ABERRATION-CORRECTED STEM ANALYSIS OF ELECTROPHORESIS SEPARATES OF ALLENDE NANODIAMOND.

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Introduction: Nanodiamond is an historically important phase for cosmochemical studies because it was the first phase identified as the carrier of nucleosynthetic anomalies indicative of formation in a star other than the Sun [1]. Present in the matrix of primitive chondrites at levels up to 2000 ppm, nanodiamonds are also arguably the most abundant presolar phase that survived incorporation into the Solar System [2]. The difficulty with this assertion is that, at present, there is no method for measuring isotope compositions, other than possibly for C, of individual ~ 2-nm nanodiamonds. Measured as an ensemble, the average C and N isotope compositions are within the range of Solar System values. Furthermore, the nucleosynthetic anomalies that provide signatures of preserved nucleosynthesis of stars pre-dating the Sun are present in very low abundance, e.g., < 1 Xe atom per 10^5 nanodiamonds. Thus, the vast majority of diamonds could have an origin in the early Solar System [3].

The existence of two or more sub-populations of nanodiamonds has been inferred from multiple lines of evidence, e.g., variations in N content and release patterns [4], bi-modal noble gas release patterns [5], variation in the noble gas content of ultrafine density [6] and electrophoresis separates [7] which contain different quantities of noble gases that are indicative of an extra solar origin [8]. These sub-populations in the nanodiamond residues have yet to be fully characterized, but aberration-corrected scanning transmission electron microscopy (STEM) is a promising tool for doing so [9]. In particular, aberration-corrected STEM, at low voltage and in UHV, is optimal for analysis of nanodiamond, and other nanoscale phases of carbon, because of the single atom sentivity for imaging and spectroscopy, as well as the greatly reduced beam etching.

Samples and Methods: Nanodiamond separates extracted from the Allende (CV3) meteorite at Washington University by established methods, were further separated into 12 fine fractions with electrophoresis methods described previously [7]. The electrophoresis technique involves application of high voltage to separate components of the colloidal suspension by competition of sedimentation and electrostatic forces. The total Xe and Xe-HL components of the 12 fractions were measured by single-step pyrolysis; additional noble gas release studies are reported at this meeting [10]. The powders were re-suspended in an ultrapure water-isopropanol mixture and pipetted as aliquots onto lacey carbon film-coated Cu TEM grids, and allowed to dry in air. The TEM grids were first cleaned with an Ar^+ plasma, to remove any volatile hydrocarbons. The grids were subsequently stored in plasma-cleaned glass vials.

Aberration-corrected STEM measurements were performed at the Naval Research Laboratory with PRISM, a custom Nion UltraSTEM200, which incorporates a 0.7 sr, windowless Bruker SDD-energy dispersive x-ray (EDX) system, and a Gatan Enfinium ER electron energy loss (EEL) spectrometer. STEM analyses of fractions 1, 2, 4, 8 and 10, representing a range of electrophoretic separation were carried out at 60kV, with a nominal probe size of 150 pm, and probe current of 50 pA.

Results: The STEM analyses confirm that all of the analyzed fractions do contain nanodiamond. However, the abundance of nanodiamond, and amounts of other phases, present on the TEM grids varied significantly. Nanodiamond was most concentrated in the #1 (Fig. 1) and #4 fractions (Fig. 2), with 10 or more clusters of nanodiamonds per grid square (~ 10^4 μm^2), compared to less than 1 cluster per square for fractions 2, 8, and 10. Fractions 8 and 10 contain silicate nanoparticles in addition to diamond.
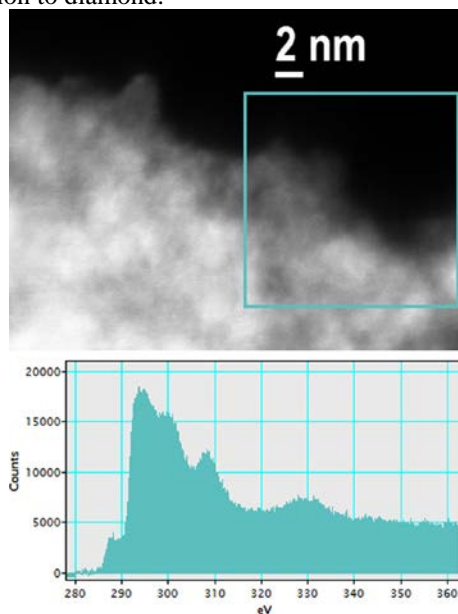

Fig. 1. STEM dark field image (top) and C K-edge EEL spectrum of Allende fine fraction #1, which has sub-nm structure. The blue box indicates the area of the EELS analysis.
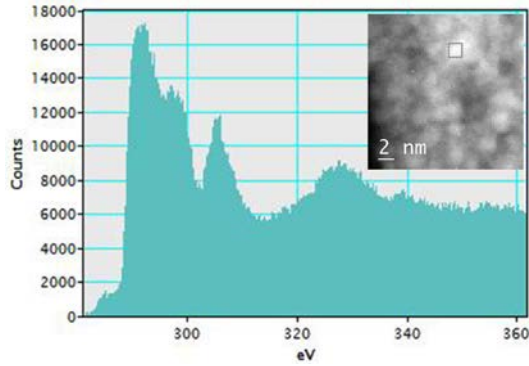
Fig. 2. C K-edge EEL spectrum of Allende nanodifine fraction #4. The inset spectrum image shows the ~ 2 nm size of the nanodiamonds and the area of the extracted spectrum (box).
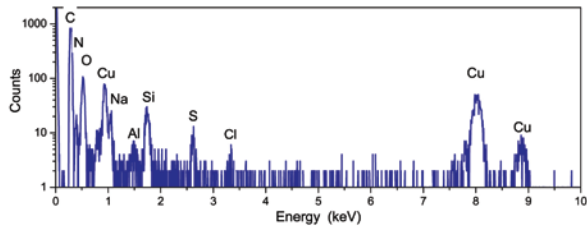

Fig. 3. Log scale STEM-EDX spectrum of a nanodiamond cluster from fine fraction #4. The Cu is a system peak associated with the support grid and microscope components.
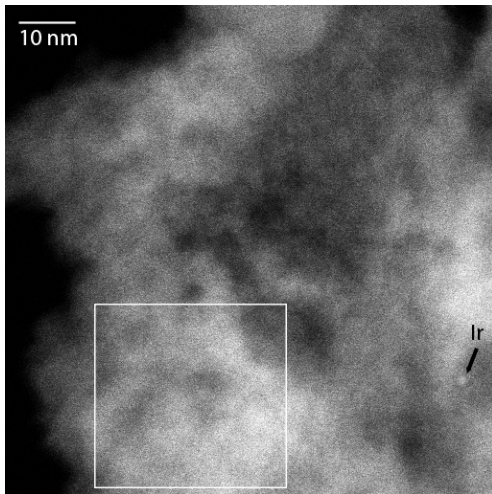

Fig. 4. STEM dark field image of fine fraction #4. A sub-nm Ir-rich particle is visible on the lower right. EDX spectra from the particle and adjacent area (white box) are shown in Fig. 5.

Elemental analysis with EDX spectroscopy of the fine fractions (e.g., Fig. 3.) revealed the prescence of variable, minor amounts of F, Na, Cl, Al and Si (< 1 at. %) in addition to C (> 90 at.%), N (<2 at.%) , O (< 4

at.%). In one cluster from fraction #4, Ir was also detected (Figs. 4 and 5.) The Ir appears to be a distinct particle, but intimately associated with the surrounding nanodiamond. EEL spectrum imaging over this area shows the expected C K-edge signature of nanodiamond. Attempts to obtain EELS spectra of the Ir were unsuccessful. Whereas the presence of F, Na, and Cl is attributable to residue from laboratory processing of the samples, terrestrial sources of the Ir are highly unlikely; none are associated with the laboratory processing of these samples.
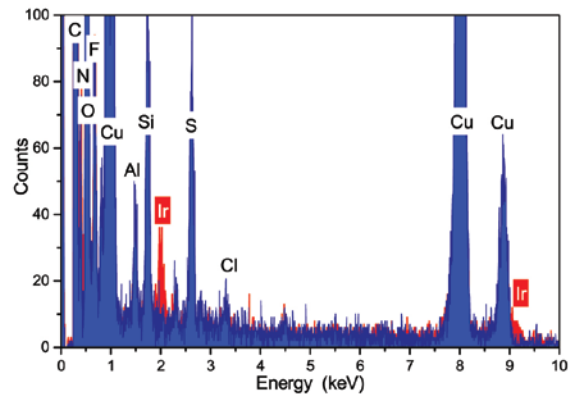

Fig. 5. STEM-EDX spectra of nanodiamond (blue) and an associated Ir-rich particle (red), plotted to show minor element content; off scale in C.

Conclusions: The STEM analyses suggest that the electrophoresis separation depends on the size of the nanodiamond particles, the degree of aggregation, and ionic surface charge associated with residual ions from the chemical processing used to isolate the nanodiamond from the meteorite. Smaller, more aggregated diamond is associated with fraction #1, and larger, more isolated diamonds are associated with fraction #4. The presence of an Ir particle in fraction #4 opens the possibility that refractory metal phases are important, previously unrecognized, carriers of nucleosynthetic anomalies in the nanodiamond residues.

References: [1] Lewis, R.S., et al. (1987) *Nature 326,* 160-162. [2] Zinner, E. (2014) *in Treat. on Geochem.*, 181-213. [3] Dai, Z.R., et al. (2002) *Nature 418*, 157-159. [4] Russell, S.S., et al. (1991) *Science 254*, 1188-1191. [5] Huss, G.R. and Lewis, R.S. (1994) *Meteoritics 29*, 811-829. [6] Verchovsky, A.B., et al. (2006) *ApJ 651*, 481-490. [7] Shatoff, E.A., et al. (2015) *LPS XLVII*, Abstract# 2688. [8] Ott, U. (2014) *Chem Erde-Geochem 74*, 519-544. [9] Stroud, R.M., et al. (2011) *ApJ Lett. 738*, L27. [10] Pravdivtseva O.V. et al. (2016) *LPS XLVII, this meeting.*