METEORITIC NANODIAMOND ANALYSIS BY ATOM-PROBE TOMOGRAPHY J. B. Lewis[1,3], D. Isheim[4], C. Floss[1,3], T. Daulton[2,3], D. N. Seidman[4], P. R. Heck[5,6], A. M. Davis[6,7,8,9], M. J. Pellin[6,7,8,9,10,12], M. R. Savina[6,9,10,12], J. Hiller[10,12], A. Mane[10,12], J. Elam[10,12], O. Auciello[10,11,12], T. Stephan[6,7,9,10,12]. [1]Laboratory for Space Sciences, [2]Center for Materials Innovation, [3]Physics Dept., Washington University, St. Louis, MO 63130. [4]Center for Atom-Probe Tomography, Dept. of Materials Science and Engineering, Northwestern University, Evanston, IL 60208. [5]Dept. of Geology, The Field Museum, Chicago, IL 60605. [6]Chicago Center for Cosmochemistry, [7]Dept. of Geophysical Sciences, [8]Enrico Fermi Institute, [9]University of Chicago, IL 60637. [10]Materials Science Division, [11]Center for Nanoscale Materials, [12]Argonne National Laboratory, Argonne, IL 60439. (*email: jblewis@go.wustl.edu).

Introduction: Meteoritic nanodiamonds were initially isolated in 1987, when they were shown to be associated with highly anomalous Xe isotopic ratios [1]. Bulk analyses of nanodiamond residues show isotopic anomalies in trace elements such as Xe, Ba, Pd, and Te [1–4], indicating a supernova origin, but near-solar $^{12}C/^{13}C$ and $^{14}N/^{15}N$ ratios [5, 6], possibly suggesting a solar system origin for some grains [e.g., 7]. Additionally, recent research demonstrates the presence of abundant glassy carbon in meteoritic nanodiamond residues [8], which leads to additional uncertainty about the carrier(s) of the observed isotopic anomalies and the origin of the nanodiamonds. Measurement of the $^{12}C/^{13}C$ ratios of individual meteoritic nanodiamonds can help determine whether isotopically different nanodiamond (or glassy carbon) populations are present in the residues and can provide additional constraints on their origins. Such analyses have only recently become feasible through the novel application of atom-probe tomography (APT) [9, 10]. We report herein new analyses of Allende nanodiamond residues and synthetic detonation nanodiamonds in our continued effort to determine the C isotopic ratios of individual nanodiamonds.

Experimental: We used focused ion-beam (FIB) lift-out and milling to prepare ~25 nm radius APT tips of nanodiamonds embedded in a Pt matrix [e.g., 9]. Two samples contained detonation-prepared synthetic nanodiamonds, and four contained Allende DM nanodiamond residue. FIB milling and APT were performed at Northwestern University with the FEI Helios Nanolab FIB and Cameca LEAP4000XSi, respectively. Atom-by-atom laser-assisted field evaporation of the microtips was conducted in the LEAP tomograph by applying up to 5 kV dc and 250–500 kHz, 0.15 nJ pulsing from a 355 nm UV laser, at a base temperature of 103 K in a vacuum of $2–5\times10^{-9}$ Pa. While data collection typically ended when the tip fractured, in one case the tip did not fracture and its radius was measured after the APT run by SEM (Fig. 1).

We used two different methods to calibrate the reconstruction volume for the Pt matrix. In one case we identified the (002) crystallographic planes of the Pt and calibrated the reconstruction to within a 2.8% relative error based on the known lattice spacing. In the other case, a V/r ratio of 127.3 V/nm for calculation of the evaporation field, E, could be derived from the diameter of the tip after the LEAP analysis (Fig. 1). We also performed more detailed analysis of data sets from prior APT measurements on two meteoritic and one synthetic nanodiamond tips [9].

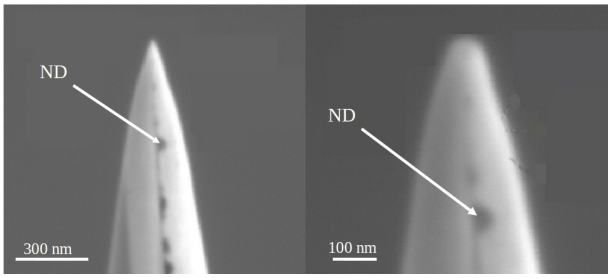

Figure 1. The same tip before and after a LEAP tomographic experiment. The lighter material is the Pt matrix, while the darker material along the uneven line down the center is the nanodiamond (ND) residue.

Carbon Loss During Field Evaporation: While we are confident of our length scale for the Pt matrix, the evaporation field for diamond is significantly higher than that of Pt (or any other viable substrate material), ~100 vs. ~45 V/nm at 78 K [11, 12]. Nanodiamond inclusions in the Pt matrix will, therefore, resist field evaporation until the surrounding Pt has been removed, exposing a smaller-radius nub on the larger tip. The higher evaporation field for C leads to preferential magnification of the C in the x- and y- directions, with regions of reduced density ('voids') in the Pt matrix and spatial distributions of C that extend outside of these voids, which trace the outlines of the nanodiamonds. Additionally, we have observed sudden spikes in the detection of C during the evaporation of nanodiamond inclusions, suggesting that clusters of C atoms are being removed from the tip, due to the weaker bonds in the Pt-nanodiamond interface relative to the diamond lattice bonds. The result is a decreased detection efficiency for nanodiamond C; indeed, C detections per nm^3 in the Pt voids are below the anticipated 1000 C atoms/nm^3 (based on 50 % detection of the ~2000 C atoms present

in a 3 nm diameter nanodiamond), even after taking the preferential magnification into account.

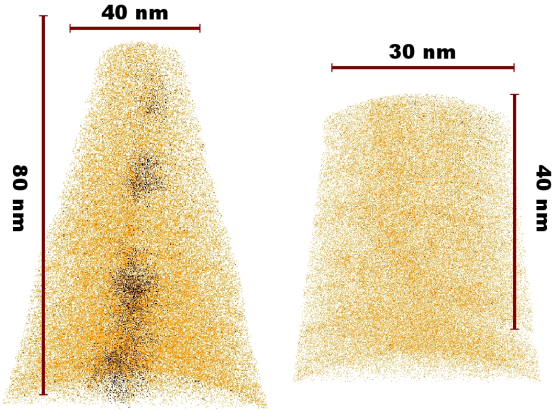

Figure 2. Three-dimensional APT reconstructions of samples with meteoritic (left) and synthetic (right) nanodiamonds embedded in a Pt matrix. Dots represent individual atoms of C (black) and Pt (orange). Note that no NDs are present in the analyzed volume on the right.

Results and Discussion: Figure 2 shows 3D APT reconstructions of two representative data sets, one with and one without nanodiamonds. Two of the synthetic nanodiamond tips did not contain any nanodiamonds. The volume density of C in these two data sets is 0.038 and 0.042 atom/nm^3, compared to typical densities of ~0.15 – 0.24 atom/nm^3 for nanodiamond-bearing data sets, providing a baseline for the amount of C contamination present in the Pt matrix from sources other than nanodiamonds.

Because of the comparatively low number of C counts for the nanodiamonds, we report background corrected $^{12}C/^{13}C$ peak ratios for entire tips, rather than for individual nanodiamonds, as a way to improve counting statistics. Based on total monatomic C counts (C^+ and C^{++}), two of the meteoritic nanodiamond samples, and the single synthetic-nanodiamond bearing microtip, have $^{12}C/^{13}C$ peak ratios of 57 ± 5 to 58 ± 6, while the other five meteoritic nanodiamond microtips have peak ratios between 74 ± 8 and 87 ± 12 (Fig. 3). The peak ratios calculated from only the C^+ or C^{++} peaks are consistent with the overall ratios in four of the microtips, but are more variable in three others. The difference can be attributed to low signal-to-noise in two microtips (experiments 15005 and 16119 in Fig. 3) with the largest discrepancies, but instrumental artifacts may also contribute to the variations.

Our continuing research will focus on identifying conditions for improved field evaporation of C from the nanodiamonds, and optimizing data processing to obtain meaningful $^{12}C/^{13}C$ ratios for individual nanodiamonds. Slower evaporation rates may help to stabilize the evaporation of C and increase the overall detection efficiencies. Varying parameters such as laser energies and tip temperatures should permit the determination of the optimum conditions for stable evaporation of C from the nanodiamond inclusions. Additional calibration of reconstruction procedures and refinement of background corrections will help us to obtain statistically significant $^{12}C/^{13}C$ ratios for individual and/or clusters of nanodiamonds. Finally, more measurements of standard samples are needed, including ones of "anomalous standards" with a broad variation of known C isotopic ratios.

References: [1] Lewis et al. (1987) *Nature* **326**, 160. [2] Lewis et al. (1991) *LPS XXII*, 807. [3] Richter et al. (1998) *Nature* **391**, 261. [4] Maas et al. (2001) *MAPS* **36**, 849. [5] Russell et al. (1991) *Science* **254**, 1188. [6] Marty et al. (2011) *Science* **322**, 1533. [7] Dai et al. (2002) *Nature* **418**, 157. [8] Stroud et al. (2011) *ApJ Lett.* **738**, L27. [9] Stadermann et al. (2011) *LPS XLII*, #1595. [10] Heck et al. (2011) *LPS XLII*, #2070. [11] Tsong (1978) *J. Phys. F: Met. Phys.* **8** 1349. [12] Southworth & Ralph (1969) *J. Micro.* **90**, 167.

This work is supported by NASA grant NNX09AC28G (C.F.). The LEAP at NUCAPT was purchased and upgraded with funding from NSF-MRI and ONR-DURIP grants. We thank R. S. Lewis for providing the Allende nanodiamond sample.

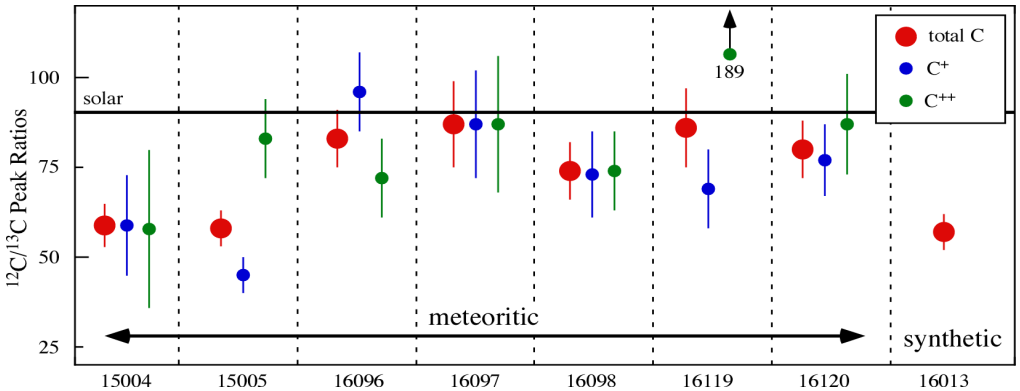

Figure 3. $^{12}C/^{13}C$ peak ratios in meteoritic and synthetic nanodiamond microtips for different experiments.