

DISCOVERY OF GLASSY CARBON IN METEORITIC NANODIAMOND RESIDUES: IMPLICATIONS FOR NANODIAMOND ORIGINS. R.M. Stroud¹, M. F. Chisholm², P. R. Heck³, C. M. O'D. Alexander⁴. 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; ⁴Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015

Introduction: Nanodiamond was the first phase identified in meteorites as the carrier of an isotopic component indicative of an extrasolar origin [1]. Large isotope anomalies in Xe isotopes [1], and small anomalies in Pd, Te, and Ba [2,3] observed during bulk analysis of residues can be only explained by nucleosynthesis in supernovae. However, the 2-nm average size of the nanodiamond precludes isotopic analysis of individual particles, and thus the origin remains controversial. Several formation scenarios have been proposed, including condensation in the interstellar medium, the outflows of supernova [4,5] and Red Giant stars, and in the solar nebula [6].

Multiple spectroscopic studies [1, 7-9] of meteoritic nanodiamond residues have indicated that a nanodiamond component comprises up to 50% of the residues. Previously, this was attributed to surface reconstruction of the nanodiamonds [10] and contamination with terrestrial carbon. However, we recently demonstrated that a disordered carbon phase with sp^2 bonding, spatially distinct from the nanodiamond, is present in two residues, the Allende DM separate and a new residue from the Murchison carbonaceous chondrite [11]. Here we present further analysis of these residues using aberration-corrected scanning transmission electron microscopy, and discuss the implications for formation of the nanodiamond and disordered carbon phase.

Experimental: Two nanodiamond residues were examined: an aliquot of the Allende DM residue prepared by Lewis et al. [1], and a new Murchison residue prepared using established CsF-HCl methods. To minimize the chance of contamination with terrestrial carbon and also optimize imaging conditions, measurements were performed on 5-nm thick, carbon-free, amorphous Si support films, which were first cleaned with an argon plasma, as well as lacey carbon and 3-nm carbon-backed lacey carbon. Conventional 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 (EELS) spectrometer.

Results: Conventional TEM imaging of each residue on ultrathin support films reveals the presence of an amorphous phase of carbon (Fig. 1). This phase is not readily observed in the same samples supported on lacey carbon, due to the low contrast of this few-nm thick phase on the ~ 25 nm thick support film and sample agglomeration over the holes.

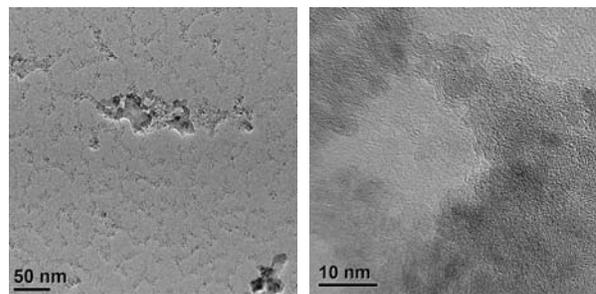


Figure 1. (left) Bright-field TEM image of Murchison nanodiamond on a 5-nm thick amorphous Si membrane. (right) High-resolution TEM of Allende DM residue on a 3-nm carbon support film.

Medium angle-dark field (MADF) aberration-corrected STEM imaging of the residues (Figs. 2&3) shows the (111) planes of individual nanodiamonds, the ring structure of the disordered carbon, and the presence of individual impurity atoms (bright spots).

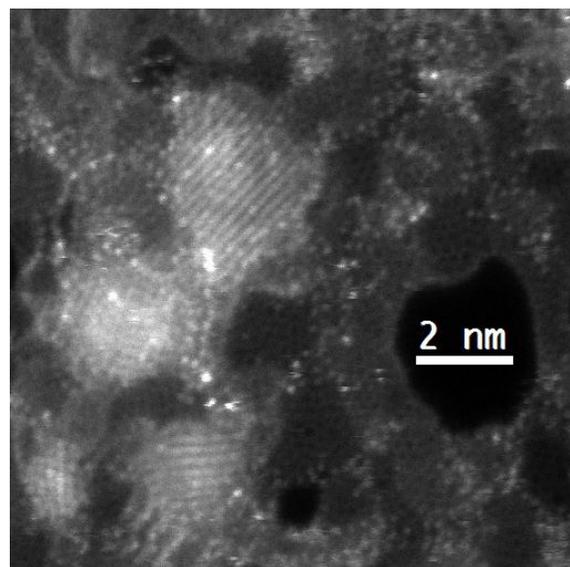


Figure 2. MADF image of Murchison nanodiamond residue.

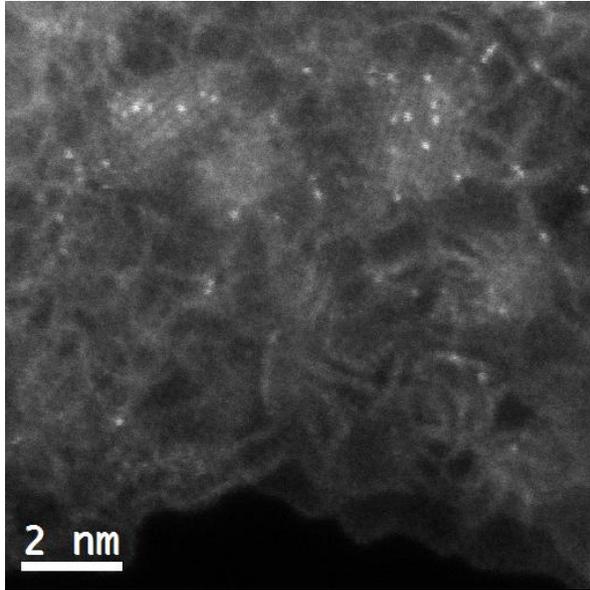


Figure 3. MADF image of Allende DM nanodiamond residue.

In each residue, the disordered carbon phase has a wrinkled-sheet morphology, and extends well beyond the surface of the individual diamonds. Variations in the MADF image intensity can be quantitatively interpreted in terms of atomic number using the relationship $I \sim Z^{1.64}$ [12] and calibration of the proportionality constant against discrete steps in the number of carbon planes. Sample thickness of 0-12 atomic planes of carbon are visible in Fig. 2. Individual impurity atoms are also visible in these images, associated both with the nanodiamonds and the disordered carbon phase. The impurities appear to be mostly inconsistent with image intensity corresponding to noble gas species; most are residual components of the acid dissolution processing.

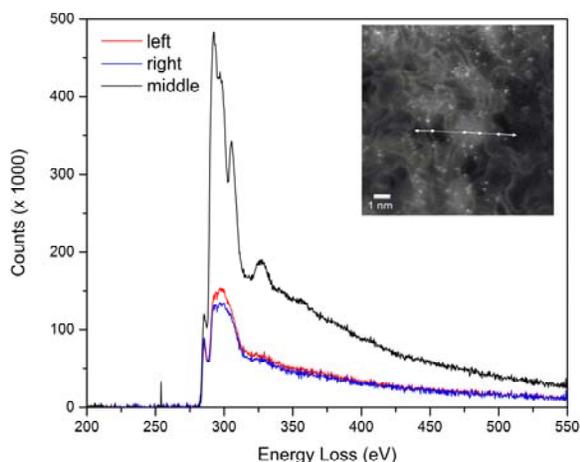


Figure 4. Electron energy loss spectra of Murchison nanodiamond residue.

EELS spectra of the C K edge obtained with a ~ 150 pm probe reveal that the disordered carbon phase (Fig. 4 left and right) is sp^2 in character, with a strong π^* peak at 285 eV, and a broad σ^* feature. Spectra obtained on a single nanodiamond (Fig. 4 middle) are characteristic of sp^3 bonded diamond. A small π^* peak is present in the nanodiamond spectra, but this is likely due to the disordered carbon phase extending above and below the nanodiamond. No N K or O K edge features are visible.

Discussion: Because the second carbon phase is present in two residues, produced in two laboratories using different chemistries, and deposited on three types of TEM grids, contamination with terrestrial carbon is unlikely. Furthermore, the nature of the second phase, i.e., extreme acid resistance, with sp^2 bonding and a disordered, wrinkled-sheet character, is consistent with a synthetic carbon material known as glassy carbon (GC), which is produced by heat treatment of organic resins [13]. The presence of GC in meteoritic nanodiamond residues raises significant questions regarding the interpretation of measurements of such residues, including the origin of the diamonds. GC contains a range of open and closed pores and varies in the degree of local graphitic ordering depending on the precursor material and details of heat treatment. The bulk density can be as low as 1.3 g/cc, and GC in the meteoritic residues may explain the reduced density of this residue compared to bulk diamond. Although we have not confirmed the segregation of noble gas impurities to the GC in the STEM images, the closed pores of the GC are a possible reservoir for storage of noble gas species. Thus, it is possible that the supernova nucleosynthesis signatures are carried by the nanodiamonds, the GC, or both. In the later case, coformation of the GC and nanodiamonds could have occurred by flash heating and ion implantation of organic mantles in a supernova shock wave.

References: [1] Lewis, R.S. et al. (1987) *Nature* **326** (6109), 160-162. [2] Richter, S. et al. (1998) *Nature* **391** 261-263. [3] Maas et al. (2001) *MAPS* **36**(6) 849-858. [4] Clayton, D.D. (1989) *ApJ* **340**, 613-619. [5] Daulton, T.L., et al. (1996) *GCA* **60**, 4853-4872. [6] Dai, Z.R. et al (2002) *Nature* **418**, 157-159. [7] Blake, D.F. et al (1988) *Nature* **332** (6165), 611-613. [8] Bernatowicz, T.J., et al (1990) *ApJ* **359**(1), 246-255. [9] Hill, H.G.M. et al. (1997) *MAPS* **32** (5), 713-718. [10] Garvie, L.A.J. (2006) *MAPS* **41**(5), 667-672. [11] Stroud, R. M. et al. (2010) *MAPS Suppl.* Abstract #5352. [12] Krivanek, O.L. et al. (2010) *Nature* **464**(7288), 571-574. [13] Harris, P. J. F. (2004) *Phil. Mag.* **84**(29), 3159 -3167.