

The Enigmatic Origin of Meteoritic Nanodiamonds – An Approach with Atom-Probe Tomography

Philipp R. Heck^{1,2}

¹ Robert A. Pritzker Center for Meteoritics and Polar Studies, The Field Museum of Natural History, Chicago, USA.

² Chicago Center for Cosmochemistry and Department of the Geophysical Sciences, The University of Chicago, USA.

Nanodiamonds are found in primitive meteorites that did not experience high degrees of thermal metamorphism on their parent asteroids [1]. Because of their resistance to acids, they can be extracted from meteorites by acid-dissolution [2]. Through mass spectrometric bulk analyses of acid residues, nanodiamonds were identified as the carriers of an isotopically anomalous xenon component and were therefore interpreted to have interstellar or circumstellar origins that predate the formation of the Solar System [2]. This presolar interpretation is supported by the discovery of isotopic anomalies of the trace elements palladium, tellurium and barium in nanodiamond-containing acid residues [3,4]. However, the carbon and nitrogen isotopic compositions of the acid residues are not anomalous and are consistent with formation of nanodiamonds in the Solar System [5]. To address these divergent genetic interpretations, which are based on mass spectrometric bulk analyses of a large number of nanodiamonds, isotopic analyses of individual nanodiamonds are needed. Such single particle analyses will reveal if there are different populations of nanodiamonds with different carbon isotopic compositions that would point to formation in different environments. Due to their small size (~2 nm in diameter [6]) single nanodiamond isotopic analyses have proven to be impossible with conventional mass spectrometry techniques. Atom-Probe Tomography (APT) has been identified as the only current technique that can obtain carbon isotopic compositions of individual meteoritic nanodiamonds [7]. In this paper I will review recent advances with the ultimate goal of constraining the origin of meteoritic nanodiamonds using on APT [e.g., 7–9].

Efforts to analyze meteoritic nanodiamonds with APT are lead by two groups in close collaboration with the Northwestern University Center for Atom-Probe Tomography (NUCAPT). One group is based at the Chicago Center for Cosmochemistry (The Field Museum of Natural History, The University of Chicago, Argonne National Laboratory) and the other one at Washington University in St. Louis. In collaboration the two groups developed three different methods that have been applied to prepare nanodiamonds for APT [7]. All methods used aliquots of the same sample: A nanodiamond-bearing acid residue prepared from the Allende meteorite [10] that was suspended in an isopropanol-water mixture. The first sample preparation method consists of drop-casting the sample with a micropipette directly onto a presharpended silicon microtip array (distributed by Cameca Inc.). After drying, open pore space was coated with alumina and tungsten by atomic layer deposition (ALD). This provided enhanced sample stability during APT analysis. Sample stability was highest with this method because it did not require the use of focused ion beam (FIB) milling. The FIB can create defects leading to less stable samples in APT. However, sample thickness is difficult to control with drop-casting directly onto microtips and therefore FIB-based methods were also used. These were two different methods where nanodiamonds were drop-cast either directly onto a silicon wafer and then ALD coated and sputter coated with a protective conductive cobalt layer or drop-cast onto a sputter-deposited nickel and platinum layer and then coated again with platinum and nickel (sandwich method). Subsequently, using SEM and/or Auger Nanoprobe

an area of interest containing the thinnest identifiable layer was selected. A FIB microscope was then used to lift out wedges, attach them to prefabricated flattop arrays (distributed by Cameca Inc.) and sharpen them with annular milling to a tip radius of <50 nm. A laser-assisted local electrode atom probe Cameca LEAP 4000 X Si [e.g., 11,12] was used for the analyses of the samples. We used synthetic nanodiamonds (UNCD and detonation nanodiamonds) as reference materials [7–9].

The tomographic datasets clearly reveal areas with high concentrations of carbon that are attributed to individual or small clusters of nanodiamonds with the meteoritic as well as the synthetic samples. This implies that nanodiamonds seem to be distinguishable based on density from other forms of carbon that are also present in the sample. TEM analyses confirmed the presence of disordered sp² carbon (similar to glassy carbon) in the meteoritic acid residues besides the nanodiamonds [13].

Analyses with APT of synthetic nanodiamonds revealed nominally anomalous ¹²C/¹³C ratios that were significantly lower than the expected terrestrial ratio. This was partly attributed to an isobaric interference of the (¹²C¹H)⁺ hydride on ¹³C⁺ leading to an overestimate of ¹³C. In contrast to singly-charged ions doubly-charged ions should not be significantly affected by hydrides. However, also the ¹²C²⁺/¹³C²⁺ ratio was significantly lower than the terrestrial ratio expected for the synthetic reference materials [7]. This bias was explained by a strong detector dead time, undercounting effect: The burst-like field evaporation of carbon from nanodiamonds (in contrast to many other materials) leads to too many simultaneous detector events that even the multi-delay line multichannel plate detector of the LEAP cannot keep up with [8]. Stephan et al. [8] developed a correction method based on Poisson statistics of correlated detection events from different isotopes of a single element. This correction was successfully applied to the tomographic dataset of synthetic nanodiamonds and resulted in correct carbon isotope ratios within 2σ uncertainty [8]. Lewis et al. [9] presented an alternative correction method based on iterative proportional fitting. Both correction methods were applied to obtain corrected ¹²C/¹³C ratios of individual and small clusters of meteoritic nanodiamonds.

Much of the effort went into optimization of sample preparation, analytical conditions and development of correction [7–9]. From the meteoritic nanodiamonds analyzed so far none of them contained significantly anomalous carbon isotopes. This implies that the fraction that carries the nucleosynthetic isotope anomalies is small. More meteoritic nanodiamonds will be analyzed with APT to quantitatively constrain the presolar fraction [14].

References:

- [1] GR Huss and RS Lewis, *Geochimica et Cosmochimica Acta* **59** (1995), p. 115.
- [2] RS Lewis *et al*, *Nature* **326** (1987), p. 160.
- [3] R Maas *et al*, *Meteoritics & Planetary Science* **36** (2001), p. 849.
- [4] S Richter *et al*, *Nature* **391** (1998), p. 261.
- [5] SR Russell *et al*, *Meteoritics & Planetary Science* **31** (1996), p. 343.
- [6] TL Daulton *et al*, *Geochimica et Cosmochimica Acta* **60** (1996), p. 4853.
- [7] PR Heck *et al*, *Meteoritics & Planetary Science* **49** (2014), p. 453.
- [8] T Stephan *et al*, *International Journal of Mass Spectrometry* **379** (2015), p. 46.
- [9] JB Lewis *et al*, *Ultramicroscopy* **159** (2015), p. 248.
- [10] RS Lewis *et al*, *Nature* **339** (1989), p. 117.
- [11] DN Seidman and K Stiller, *MRS Bulletin* **34** (2009), p. 717.
- [12] TF Kelly and DJ Larson, *Annual Review of Materials Research* **42** (2012), p.1.
- [13] RM Stroud *et al*, *The Astrophysical Journal Letters* **738** (2011), p. L27.
- [14] The author acknowledges funding from NASA Cosmochemistry (NNX11AG77G and NNX15AC53G) and the Tawani Foundation.