ATOM-PROBE TOMOGRAPHIC CHARACTERIZATION OF METEORITIC NANODIAMONDS AND PRESOLAR SiC.

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Introduction: Analysis of the isotopic and elemental compositions of presolar grains can provide information about the stellar environments in which they originated. However, many standard analytical techniques have insufficient spatial resolution to adequately study the smallest presolar grains. Particularly problematic are meteoritic nanodiamonds, which remain poorly understood, although they were the first presolar phase to be identified [1] and are the most abundant presolar grain type. The presence of Xe-HL in nanodiamonds indicates a supernova origin for at least some grains [1], but average C and N isotopic compositions of nanodiamonds are close to solar [2, 3]. The isotopic signatures observed could be hosted in different components in nanodiamond residues, including distinct populations of nanodiamonds with different isotopic compositions and origins [2, 3] or a distinct C phase [4]. However, such suggestions remain difficult to assess without a method to measure the C isotopic compositions of individual grains. Atom-probe tomography [5] offers a novel method for analyzing meteoritic nanodiamonds, as well as other small presolar grains such as sub-µm inclusions in larger host grains [6, 7]. Here we present results of our ongoing efforts to characterize meteoritic nanodiamonds using this approach. We also report new data from our work on a large inclusion-bearing presolar SiC grain [6].

Experimental: Atom-probe measurements were carried out at Northwestern University using the LEAP4000XSi Local-Electrode Atom-Probe (LEAP) tomograph with UV-laser assisted field evaporation.

We initially prepared nanodiamonds for LEAP analysis by embedding thin layers of nanodiamonds between layers of high purity Au to form a nanodiamond sandwich [6]. This structure was then mounted and sharpened into a tip with the FEI Helios Nanolab focused ion-beam (FIB) instrument at Northwestern University. Unfortunately, tips prepared in this manner consistently fractured during the measurements, typically at the boundary between the Au-nanodiamond-Au sandwich and a Ni cover layer that was added to assist in the FIB preparation. In our modified approach, Pt and Ni are used to create a sandwich structure. We expected that the reduced difference in evaporation rates between Ni and Pt would help both with the shaping of the tips and with the actual LEAP tomographic measurements. After deposition of a thin (170 nm) layer of Pt onto a high purity Ni substrate, we deposited nanodiamonds from suspension in alcohol and water. This was followed by another Pt layer over the nanodiamonds to protect and embed the grains, followed by a final 500 nm layer of Ni to serve as a cover for the FIB work, thus creating a Ni-Pt-diamond-Pt-Ni sandwich structure.

The SiC sample is a large (7 µm) mainstream grain from the LS+LU fraction of Murchison [8] and was extracted using standard FIB lift-out procedures, followed by mounting and sharpening into a tip for LEAP tomographic analysis [6].

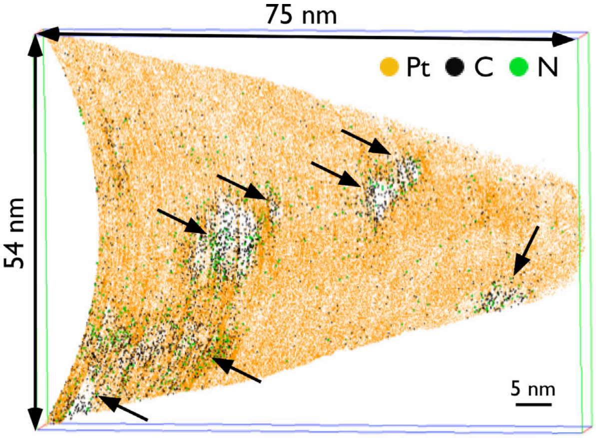

Fig. 1. Three-dimensional reconstruction showing meteoritic nanodiamonds from Allende embedded in a Pt matrix for LEAP tomographic analysis. Individual atoms are shown as colored dots.

Nanodiamonds: Sample tips prepared with synthetic detonation diamonds showed that we could successfully analyze tips made using the Ni and Pt sandwich structure. We have now prepared and measured similar samples using meteoritic nanodiamonds from Allende [1]. Figure 1 displays a three-dimensional reconstruction of several clusters of meteoritic nanodiamonds, indicated by the arrows, embedded in Pt. Shown is a 2 nm thick slice cut through the data set along the plane of the original diamond deposition layer. Nitrogen atoms in the analyzed volume are spatially correlated with the presolar nanodiamonds. Raw background-corrected $^{12}C/^{13}C$ ratios for the entire volume are 61 ± 4 for singly charged (C^+) and 54 ± 4 for doubly charged (C^{++}) ions. As the Pt matrix contains less than 0.1 at.% C, these values represent the average composition of the diamond clusters in the analysis volume. Identical measurements currently underway on synthetic diamond samples will provide an isotopic standard, allowing us to constrain the actual C isotopic composition of the Allende nanodiamonds.

SiC: Presolar SiC grains typically have relatively high trace element abundances, but our initial measurement of this grain [6] showed little evidence for trace elements in the volume analyzed, supporting observations that at least some of these elements are hosted within discrete inclusions in the SiC [e.g., 9, 10] and that such inclusions were not sampled by our analysis. Additional data for the same grain show the presence of Al at a concentration of ~280 at. ppm. Notably, the Al is not distributed homogeneously or as discrete inclusions, but rather is present in bands that extend with depth into the volume of the grain (Fig. 2). This banded structure may indicate that Al is segregated along planar defects in the SiC without forming discrete Al-bearing phases; such planar defects are common in some presolar SiC grains [11]. Recent TEM study of some mainstream SiC grains also showed variations in Al across the grain [10]. Aluminum may be present in solid solution in the SiC, possibly in the form of AlN, which is isostructural with SiC [11]. Nitrogen is also present in the SiC grain (~550 at. ppm), but it exhibits only a limited correlation with the Al bands (Fig. 2). $^{12}C/^{13}C$ ratios determined for the SiC grain from singly charged (C+) and doubly charged (C++) ions are 67 ± 8 and 38 ± 1, respectively. NanoSIMS measurement of the same grain indicates a $^{12}C/^{13}C$ ratio of ~76.

Conclusions: We have successfully carried out LEAP tomographic measurements on meteoritic nanodiamonds. Continued work will help address outstanding issues in understanding the origin of nanodiamonds, including the size and shape distributions of individual grains, their surface properties, major and minor elemental as well as isotopic compositions, and the identification of distinct groups in the nanodiamond population. Atom-probe tomography is also providing information on trace element abundances in presolar SiC and their distributions within the host grain.

References: [1] Lewis R. S. et al. (1987) *Nature* **326**, 160. [2] Russell S. S. et al. (1991) *Science* **254**, 1188. [3] Russell S. S. et al. (1996) *MAPS* **31**, 343. [4] Stroud R. M. et al. (2010) *MAPS* **45**, A198. [5] Seidman D. N. (2007) *Ann. Rev. Mat. Res.* **37**, 127. [6] Stadermann F. J. et al. (2010) *LPS XLI*, #2134. [7] Heck P. R. et al. (2010) *LPS XLI*, #2112. [8] Amari S. et al. (1994) *GCA* **58**, 459. [9] Bernatowicz T. J. et al. (1992) *LPS XXIII*, 91. [10] Hynes K. M. et al. (2010) *MAPS* **45**, 596. [11] Daulton T. L. et al. (2003) *GCA* **67**, 4743.

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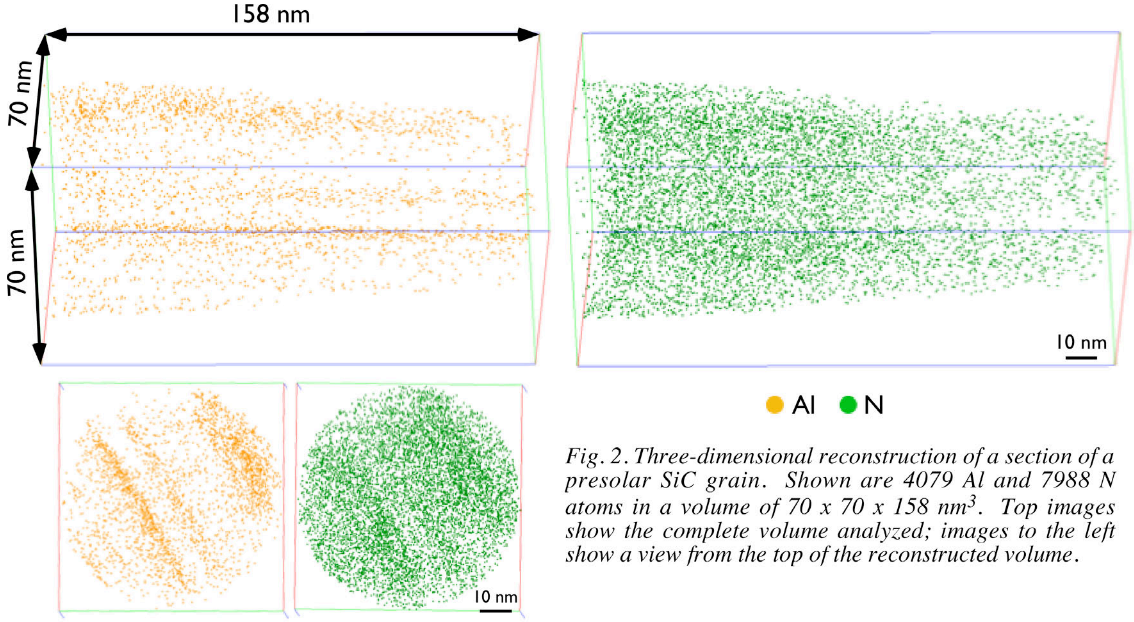

Fig. 2. Three-dimensional reconstruction of a section of a presolar SiC grain. Shown are 4079 Al and 7988 N atoms in a volume of 70 x 70 x 158 nm^3. Top images show the complete volume analyzed; images to the left show a view from the top of the reconstructed volume.