Every Atom has a Story to Tell: Using Single-Atom-Sensitivity Imaging and Spectroscopy to Determine Origins of Cosmic Nanodiamonds

R. M. Stroud[1] and N. D. Bassim[1]

[1.] Materials Science and Technology Division, Naval Research Lab., Washington, DC 20375 USA.

Nanodiamonds isolated from meteorites represent a milestone in the study of the evolution of the Solar System, because they are the first distinct phase identified as the carrier of isotope anomalies indicative of an origin before the formation of the Solar System [1]. The small size of the nanodiamonds, typically 2 nm, precludes most isotopic measurements of individual diamonds, with the possible exception of atom-probe analysis of C isotopes. Instead, isotope composition measurements are made on ensembles of nanodiamonds. Multiple lines of evidence indicate that the nanodiamond isolates contain two or more subpopulations, with origins in supernovae, AGB stars and/or the Early Solar System. Identification of these subpopulations requires single-atom-sensitivity imaging and spectroscopy with an aberration-corrected electron microscope, in order to identify variations in minor (N, O) and trace element concentrations (any), and/or variations in surface bonding arrangements. Our earlier work revealed that many of the of nanodiamond isolates also contain up to 50% amorphous sp^2 carbon, and that this second phase of carbon may also be a carrier of the isotope anomalies [2]. Accelerator mass spectrometry of meteoritic nanodiamond isolates has revealed a range of impurity species, some likely due to incomplete digestion of the meteorite matrix, and some indigenous to the diamond. One of the highest abundance impurities is Si, to which some attribute an indigenous origin, and associate with the diamond SiV defect photoluminescence feature [3].

In order to better decipher the clues provided by the heterogeneity of the nanodiamonds as to their origins, we are performing single-atom sensitivity imaging and spectroscopy of nanodiamond isolates, with a Nion UltraSTEM 200 at the Naval Research Lab (NRL). The NRL UltraSTEM is equipped with a 0.7 sr, windowless, Bruker SDD energy dispersive X-ray (EDX) detector, and a Gatan Enfinium ER electron energy-loss spectrometer. The typical operating conditions for our nanodiamond analyses are: 60kV operating voltage, 50 pA-150 pA probe current, and 100 pm to 200 pm probe size. High and medium angle dark field images, EDX spectra, and EELS low-loss and C core loss spectra are obtained for each sample. Three types of nanodiamond isolates are under investigation: nanodiamond from the original Allende meteorite isolate prepared at the University of Chicago, Allende nanodiamond further separated into fine fractions by electrophoresis at Washington University, and nanodiamond from the Murchison meteorite prepared by a CsF variation of the standard extraction method, at the Carnegie Institution of Washington. The electrophoresis separation method balances sedimentation forces against surface charge, to achieve spatial separation of distinct subpopulations.

Compared to the original Allende sample and the Murchison sample [2], the Allende electrophoresis separates show less associated amorphous sp^2 carbon. This can be observed in both the MAADF images, and the EELS measurements (Fig. 1). In the C-K EEL fine-structure of the electrophoresis separates, the π^* peak, associated with sp^2 carbon, and also attributed to surface reconstruction in nanodiamond, is significantly reduced, and sometimes completely absent (Fig. 2). Individual, mobile Si and S atoms are present in all of the separates, and can be identified with targeted raster EDX spectral acquisitions in as few as 8 seconds (Fig. 3). Other identified impurities include Ir, present in at least one

electrophoresis separate as sub-nm particles. Our results indicate that with our STEM, EDX spectroscopy is the most effective method for identifying the individual unknown impurity atoms and evaluating the local variation in N content at the sub 1 at% level, whereas EELS provides single-atom sensitivity characterization of the carbon bonding, and the local bonding of some of the EDX-identified impurity species.

References:

[1] Lewis, R.S., et al. *Nature 326,* (1987) 160-162.
[2] Stroud, R.M., et al. *Astrophys. Journal Lett. 738*, (2011) L27.
[3] Shiryaev, A.A., et al. *Meteoritics and Planet. Sci.*, (2015) 177.
[4] The authors acknowledge funding from the NASA Cosmochemistry and SSERVI programs. RMS thanks P. Heck, C. M. O'D. Alexander and O. Pravdivtseva for providing nanodiamond samples.
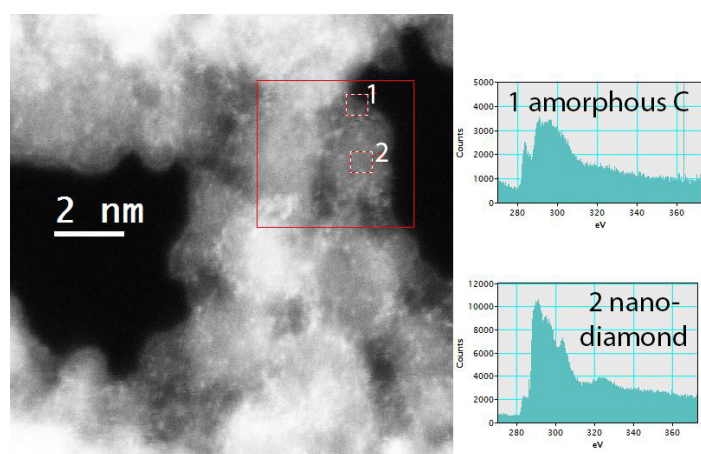
Figure 1. Dark field STEM image and sub-nm EEL spectrum imaging of an Allende electrophoresis separate. Amorphous carbon (1) surrounds nanodiamonds (2). White dots are impurity atoms. The large red box indicates the area over which a C EEL spectrum image was obtained. Spectra extracted from the boxes 1 and 2 are shown on the right.
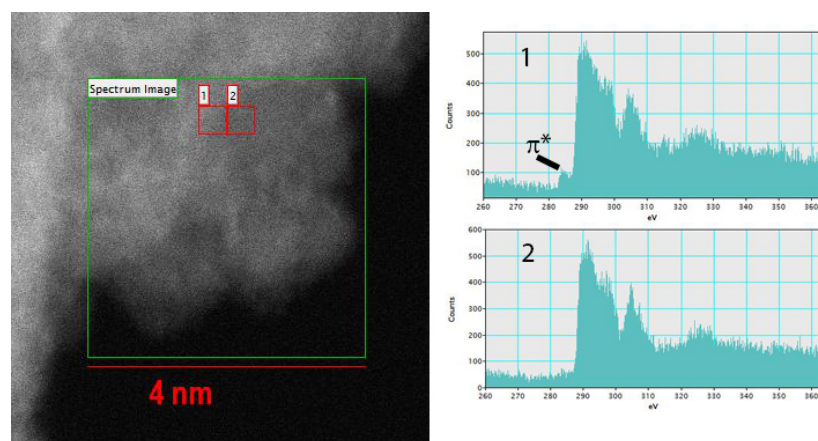

Figure 2. EEL fine structure of C-K edge of an Allende nanodiamond electrophoresis separate. Adjacent pixels of the spectrum image show (1) mixed sp^2-sp^3 bonding and (2) pure sp^3 bonding, demonstrating that nanodiamonds do not always require a sp^2 surface reconstruction.
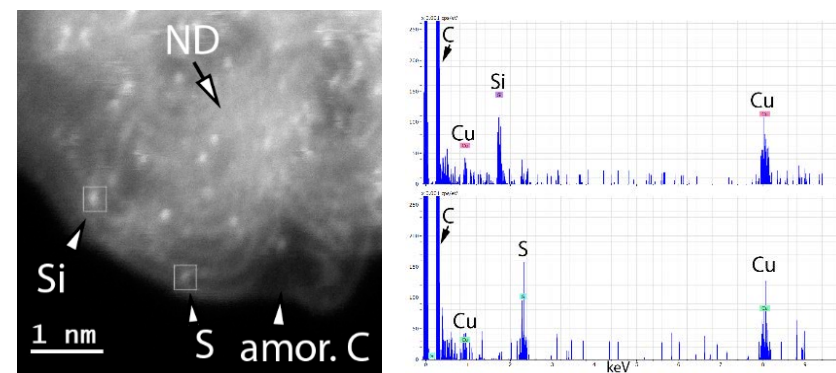

Figure 3. Annular dark field STEM image of a Murchison nanodiamond (ND) separate, and single atom sensitivity EDX spectra of single Si and S impurities. The spectra were collected for 9 and 8 seconds respectively. The Cu counts are from secondary scattering off of the sample grid, holder and pole piece.