

## STRUCTURAL AND ELEMENTAL TRANSFORMATION OF METEORITIC NANODIAMONDS DURING IN SITU HEATING IN A UHV SCANNING TRANSMISSION ELECTRON MICROSCOPE

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**Introduction:** Nanodiamond isolates from meteorites carry nucleosynthetic anomalies indicative of a presolar supernova origin [1]. However, the major element (C, N) isotope compositions of the bulk isolates are consistent with solar system values. Thus, the origins of meteoritic nanodiamonds remain enigmatic. Possible origins include formation by condensation in the dusty outflows of supernova and AGB stars, or by shock and radiation processing of carbonaceous matter in the interstellar medium or the solar nebula. If the nucleosynthetic anomalies were distributed uniformly in the nanodiamond isolates, up to 1 in 10 nanodiamonds might retain a signature of a presolar origin. However, in addition to diamond, the isolates also contain varying amounts of  $sp^2$  carbon, presolar SiC, and refractory metal nuggets, which may also be carriers. The temperature release patterns of noble gases from the isolates identify multiple noble gas components with different cosmochemical histories, e.g., the P3 planetary gases, which reflect early solar system processes, and “HL” gases that are indicative of the supernova component, released at low and high temperature, respectively [2]. By performing heating stage experiments on the nanodiamond isolates *in situ* in a UHV STEM we aim to identify structural and elemental changes that correlate with the noble gas release patterns, in order to constrain the specific carriers.

**Methods:** An aqueous suspension of Allende DM nanodiamond was pipetted onto a holey carbon film on a heating stage compatible with the Protochips Fusion heating holder. The nanodiamond samples were subsequently analyzed with the Nion UltraSTEM 200-X aberration-corrected scanning transmission electron microscope at the Naval Research Lab, equipped with a Bruker Xflash 100 energy dispersive X-ray (EDX) spectrometer, and a Gatan Enfium HR electron energy loss (EEL) spectrometer. The Nion was operated at 60 kV, with a nominal 0.15 nm, 50-100 pA probe. Heating stage experiments to observe the transformation of the isolates were performed in the Nion with a Protochips Fusion system. The temperature was raised in 50°C increments at a rate of 1°C per second, and an EEL spectrum and dark-field images were recorded at each temperature step, up to a maximum of 1200°C.

**Results:** The as-deposited sample showed the characteristic C-K edge EEL fine-structure of diamond, along with a small  $\pi^*$  peak at 284.3 eV, indicative of the  $sp^2$  component common to nanodiamonds. In addition, there was a small peak at ~282.4 eV, reported to be associated with N impurities in diamond (N-V center) [3], or with partially H-passivated surface defects [4]. Based on our earlier EDX analysis of Allende DM nanodiamond aliquots, the N content is ~0.1 to 0.3 at%.

On heating to between 400°C and 600°C, the N defect peak in the EELS spectrum dramatically decreased in intensity. This rules out the possibility of attributing this feature to surface H, which would be desorbed under the electron beam at much lower temperature. Continued heating of the sample to 1200°C under UHV conditions resulted in a gradual increase in graphitization, demonstrated by the relative intensity increase of the  $\pi^*$  peak, a shift of the centroid to 285.3 eV, and changes in the extended structure at higher energies. The most dramatic changes occurred above 900°C, including increased porosity and formation of linear channels, consistent with the onset of the release of HL components in pyrolysis experiments. By 1200°C, the sample consisted of at least 50% graphitic carbon, and remained that way on cooling back to room temperature.

**Discussion:** The direct observation in the STEM of the low temperature release (400°C to 600°C) of N is important because published stepped combustion studies show the low temperature N release to be the least isotopically anomalous. However, the stepped combustion data could not provide definitive evidence that the N was carried by the diamond, rather than  $sp^2$  carbon or other components in the isolates. Our preliminary data show direct evidence that the low-temperature-released N is intrinsic to the diamond, and thus these N-bearing diamonds are most likely formed in the solar system. Additional heating studies *in situ* in the Nion STEM, and *ex situ* in air, are planned in order to provide new context for interpreting nanodiamond pyrolysis and stepped combustion experiments, and to offer new constraints as to the nanodiamond formation histories.

### References:

[1] Lewis R. et al. *Nature* (1987) 326:162-165. [2] Ott U. et al. (2012) *Publications of the Astronomical Society of Australia* 29:90-97. [3] S. L. Y. Chang et al. (2016) *Nanoscale* 8:10548-10552. [4] Garvie L. A. J. (2006) *Meteoritics & Planetary Science* 41:667-672.

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