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Correlated Atom-Probe Tomography and Transmission Electron Microscopy of Meteoritic Nanodiamonds

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Primitive chondritic meteorites contain high concentrations of ~3 nm nanodiamonds (NDs) [1]. NDs are isolated from meteorites by acid dissolution, and these isolates exhibit isotopic anomalies in trace elements, notably Xe, which suggest at least some are presolar in origin [2]. The carbon isotopic composition would provide a better indication of origin, but ND isolates are not pure, containing particles of amorphous, sp2-bonded carbonaceous particles of potentially different origins than the NDs [3]. We are applying atom-probe tomography (APT) to measure the $^{12}C/^{13}C$ composition of individual NDs. To identify NDs, it is necessary to confirm the size, density, and structure of the particles in reconstructed APT nanotips [4–6]. Transmission electron microscopy (TEM) is proving increasingly useful for correlated studies of nanostructures and nanoparticles with APT [7–9]. We report the results of correlated TEM/APT studies on two samples containing carbonaceous acid residue from the meteorite Allende.

A droplet of ND-containing Allende residue suspended in deionized water was deposited on a Pt substrate, while ultrasonicating to disperse the particles. The resulting deposit was covered by another layer of sputter-deposited Pt. Focused Ion-Beam (FIB) milling was utilized to lift out sections of the multilayer and attach them to posts on a Cu TEM half-grid. Samples were FIB-sharpened into nanotips designated HG01-B and -C, each with ~20 nm apex radii, suitable for APT (Fig. 1a). These nanotips were studied by TEM using a JEOL 2100F instrument at Washington University. Following TEM, a ~50 nm Ni-layer was sputter-deposited on the nanotips. APT was conducted using a LEAP 4000X Si at Northwestern University. The last few hundred-million atoms were field evaporated from the nanotips utilizing ~10 kV DC voltage and thermal activation from a base temperature of 60 K combined with 80 pJ pulses from a 355 nm laser. APT reconstructions gave 3D positions and mass-to-charge-state ratios of ~50% of the atoms within the volume analyzed.

Conventional TEM bright-field and scanning HAADF images (Fig. 1b–d) show discrete, low-density features 1–10 nm in diameter. Images taken at tilt angles from 0–35 degrees demonstrate that these features are coplanar, consistent with NDs embedded in Pt. However, they are also consistent with amorphous C or voids in the acid residue/Pt interface. APT reconstructions reveal hydrocarbon contamination on nanotip HG01-C, deposited by the TEM beam (Fig. 1e). ND deposition layers were identified in reconstructions of nanotips HG01-B and -C, distinguished from hydrocarbon contamination by location in the Pt, planar orientation, and the presence of residual salts and acids from separation treatments. While the deposition layers are filled with C at significantly higher atomic density than the surrounding Pt, no discrete features were observed with the size and density expected for NDs.

The features observed by TEM suggest three possibilities. They are either voids created as Pt sputter-coated a rough sample deposit, clumps of amorphous C, or NDs that were undetected by APT. A thick

acid residue may weaken the attachment of NDs to the Pt, leading to NDs being plucked from the nanotips mostly whole during field-evaporation. In all cases, the C in the reconstructed deposition layers most likely represents amorphous C.

Based on the results of this study, we will target lower-density regions of the acid residue deposit for our next samples. Correlated TEM/APT of nanotips containing only isolated, nanodiamond-sized carbonaceous regions, as has been previously observed in some cases [4–6], should resolve the question of whether we are imaging voids or clumps of acid residue in the TEM, and minimize the deleterious effects of a thick deposit on APT reconstructions [10].

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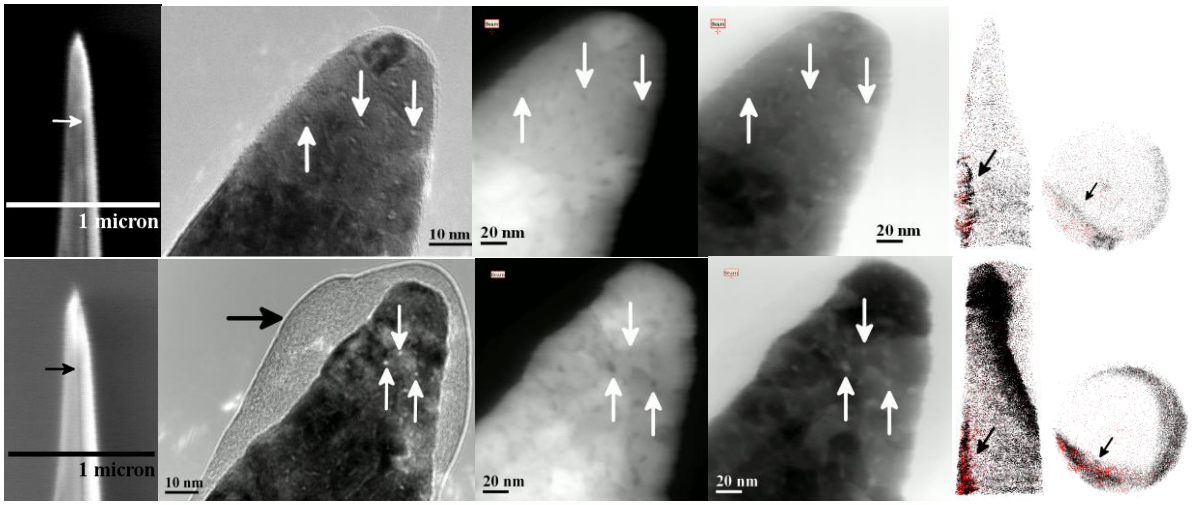

Figure 1: Secondary electron images of nanotips HG01-B (top row) and HG01-C (bottom row) prior to TEM analysis **(a),** showing the nanodiamond deposition layer (arrow) between Pt layers. TEM bright-field **(b)** as well as high angle annular dark field **(c)** and bright field **(d)** images show nm-sized low-density features, as well as hydrocarbon contamination on HG01-C. APT 3D maps **(e)** of carbon (black) and NaO (red) ions show the carbon-filled deposition layers, and, for HG01-C, the hydrocarbon cap.

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