WHERE ARE THE NANODIAMONDS IN PRIMITIVE METEORITES? PRELIMINARY TEM RESULTS

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Introduction: Nanodiamonds are abundant in primitive meteorites. The work of [1] shows that most primitive meteorites have similar matrix normalized nanodiamond concentrations (within a factor of ca. 2.2), consistent with their location in the matrix. Huge numbers of meteoritic nanodiamonds occur in primitive meteorites, on the order of 3 x 10^{17} per gram of matrix. Nanodiamonds from primitive meteorites display a uniform size distribution and a mean diameter near 2 to 3 nm [2, 3]. They occur in the primitive members of all classes of chondrites [1, 4-7], with matrix-normalized values from ca. 700 to 1500 ppm [1, 6]. Despite their abundance in primitive meteorites, they may be scarce in fragile, C-rich IDPs thought to have originated form comets [8]. At least some nanodiamonds are believed to be pre-solar based on their excesses of the heavy isotopes of noble gases such as Xe and the trace elements Te and Pd [9-12]. These isotopes may have a supernova origin.

Diamond dominates the residues of primitive meteorites after extreme acid dissolution and chemical oxidation. The dissolution removes the majority of minerals and sp^2-bonded carbon leaving primarily diamond with a few percent of acid resistant minerals, e.g. [1]. Transmission electron microscopy (TEM) images of the residue show a mélange of nanometer-sized diffracting domains. Despite many decades of research on nanodiamonds, relatively little is know about their location within the meteorite matrix. To begin to answer this question I have started to undertake work on locating nanodiamonds in the primitive meteorite matrices. Initial work is being done to find diamonds in the HF/HCl residue used to prepare the insoluble organic matter (IOM). The experience with finding diamonds in the IOM residue is then used to find diamonds in the raw, but disaggregated, meteorite matrix.

Nanodiamonds in the IOM: There have been few TEM studies of nanodiamonds in the IOM residue, though they are detectable by nuclear magnetic resonance (NMR). During my TEM and electron-energy loss spectroscopy (EELS) studies of the IOM I have frequently encountered nanodiamonds, both on the HRTEM images and by EELS (Fig. A and B). The example given here is for the Orgueil residue.

The Orgueil carbonaceous residue is composed primarily of an aggregate of carbonaceous particles, with a range of structures and chemistries [13]. Our preliminary works shows that some of the particles contain diamonds. The diamond-bearing particles typically show HRTEM images with small stacks of curved graphitic material, whereas thin areas of carbon that lack this structure are typically diamond free. Some of the diamonds appear to have a fullerene-like coating, and are akin to synthetic bucky-diamonds, e.g., [14]. Interestingly, no nanodiamonds are visible by HRTEM or detected by EELS in the nanoglobules, suggesting distinct and non-overlapping synthesis routes.

Just this preliminary data for Orgueil alone has several important implications. Firstly, the data suggests that at least some nanodiamonds are associated with a structurally distinct IOM. Secondly, if nanodiamonds are normally associated with, or embedded in, a poorly graphitized carbon then this would have important implications for their formation mechanisms and for their identification in extrasolar settings.

Nanodiamonds in the matrix: The challenge is to find and characterize the nanodiamonds sans chemical processing. Only a small amount of material is dispersed onto a TEM grid. It is readily possible and routine to isolate, crush, and disperse a <100 micron-sized fragment of meteorite matrix onto a TEM grid. ***Note on sample preparation*:** Gentle disaggregation of the primitive meteorite matrix material does not crush the individual submicron-sized particles. Instead, this technique separates the individual particles, thus allowing TEM analysis of the individual matrix grains e.g., [15, 16], without the numerous problems associated with ion milling and preparation by FIB. Also, the dispersing agent used in my studies (water or methanol) will not separate or dislodge the nanodiamonds from the materials they are attached to, since special chemical processing is required to bring nanodiamonds into suspension [17, 18]. Therefore, any "nanodiamond-matrix component" association revealed by TEM is a true measurement of their association in the meteorite.

During the authors search for and characterization of the nanoglobules in the primitive meteorites, an EELS C *K*-edge spectrum indicative of diamond was frequently encountered within discrete patches of poorly ordered, dominantly sp^2-bonded carbon. These nanometer-sized carbonaceous clumps are readily located by energy-filtered TEM (EFTEM) (Fig. C and D). The EELS spectra from these clumps show a sharp peak at 285 eV, which is attributed to transitions to unoccupied π^* states of sp^2-bonded C, and is a measure of their aromaticity. The intense π^* peak masks the relatively weak intensity peaks below 288 eV from the nanodiamonds. Despite these spectral overlaps, nanodiamonds are readily recognized by EELS even when embedded in amorphous C.

Discussion: TEM and EELS is a suitable combination for finding and characterizing the small and dispersed diamonds in the primitive meteorites. The preliminary work shows that at least some nanodiamonds are associated with submicron-sized particles of amorphous carbon. These particles are readily located with EFTEM and can be characterized by HRTEM and EELS. This research is generating fundamental new knowledge regarding meteoritic nanodiamonds - one of the most ubiquitous components in primitive samples. In particular, new data, such as location, associations, compositions, and structures, will be used to determine whether the current nanodiamond population consists of a mixture of true presolar grains and diamonds formed during the early stages of the formation of our solar system.

References:

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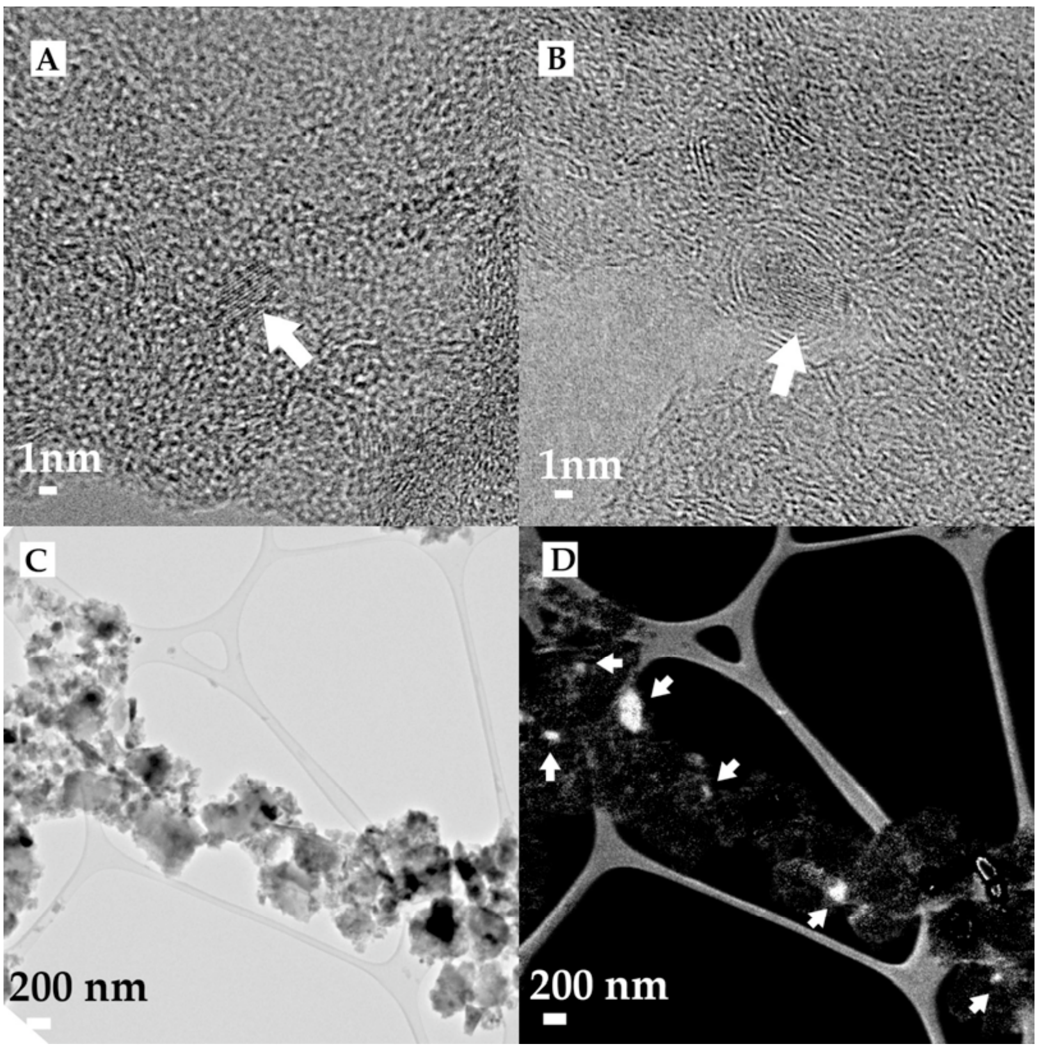

HF/HCl residue from the A) Tagish Lake and B) Orgueil meteorites. The white arrows point to individual, isolated nanodiamonds associated with the IOM. The Orgueil diamond appears to have a graphitic coating. C) TEM image of a cluster of Murchison matrix particles adhering to the TEM grid. D) C map showing isolated C-rich particles (arrowed).