NANO-DIAMONDS IN INTERPLANETARY DUST PARTICLES (IDPs), MICROMETEORITES, AND METEORITES. Z. R. Dai\textsuperscript{1}, J. P. Bradley\textsuperscript{1}, D.J. Joswiak\textsuperscript{2}, D. E. Brownlee\textsuperscript{2}, and M. J. Genge\textsuperscript{3}, \textsuperscript{1}School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA, \textsuperscript{2}Dept. of Astronomy FM-20, University of Washington, Seattle, WA 98195, \textsuperscript{3}Department of Mineralogy, The Natural History Museum, London SW7 5BD.

Introduction: The average abundance of nano-diamonds in chondritic meteorites is ~400 ppm, they are between 1 and 10 nm in diameter with a log-normal size distribution, and they have an average diameter of ~3 nm [1]. Although their bulk $^{13}$C/$^{12}$C composition is solar, they are widely assumed to be presolar in origin because of their association with a noble gas carrier, specifically an anomalous Xe-HL component that has been linked to a supernova origin [2]. The abundance of Xe is such that only 1 in $10^6$ nano-diamonds contains a Xe atom and, since it is not yet possible to measure the isotopic composition of a single nano-diamond, it is an unclear whether all nano-diamonds are indeed presolar [3]. The relative abundance of nano-diamonds in asteroidal versus cometary materials may provide insight about their origins because presolar grains should be more abundant in the most primitive parent bodies located at large heliocentric distances. We have examined HF acid-etched thin sections of Orgueil (CI) and Murchison (CM) meteorites, two unmelted “CM-like” polar micrometeorites, and 9 chondritic IDPs (Table 1). Eight of the 9 IDPs are anhydrous chondritic porous (CP) particles, 4 are cluster particles one of which is hydrated [4].

Experimental procedures: IDPs, micrometeorites, and meteorite fragments were embedded in sulfur and thin sectioned using ultramicrotomy. The sections were mounted on continuous carbon films on gold TEM grids and etched using an \textit{in-situ} acid-etching procedure [5]. The etched sections were examined using an atomic resolution 400 kV TEM and a 200 kV analytical field emission TEM. Lattice-fringe imaging was used to determine crystal structures and energy-dispersive x-ray spectroscopy (EDS) was used to measure the compositions of nanocrystals within etched regions of the sections. Lattice-fringe image simulations were performed using the Cerius-2 software package (Fig. 1), and calibration of experimental lattice fringe images was obtained \textit{in-situ} using gold \{111\} and graphite \{002\} spacings.

Results: All of the etched samples contain mostly carbonaceous material and Fe-rich sulfide crystals. One of the micrometeorites (AMMSRU2-2) contains a single submicrometer SiC grain but, since the particle was extracted from a thick-flat specimen polished with SiC, the origin of the grain is questionable. EDS spectra typically show major C and minor but variable amounts of Si and O in all etched samples. (We observe similar compositions for \textit{bulk} nanodiamond-rich acid residues from Murchison and Orgueil). In addition, minor or trace Au, Pd, or Sn peaks are present in EDS spectra from several of the etched specimens and they are associated with nanometer-sized particulate materials. The Au and Pd-rich materials are crystalline and the Sn-rich material is amorphous. The Au and Pd likely indicate partial dissolution and reprecipitation of Au from the (Au) TEM grid and Pd that had been applied to some particles as a conductive coating before sectioning. The source of the Sn remains unknown.

Figure 1 shows simulated [110] lattice-fringe images of C (diamond), Au, Pd, PdF$_2$, and Sn. In this orientation the Pd, PdF$_2$, Au, and α-Sn spacing are 2.246 Å \{111\}, 3.030 Å \{111\}, 2.355 Å \{111\}, and 3.751 Å \{111\} respectively and they differ from the 2.059 Å \{111\} nano-diamond spacing by ≥ 9%.

Figure 2 shows experimental lattice-fringe images. In micrometeorite AMMSRU2-2 (Fig. 2a), a crystal with 0.206 nm spacing is identified as nano-diamond, despite its proximity to what we believe is a PdF$_2$ crystal. Figures 2b through 2d show images of nano-diamonds in cluster particles in U2-20GCA, RB12A44, and U230C-1G-D.

Discussion: Unambiguous identification of individual nano-diamonds in thin sections prepared using the \textit{in-situ} etching method has been a formidable under-

\begin{table}
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\caption{Nano-diamonds?}
\begin{tabular}{|l|c|}
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Meteorites & \text{\texttt{\textbackslash Verbatim{}}} \\
Murchison (CM) (2 samples) & √ \\
Orgueil (CI) (2 samples) & √ \\

Polar Micrometeorites & \\
AMMSRU2-2 (CM) & √ \\
AMM94-2/14 (CM) & √ \\
Cluster IDPs & \\
RB12A44-3 (CM) & √ \\
U2-20GCA (3 samples) & √ \\
U2-30C-1G-B & √ \\
W7110A-2E-D & X \\

Non-cluster IDPs & \\
W7027A-8D & X \\
U2-20A-23A & X \\
U217B1 & X \\
U2073B-1F & X \\
U2073B-4C & X \\
\hline
\end{tabular}
\end{table}
taking for the following reasons. First, since typical nano-diamonds are 2-4 nm thick and they are supported on carbon substrates ~20 nm thick, measurement of their compositions using EDS (or EELS) is at best ambiguous. Second, contamination from Au, Pd, and Sn is a problem that demands precise in-situ image calibration (e.g. see Fig. 2a). Third, the nano-diamonds are so sparsely distributed it is not possible to obtain useful electron diffraction (or EELS) data. Despite these problems using carefully calibrated lattice-fringe images we have identified nano-diamonds.

**Conclusions:** We find nano-diamonds in Murchison, Orgueil, and in two “CM-like” micrometeorites. This is the first direct observation of nano-diamonds in a micrometeorite. We also find nano-diamonds in three of four cluster particles, one of which (RB12A44-3) is a hydrated particle with CM mineralogy [4]. Assuming the meteorites, micrometeorites, and IDP (RB12A44-3) share an asteroidal origin, it is not unexpected that all of them should contain nano-diamonds. By implication the other two anhydrous cluster particles U2-20GCA and U2-30C-1G-B may also be asteroidal, consistent with the observation that cluster particles generally do not appear to have been strongly heated during atmospheric entry [6]. Although we did not observe nano-diamonds in one of the cluster particles (W7110-2E-D), we point out that the distinction between cluster and non-cluster particles is in some cases difficult. The conspicuous absence of nano-diamonds in the five non-cluster “CP” particles suggests the existence a class of very primitive solar system materials in which nano-diamonds are either depleted or NOT present. Some or all of these IDPs are likely of cometary origin. If returned STARDUST comet samples are also “diamond-free” then the origin of nano-diamonds, perhaps the most exotic type of presolar grain ever identified in meteorites, may need to be re-evaluated.

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Figure 1: [110] lattice-fringe images simulated under the following conditions: defocus=-40.2 nm, thickness=2.5 nm, E=400 kV and Cs=1.0 mm. All indicated spacings are {111} except in (F) where they are {001}.

Figure 2: Actual lattice-fringe images of nano-diamonds in micrometeorite AMMSRU2-2, cluster particles U2-20-GCA and RB12A44, U2-30C-1G-B.