# ATOM-PROBE TOMOGRAPHIC ANALYSIS: TOWARDS CARBON ISOTOPE RATIOS IN INDIVIDUAL NANODIAMONDS.
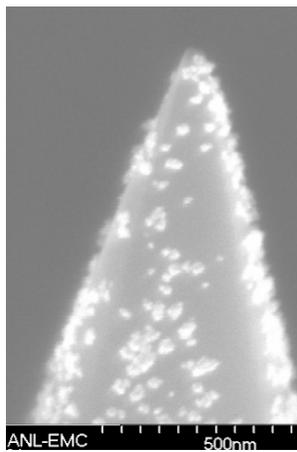
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**Introduction:** Twenty-five years after the discovery of meteoritic nanodiamonds, their origins are still unknown. Isotopic anomalies in Xe, Ba, Pd, and Te found in bulk samples of nanodiamonds can be only explained by stellar nucleosynthesis and hence indicate a presolar origin [1–4]. In contrast, C and N isotopic ratios of bulk nanodiamonds are close to solar and suggest formation within the Solar System [5]. Carbon isotopic analyses of individual nanodiamonds are required to help constrain their origin. A knowledge of the distribution of $^{12}C/^{13}C$ ratios of individual meteoritic nanodiamonds would help to identify populations of diamonds with different origins—analogous to the classification of presolar SiC grains. What fraction of nanodiamonds is presolar? What are the different sources of the presolar nanodiamonds? Are they mainly stellar, such as supernovae [1] or AGB stars [6], or are nanodiamonds shock products of organic matter in the interstellar medium [7]? The problem has become more complicated since the recent discovery that meteoritic nanodiamond residues contain not only diamonds but also disordered $sp^2$ bound glassy carbon [7]. Thus, the isotopic anomalies might be carried by the nanodiamonds, by the glassy carbon, or by both. The atom-probe tomograph (APT) is currently the only instrument that has the spatial resolution and sensitivity to analyze the C isotopic compositions of individual meteoritic nanodiamonds (avg. diameter ~3 nm [8]). We have developed sample preparation and analytical protocols that lead to stable tomographic analyses of nanodiamonds at the required sub-nm spatial resolution [9–13].

**Samples & Methods:** We prepared samples by direct deposition of Allende DM nanodiamond residue [14] suspended in an isopropanol-water solution onto pre-sharpened Si microtips at the Field Museum. By carefully adjusting the diamond concentration, the dispersion on the tip surfaces can be optimized. To provide mechanical sample stability we used atomic layer deposition of $Al_2O_3$ and W [15] at Argonne National Laboratory (ANL) to fill open pore space. Initially, we also prepared a few samples with direct deposition of the sample onto flat-top microtip arrays and then used fo-cused ion beam (FIB) milling to sharpen the tips [16,11,13]. Two types of synthetic nanodiamond were used as analytical standards: detonation nanodiamonds obtained from Lawrence Livermore National Laboratory, which were deposited onto the tips analogously to the meteoritic nanodiamonds; and ultrananocrystalline diamonds (UNCD®), which were grown directly on the presharpened microtips at ANL (Fig. 1). Analyses were performed with a local electrode atom-probe LEAP tomograph 4000XSi (Cameca Instruments) at the Northwestern University Center for Atom Probe Tomography [17,18].

**Results & Discussion:** The best results were obtained with nanodiamonds on the presharpened microtips. The distribution of C is heterogeneous and clumpy. These samples were the most stable during field evaporation and had the best dispersion, hence, we were able to analyze individual meteoritic nanodiamonds and clusters of them, and we obtained mass spectra of these nm-sized regions of interests [13]. The number of C atoms (~2000) in subvolumes of nominal size of nanodiamonds is consistent with what is expected from TEM studies [8]. The samples on the flat-top microtips were slightly less stable—possibly because of the higher abundance of closed pore space that could not be filled and stabilized with ALD deposition, which could have occasionally triggered tip fractures. The lack of dispersion in these samples provided no contrast, and, unlike the presharpened microtip sample, single nanodiamonds could not be identified. We generally obtained $^{12}C/^{13}C$ peak ratios much smaller than expected; this was true for



**Fig. 1.** SEM image of a Si micropost with UNCD® nanodiamonds deposited directly onto a presharpened Si tip.
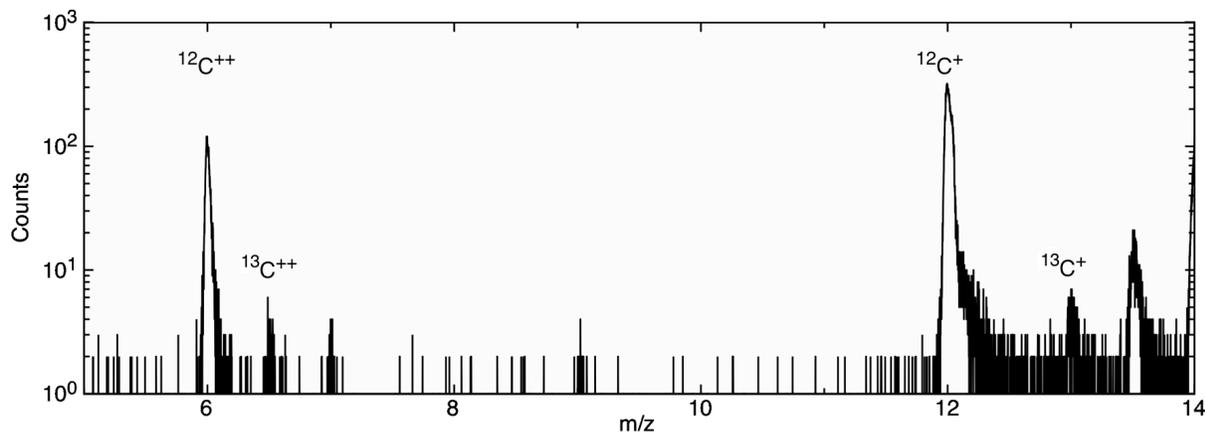
bulk and individual nanodiamonds, for meteoritic and synthetic nanodiamonds, and for both singly and doubly charged ions. The cause of this is a combination of different effects: an unresolved $^{12}C^1H$ hydride interference with $^{13}C$ (mainly important for singly-charged ions); a small uncertainty in the background correction for the $^{13}C$ peaks; and an instrumental bias that results in an apparent mass fractionation. The hydride interference is hard to control and strongly depends on the residual gas pressure in the analysis chamber. Hydrogen may also be released from the sample itself and contributes to hydride formation. The probability of forming hydrides of doubly-charged C ions is much smaller than for singly-charged ones; thus, the magnitude of the hydride interference with $^{13}C^{++}$ should be much smaller than on $^{13}C^+$. The background is usually only a few counts and therefore only a small correction is necessary. The doubly charged $^{13}C$ peaks can, however, be very small and therefore the uncertainty in the background correction becomes important. By further optimizing the analytical conditions, we can obtain larger signals for doubly charged ions and can reduce these uncertainties. By comparing peak ratios from doubly-charged ions with the ones from singly-charged ones, we can quantify the hydride interference. To correct for the instrumental bias we need to analyze synthetic nanodiamonds that have different isotopically anomalous C compositions. Analyzing a suite of such samples should enable us to determine an empirical correction for the instrumental bias that we can apply to obtain true isotope ratios for the analyzed individual meteoritic nanodiamonds. This will help us answer the questions concerning the origin of the meteoritic nanodiamonds. We are preparing isotopically anomalous UNCD® LEAP samples at ANL.

**Summary:** We successfully analyzed individual meteoritic and synthetic nanodiamonds with highly improved sample stability. The direct deposition or growth of nanodiamonds onto presharpened microtips provides

better stability during LEAP tomographic analysis, eliminates FIB-milling and can provide a well-dispersed sample. The time-of-flight mass spectra have a low background and display well defined C peaks (Fig. 2). Instrumental bias is present and needs to be corrected. Tomographic reconstructions to a depth of about 100 nm were performed.

**References:** [1] Lewis R. S. et al. (1987) *Nature 32,*160–162. [2] Lewis R. S. et al. 1991, *LPSC* 22, 807 [3] Richter S. et al. (1998) *Nature* 391, 261–263. [4] Maas R. et al. (2001) *MAPS* 36, 849–858. [5] Russell S. S. et al. (1996), *MAPS* 31, 343. [6] Verchovsky A. B. et al. (2006) *ApJ* 651, 481. [7] Stroud R. M. et al. (2011) *ApJL* 738, L27. [8] Daulton T. L. et al. (1996) *GCA* 60, 4853–4872. [9] Heck P. R. et al. (2010) *LPS XLI*, #2112. [10] Stadermann F. J. et al. (2010) *LPS XLI*, #2134. [11] Heck P. R. et al. (2011) *LPS XLII*, #2070. [12] Stadermann F. J. et al. (2011) *LPS XLII,* #2134. [13] Heck P. R. et al. (2011) Workshop on the Formation of the First Solids of the Solar System, Kauai, #9096. [14] Lewis R. S. et al. (1989) *Nature* 339, 117–121. [15] Elam J. W. et al. (2006) *Appl. Phys. Lett.* 89, 053124. [16] Larson D. J. et al. (1999) *Ultramicroscopy* 79, 287. [17] Seidman D. N. and Stiller K. (2009) *MRS Bull.* 34, 717–721. [18] Miller M. K. and Forbes R. G. (2009) *Mater. Charact.* 60, 461–469.

**Fig. 2.** Time-of-flight mass spectrum of Allende DM nanodiamond sample integrated for one microtip. Note the sharp peaks and low background. The mass-to-charge state ratio range was selected to show peaks of C ions.