

ATOM-PROBE TOMOGRAPHIC ANALYSES OF METEORITIC NANODIAMOND RESIDUE FROM ALLENDE.

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Introduction: Meteoritic nanodiamonds are the most abundant type of refractory material associated with a presolar component. They were first isolated in the 1980s at the University of Chicago [1]. Yet their origins remain elusive because of their small size (avg. diam. ~3 nm [2]). Bulk analysis of nanodiamonds found unambiguous presolar isotopic anomalies in trace elements [e.g., 1], but no anomalies in the isotopic ratios of the major element C and the minor element N [3]. This, in part, has led to a hypothesis that a large fraction of the diamonds is not presolar [4]. Stroud et al. [5] recently hypothesized that some of the presolar isotopic anomalies could be carried by an sp² C phase that is also present in abundance. Unfortunately, individual diamonds are too small for isotopic analysis with conventional methods, even with the NanoSIMS ion microprobe (~50 nm spatial resolution). Nevertheless, measurement of the C isotopic composition of individual nanodiamonds and associated phases would provide insight into their origins: e.g., what is their presolar fraction? The atom-probe tomograph (APT) has the required sub-nm spatial resolution [6, 7] for such an analysis.

Recently, we presented the first APT analysis of three presolar SiC grains from the KJE separate from Murchison (one grain exhibited a sub-nm chemical heterogeneity) and an analysis of two synthetic SiC grains [8]. At the same time, an APT analysis of a large presolar SiC grain from the Murchison LS+LU separate has also been presented [9].

Nanodiamond APT analyses failed so far due to sample instability. Here, we present the first APT results of an atom-by-atom study of nanodiamond residue from Allende. Significantly improved sample stability was achieved with newly developed sample preparation techniques, which are also presented here.

Sample Preparation: We deposited Allende DM nanodiamond separate [1] suspended in a high-purity isopropyl alcohol-H₂O solution directly onto a commercially available Si flat-top microtip array sample mount. This technique eliminates the previously used time-consuming liftout and welding process. These welds proved to be too weak and lead to tip fracture before the diamond sample was reached during APT measurement [8]. To provide further stability, the open pore space in the post was filled with Al₂O₃ and W using atomic-layer deposition (ALD) [10]. A cap layer of Co was sputter-deposited to protect the specimen within the micropost from 30 kV Ga sputtering during subsequent focused ion beam (FIB) milling.

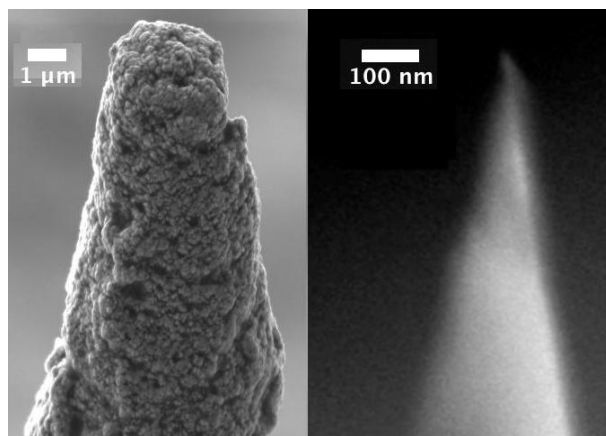


Figure 1: SEM images of Si a micropost with nanodiamonds embedded in an Al₂O₃-W matrix and coated with Co. Tip before (left) and after sharpening (right) where the Co cap is almost completely removed.

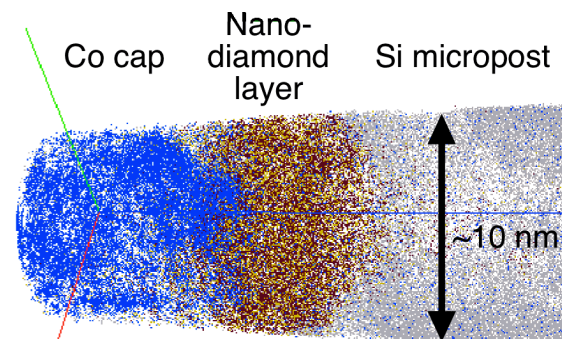


Figure 2: 3D-tomographic reconstruction of a nanodiamond sample deposit. Each dot represents a detected atom, Co in blue, Si in grey, C in brown, H in yellow.

Annular FIB milling shaped the post into the required sharp tip [11] where only a small fraction of the Co cap remained. FIB milling was completed at Argonne National Laboratory with a Zeiss 1540 Cross-beam workstation and at Northwestern University with a FEI Helios NanoLab.

APT analysis was performed with a Cameca LEAP4000XSi tomograph equipped with a pulsed and highly focused UV (355 nm wavelength) laser at Northwestern University. The samples were held at 118 K. A laser energy of 300 pJ per pulse and a pulse repetition rate of 250 kHz was used.

Results & Discussion: With three tips we acquired a complete tomographic dataset from the Co cap, through the C-rich sample deposition layer, down to the Si post. We illustrate this in the 3D tomographic reconstruction of one sample shown in Fig. 2. Carbon atoms are shown as brown dots in Fig. 2. We note that the contrast between the nanodiamonds and the associated sp^2 C phase is very low. We are currently exploring different approaches to enhance this contrast to visualize the diamonds. Compared to our previous analyses not employing a focused UV-laser, mass spectra now have a dramatically reduced background signal (Fig. 3). We attribute this primarily to reduced thermal tails due to the smaller laser spot of the focused laser. Hence, many peaks of interest are clearly separated, including ^{13}C peaks (Fig. 3).

After performing a simple background correction by subtracting the baseline we are able to obtain raw C and Si isotopic ratios. We use the Si micropost as an analytical Si isotopic standard. Relative Si isotopic ratios (δ -values) of four different sub-volumes of the same standard vary by less than 2% for singly-charged ions and by 20% for doubly-charged ions.

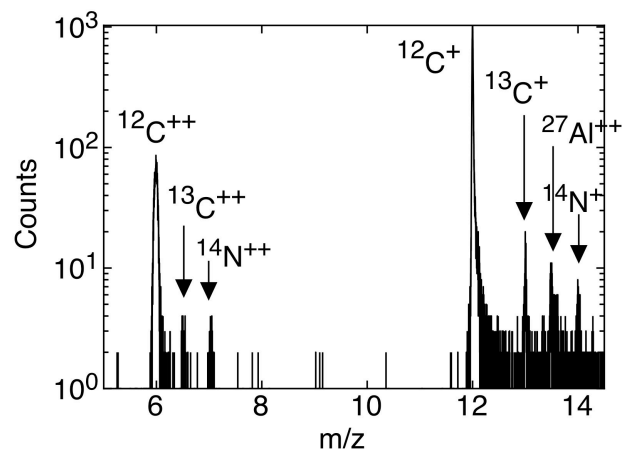


Figure 3: Mass spectrum of nanodiamond separate. The mass-to-charge state ratio (m/z) range was selected to show C isotopic peaks.

Within 2σ uncertainties, the determined Si isotopic ratios are identical and within 3% and 15% of normal Si, respectively. No correlation of Si isotopic ratios with DC voltage applied to the tip is observed. Raw, background-corrected $^{12}\text{C}/^{13}\text{C}$ ratios of the nanodiamond sample volumes of two tips are 58 ± 6 and 65 ± 6 (2σ) for C^+ and 68 ± 16 and 49 ± 10 (2σ) for C^{++} . The third sample analysis yielded low C counts. All samples were very clean and no “terrestrial dirt” with unambiguously normal C was measured that could be used as a reference. Analysis of C isotopic standards will need to be performed to correct for possible instrument bias, before a cosmochemical interpretation can be given.

Conclusions & Outlook: New instrument developments coupled with optimized analytical conditions lead to mass spectra with very high signal-to-noise ratios. We show that all C and Si isotope peaks are clearly resolved. With the fixed analysis conditions, instrumental bias for Si isotopes is below 3% for singly charged ions and below 20% for doubly charged ions.

We will continue to investigate potential instrumental bias (particularly C) by analyzing more standards. We will also analyze more samples of nanodiamond residues from Allende and other meteorites. Additionally, we will further develop and improve sample preparation and techniques for data visualization and analysis. Subgrains in presolar SiC and other types of presolar materials will be also considered for future APT analysis.

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