

CONSTRAINING THE ORIGIN OF METEORITIC NANODIAMOND RESIDUES WITH SINGLE-ATOM SENSITIVITY ELECTRON MICROSCOPY. R. M. Stroud¹, M. F. Chisholm², P. R. Heck³, C. M. O'D. Alexander⁴, L. R. Nittler⁴. ¹Materials Science and Technology Division, Naval Research Laboratory, Washington, DC 20375; ²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6069; ³Robert A. Pritzker Center for Meteoritics and Polar Studies, The Field Museum, Chicago, IL 60605; ⁴Dept. of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015.

Introduction: Although meteoritic nanodiamonds were discovered more than twenty years ago [1], their origin(s) remain controversial. The nanodiamond residues carry isotopic anomalies in trace elements Xe [1], Pd [2], Te [3] and Ba [4], that can only be explained as the products of supernova nucleosynthesis. However the isotopic composition of the residues' major elements, C and N, are within solar system values. In the absence of isotopic data from individual nanodiamonds, which are not yet technically feasible to obtain, multiple formation scenarios have been proposed. These include condensation and shockwave transformation in the interstellar medium and outflows of supernova [5], and condensation in Red Giant stars [6], and the solar nebula [7]. New analytical methods that permit atom-by-atom analysis of the nanodiamond residues [8,9] are needed in order distinguish among these competing formation models. We discuss here results from single-atom-sensitivity scanning transmission electron microscopy (STEM) studies of Murchison and Allende nanodiamond residues [10], and the implications of these results for constraining nanodiamond origins.

Experimental: We analyzed two nanodiamond residues: an aliquot of the Allende DM residue prepared by Lewis et al. [1], and a new Murchison residue prepared using established CsF-HCl methods. For optimal imaging conditions with minimal terrestrial carbon contamination, samples were placed on 5-nm thick, carbon-free, amorphous Si support films, which were first cleaned with an argon plasma, as well as on lacey carbon and 3-nm carbon-backed lacey carbon films. Bright-field and high-resolution imaging was performed with a JEOL 200 kV transmission electron microscope at the Naval Research Laboratory. Aberration-corrected STEM imaging and electron energy loss spectroscopy was performed with a Nion UltraSTEM at Oak Ridge National Lab operating at 60 kV, and a Gatan Enfina electron energy-loss spectrometer.

Results: Bright-field TEM images of the residues supported on the Si (Fig. 1) and ultra-thin carbon supports clearly demonstrate the presence of an amorphous second phase. The second phase is difficult to observe in bright-field TEM images on lacey carbon, due to the thickness of the carbon support and the aggregation of the diamonds.

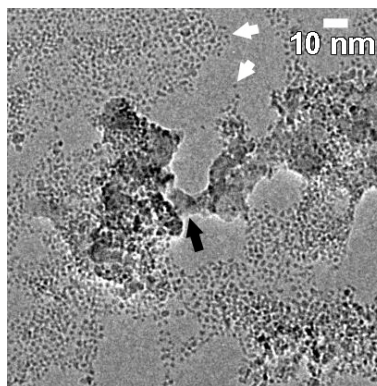


Figure 1. Bright-field TEM image of Murchison nanodiamond on a 5-nm thick Si membrane. The white arrows indicate nanodiamonds and the black arrow indicates amorphous carbon.

In medium angle dark-field STEM images (Fig. 2), the nanodiamonds can be distinguished from the second phase by the difference in density and crystallinity. The diamonds are brighter, and often show 0.2 nm (111) lattice spacings, whereas the second phase is darker (thinner) and has a disordered ring structure. Individual impurity atoms are also present, and appear as isolated white spots.

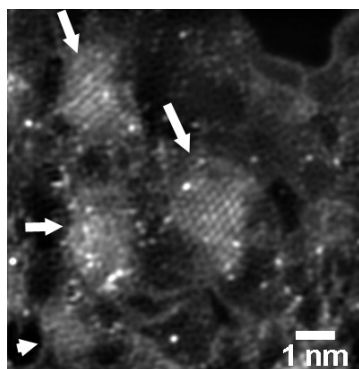


Figure 2. MAADF STEM image of Allende nanodiamond residue. White arrows indicate nanodiamonds. The surrounding material is disordered, sheet carbon. The image has been filtered for noise reduction.

The nature of the carbon bonding in the two phases can be determined with electron energy-loss spectroscopy (EELS). In the C K-edge spectra (Fig. 3 right), the second phase shows a strong π^* peak at 284 eV, and a broad, featureless σ^* peak. The nanodiamond shows a small π^* peak, and a series of σ^* peaks characteristic of the sp^3 bonding of diamond. In the low loss spectra (Fig. 3 left), there are two features: one corresponding to the plasmons from diamond (33 eV) and amorphous carbon (22 eV), and the other at ~ 5 eV, corresponding to a π - π^* interband transition.

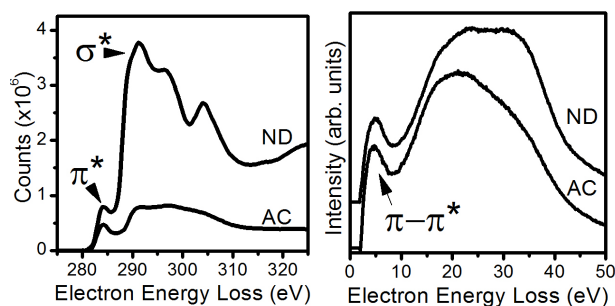


Figure 3. Electron Energy Loss Spectra of Allende. ND and AC refer to nanodiamond and amorphous carbon. The zero loss peak was subtracted from the low loss spectra (left).

Discussion: The presence of the second phase of carbon raises multiple questions about the interpretation of results from prior bulk analyses of the nanodiamond residues, i.e., what is the second phase and why was it not previously observed? Are the measured isotopic anomalies carried by only one or both phases? The first question can be answered with the existing data. The disordered-ring structure and π bonding revealed by the MAADF and EELS data, respectively, indicate the second phase is a form of sp^2 -bonded amorphous carbon. That this phase survives the acid treatments used to isolate the nanodiamond from the host meteorites indicates that it is a specific form of amorphous carbon called “glassy” or “vitreous” carbon. Based on the reported densities of nanodiamond residues, bulk diamond and synthetic glassy carbon, the residues contain a mixture of roughly equal amounts nanodiamond and glassy carbon. Although previous spectroscopic studies also have indicated that up to 50% of the residue materials are in a disordered, non-diamond form, the electron microscopes used for those studies did not have sufficient sensitivity to image individual carbon monolayers. The ultrathin support films that greatly improve the contrast for imaging monolayer variation in carbon sample thickness have also only recently become available.

More analyses will be needed to answer the question of whether the isotopic anomalies are carried by either the nanodiamond or the glassy carbon or both. Synthetic glassy carbon is known to be a gas impermeable phase, and could serve, in addition to or in place of the nanodiamond, as a reservoir for noble gas species. The MAADF STEM images do show impurity atoms associated with both phases. However, most of these impurities move under the electron beam during STEM imaging, and likely are surface adsorbed contaminants from the acid processing. The contrast in the MAADF image can be used to determine the atomic number of the impurity atoms [8]. Those identified so

far are mostly Fe, Ti, and S, with one possible Ne atom associated with the glassy carbon. Additional imaging to identify specific impurities in very fine density separates could address the possibility of one or more sub-populations of the glassy carbon and nanodiamond as the carriers of the different anomalies.

The coexistence of nanodiamond and glassy carbon in the residues suggests, but does not require, that they have a common origin, or origins. Support for the idea of common origin(s) comes from recent work [10] on crushed fragments of Murchison matrix that revealed disordered carbon, possibly “glassy”, surrounding individual nanodiamonds. The most common method for commercial synthesis of glassy carbon is by heat treatment of organic resins. Direct transformation of glassy carbon into nanodiamond by high temperature-high pressure treatment has also been experimentally demonstrated. Thus, it is plausible that a two-phase mixture of glassy carbon and nanodiamond could be produced in astrophysical settings by shock-induced high-temperature, high pressure transformation of pre-existing organic molecules. In particular, a supernova-shock wave incident on the warm intercloud interstellar medium could generate the appropriate conditions to reproduce all of the nanodiamond residue features: ambient organic molecules with solar carbon isotopic composition available for carbonization; pressure and temperature suitable for formation of glassy carbon and nanodiamond; and ion implantation from both the supernova wind and the ambient interstellar gas. Shock transformation of organics in other settings, i.e., shocks in the solar nebula or interaction between reverse shocks in a type II supernova and organic molecules in the surrounding circumstellar envelope are also possible, but would require multiple events to explain all of the isotopic data. The presence or absence of multiple nanodiamond and glassy carbon populations in a single residue, as determined by future atom-by-atom analysis, might distinguish contributions of materials from the different formations scenarios.

References: [1] Lewis, R. S. et al. (1987), *Nature*, 326, 160. [2] Richter, S., Ott, U., & Begemann, F. (1998), *Nature*, 391, 261. [3] Maas, R. et al. (2001) *MAPS*, 36, 849. [4] Lewis, R. S., Huss, G. R., & Lugmair, G. (1991) *LPSC XXII* #807. [5] Clayton, D. D. (1989) *ApJ*, 340, 613. [6] Alexander, C. M. O'D. (1997), in *Astrophysical implications of the laboratory study of presolar materials*, eds. T. J. Bernatowicz, & E. K. Zinner (Woodbury: AIP Conference Proceedings), 567. [7] Dai, Z. R., et al. (2002) *Nature*, 418, 157. [8] Krivanek, O. L., et al. (2010) *Nature*, 464, 571. [9] Heck, P. R. et al. (2011) *74th MetSoc Abstract* #5372. [10] Stroud, R. M. et al. (2011) *ApJ Lett.* 738 L27. [11] Garvie, L. A. J. (2010) *LPSC XLI* #1388.