present at ppm-level abundances in various primitive solar system materials [1]. Careful analysis of the composition of these grains can provide information about their origin in stellar environments. Particularly challenging is the analysis of nanometer-sized presolar diamonds [2] where most of our compositional knowledge comes from bulk measurements that are averaged over extremely large numbers of grains [e.g., 3]. An insufficient spatial resolution of many standard analytical techniques (e.g., SIMS) can also be a limiting factor in the analysis of ‘larger’ (i.e., micrometer-sized) presolar grains, when small sub-grains are studied. Since such inclusions are cogenetic with their host material, a detailed characterization of these sub-grains (and possibly their rims) can provide important additional constraints about the formation conditions in stellar environments [4, 5]. These examples indicate the need for a novel analytical approach that allows detailed elemental and structural characterizations at an atomic resolution.

We have recently begun to develop methodologies for atom-probe tomographic studies of presolar grains. Atom-probe tomography allows the analysis of sample volumes up to 100x100x100 nm^3 with the same atomic detection efficiency of >50% for all elements [6]. The three-dimensional position of each atom is recorded along with its mass-to-charge ratio by position-sensitive time-of-flight mass spectrometry. This makes it possible to reconstruct the full three-dimensional structure of the analysis volume and visualize elemental distributions in their spatial context. It is also possible to determine elemental (and to a limited extent isotopic) compositions of specific sub-volumes [6]. Even though atom-probe tomography is a well-established analytical technique in material sciences and the actual measurements are fairly routine, the sample preparation can be difficult, especially in the case of loose small particles. Here we describe our ongoing efforts to analyze presolar nanodiamonds and SiC grains in the atom-probe and present first results from the analysis of presolar SiC.

Experimental: Atom-probe measurements were performed at Northwestern University with a LEAP4000XSi Local-Electrode Atom-Probe (LEAP) tomograph, manufactured by Imago Scientific Instruments, with UV-laser assisted field-evaporation. Due to the different sample sizes, we used two fundamentally different approaches for the sample preparation of meteoritic nanodiamonds and presolar SiC. Common to both approaches (and all atom-probe measurements) is that the samples have to be prepared into a fine tip, as shown in Fig. 1.

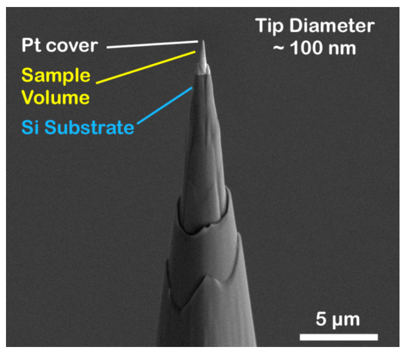

Figure 1: A specimen prepared into a fine tip for atom-probe tomography.

Nanodiamonds cannot be analyzed as loose powder, but significant experience exists with the characterization of nanometer-scale inclusions in a host matrix [6]. To utilize this experience, we have embedded a thin layer of nanodiamonds from the Allende meteorite [2] between layers of a Au host metal to form inclusions. This nanodiamond sandwich structure was then mounted and sharpened into a tip with the FEI Helios Nanolab focused ion beam (FIB) instrument at Northwestern University. Unfortunately, repeated LEAP measurements of these tips were unsuccessful, due to mechanical failure of the tips. A modified sample preparation approach that uses Ni and Pt instead of Au to embed the nanodiamonds is currently being evaluated.

For the measurements of SiC grains, we selected a large grain from the Murchison LS+LU fraction [7]. Previous NanoSIMS isotopic measurements have identified this grain as member of the ‘mainstream’ group of SiCs which have a likely origin in asymptotic giant branch (AGB) stars [1]. Imaging measurements of this 7 µm diameter grain also indicate the presence of numerous small inclusions of unknown composition. We performed a FIB extraction of some material from this grain in the direct vicinity to these inclusions. The extracted SiC material was then mounted and sharpened into a tip for subsequent LEAP analysis.

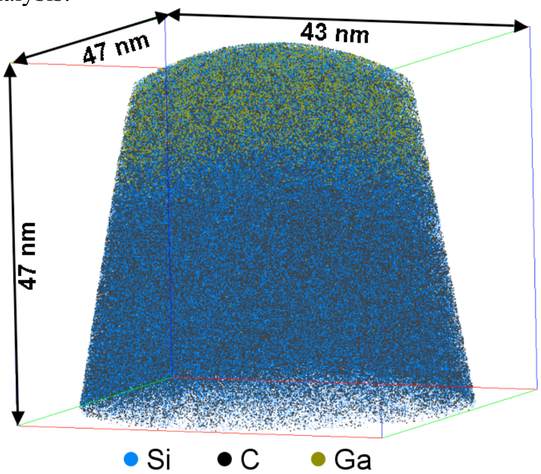

Figure 2: Three-dimensional LEAP reconstruction of a section of a presolar SiC grain.

Results: A three-dimensional reconstruction of the analysis volume from one SiC measurement is shown in Fig. 2. The reconstruction box is 43x47x47 nm^3 in volume and contains 1,304,409 atoms. Displayed are Si, C, and Ga atoms. The presence of Ga is due to the LEAP tip preparation by FIB milling with 5kV acceleration voltage. An extracted mass spectrum from the lower portion of this volume (Fig. 3) indicates that this region is affected very little by the Ga. The maximum Ga concentration, after background correction, in this part of this analysis is 138 ± 15 at. ppm (92 out of 666,468 individual atoms). We can therefore assume that this region is representative of the native composition of the presolar SiC grain. Since the analyzed volume in this case does not contain any inclusion, we can determine minor and trace element contents of the host SiC grain from the mass spectrum. Overall, the spectrum shows only few peaks other than those associated with Si, C, and some H. This suggests that the relatively high trace element abundances observed in many presolar SiC grains are not homogeneously distributed and might be carried by secondary phase inclusions. The mass resolution is sufficiently high to see that O is only present at a background level (20 ± 24 at. ppm). While the mass resolution of the time-of-flight mass spectrum is insufficient to resolve many isobaric interferences, such a spectrum can still be used to place lower limits on many isotopic ratios.

Conclusions: The atom-probe technique is a promising new analytical approach for the study of presolar grains or parts thereof. Continued studies will provide detailed information on the compositions of small inclusions in SiC and their relationship to the host grain. Possible coatings or rims on individual inclusions [5] can also be studied in detail. With respect to nanodiamonds, the atom-probe may in fact be the only technique capable of providing detailed elemental and limited isotopic information on individual grains. This may help address questions about whether all meteoritic nanodiamonds are presolar and whether there are different populations with distinct isotopic and minor element properties.

References: [1] Zinner E. (2004) in *Treatise on Geochemistry 1*, (eds. H. D. Holland and K. K. Turekian; vol. ed. A. M. Davis) 17. [2] Lewis R. S. et al. (1987) *Nature 326*, 160. [3] Huss G. R. and Lewis R. S. (1994) *Meteoritics 29*, 791. [4] Stadermann F. J. et al. (2005) *GCA 69*, 177. [5] Croat T. K. et al. (2003) *GCA 67*, 4705. [6] Seidman D. N. (2007) *Ann. Rev. Mat. Res. 37*, 127. [7] Amari S. et al. (1994) *GCA 58*, 459-470. **Acknowledgement:** This study is supported by NASA grant NNX09AC28G to FJS.

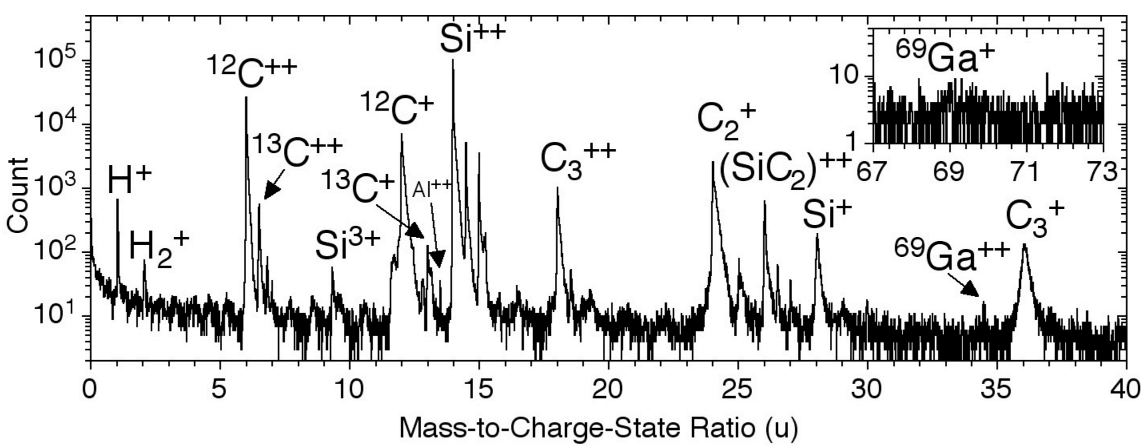

Figure 3: Extracted mass spectrum from the lower part of the analysis volume (below the Ga-rich region).