Analysis of Allende nanodiamond residue by correlated transmission electron microscopy and atom-probe tomography

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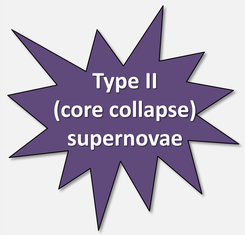
Motivation

The origins of meteoritic nanodiamonds , first separated from meteorites in 1987 by acid dissolution and size separation [1], remain an enigma: Isotopic anomalies in trace elements Xe [1], Te [2], Pa [3], and Ba [4] suggest a Type II supernova origin for at least a subpopulation of the NDs, to provide r-process and p-process nucleosynthesis.

However, the bulk measured C [5] and N [6] are consistent with formation in the Solar System. To resolve this conundrum, we are measuring the $^{12}C/^{13}C$ ratios of individual nanodiamonds and a suite of standards using atom-probe tomography (APT). It is necessary to assess the size, density, and structure of the particles in reconstructed APT microtips [7–9]. For this purpose we utilize transmission electron microscopy (TEM).

Where did the nanodiamonds originate?

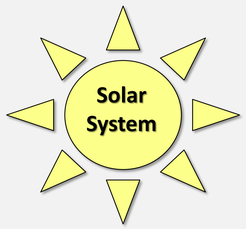
In the absence of grain-by-grain isotopic data, many mechanisms have been suggested. The nanodiamonds are likely to be drawn from some combination of these sources.



- Condensation in the expanding remnant, mixing between ^{12}C- and ^{13}C-rich shells, inclusion of trace elements from r- and p-process nucleosynthesis.

- Condensation in the outflows of AGB stars [11].

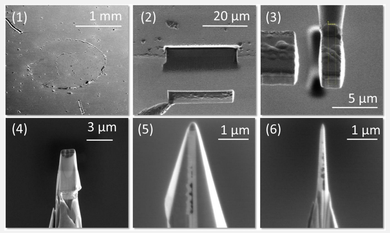
- Shock-transformation of amorphous, sp2-bonded sheets [10].

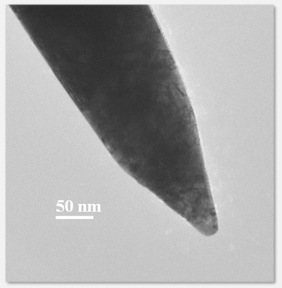


- Condensation or shock formation in the circumstellar disk. Infrared signals consistent with emission from hydrogenated nanodiamond surfaces have been observed in the circumstellar disks around young stars [12,13].

Experimental

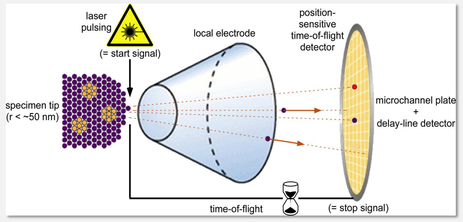
Using focused ion beam microscopy, **(1)** nanodiamonds from the Allende DM residue are embedded between sputter-deposited Pt layers, **(2)** lifted out, **(3)** attached to an electropolished micropost on a TEM half-grid, and **(4-6)** sharpened.





Transmission electron microscopy (TEM) at 200 keV, electron energy loss spectroscopy (EELS), and energy dispersive x-ray spectroscopy (EDS) are used to find and characterize the position, size, and crystal structure of carbonaceous features in microtips. Instrument: JEOL 2100F at the Institute for Materials Science and Engineering at Washington University.

Atom-probe tomography is used to conduct point-projection-microscopy and time-of-flight mass spectrometry, allowing us to reconstruct the carbonaceous features and identify ^{12}C and ^{13}C isotopes. Instrument: LEAP 4000x SI at Northwestern University.



Atoms detected per sample = ~10^7 T = 60 K

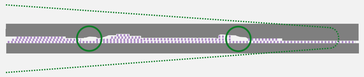
Pulse rate = 500 kHz Evaporation-assist laser energy = 120 pJ

Discussion

TEM showed low-density features consistent with nanodiamonds, that were not detected by APT on the sample microtips.

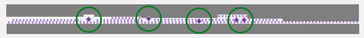
Possible explanations:

- Voids created as Pt (top, gray) sputter-coated a rough sample deposit (purple dash), onto a Pt substrate (bottom, gray). The dashed green line indicates the final microtip shape.



- Clumps of amorphous, sp2-bonded C.

- NDs that were undetected by APT.

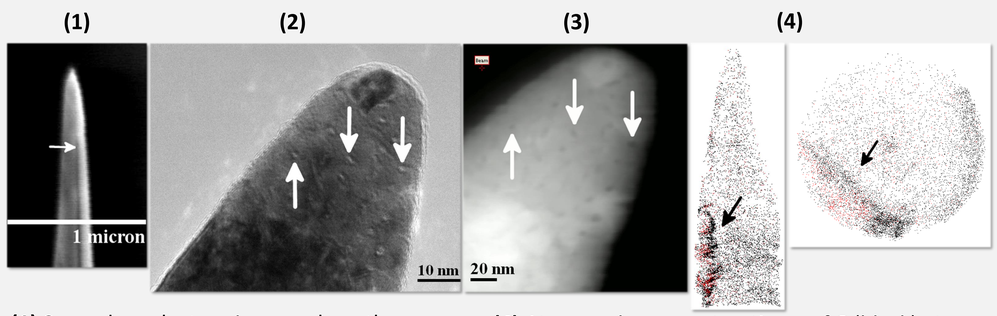


In each case, the C in the reconstructed deposition layers most likely represents amorphous, sp2-bonded C. The density is too low for precise isotopic measurements.

We are targeting lower-density regions of the acid residue deposit for our next samples. Correlated TEM/APT of microtips containing only isolated, nanodiamond-sized carbonaceous regions, as has been previously observed in some cases [7–9], should resolve the question of which of the above explanations is correct.

Results

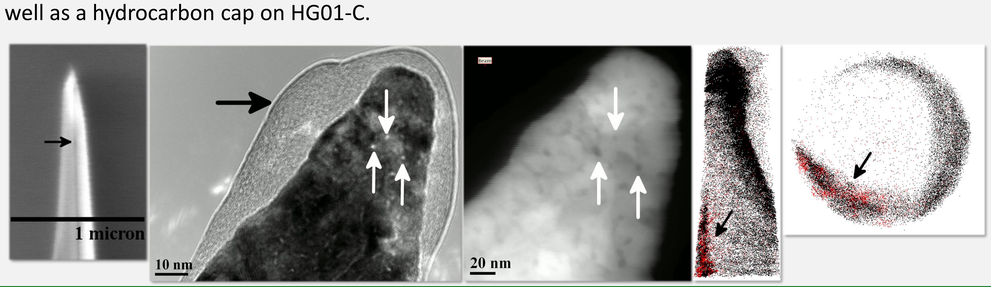
HG01-B: a FIB-sharpened sample microtip with a layer of Allende DM residue, demonstrating void-like features (indicated by arrows).

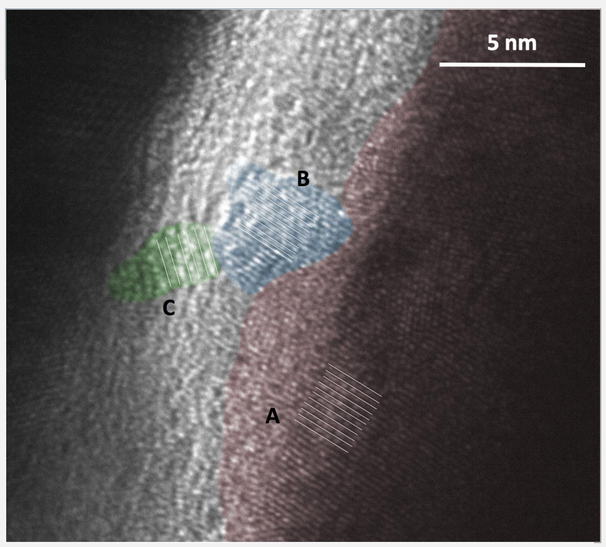


(1) Secondary electron images show the Allende DM acid residue deposition layer (arrow) between Pt layers. **(2)** TEM bright-field images and **(3)** high angle annular dark field images show low-density features, as well as a hydrocarbon cap on HG01-C.

(4) Atom-probe reconstructions of C (black) atoms contain C-strewn deposition layers (arrows) contaminated with NaO (red). The reconstructions do not, however, include nanodiamonds or voids consistent with the TEM images.

HG01-C: Demonstrates we can distinguish between the sample layer and contamination (hydrocarbon cap laid down by the ion beam).





HG04-C: Deposition is oriented parallel to the electron beam. Based on elemental identification using EELS and EDS, and lattice spacings, we identify **(A)** Pt surrounding the low-density layer. In the low-density layer we find features consistent with **(B)** diamond surrounded by **(C)** graphite.

References

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