ORGANIC COATINGS ON INDIVIDUAL GRAINS IN CP IDPs: IMPLICATIONS FOR THE FORMATION MECHANISM OF PRE-BIOTIC ORGANIC MATTER AND FOR GRAIN STICKING IN THE EARLY SOLAR SYSTEM. G. J. Flynn[1], S. Wirick[2], L. P. Keller[3], C. Jacobsen[2], and S. A. Sandford[4]. [1]Dept. of Physics, SUNY-Plattsburgh, Plattsburgh NY 12901 USA (george.Flynn@plattsburgh.edu). [2]Dept. of Physics and Astronomy, SUNY- Stony Brook, Stony Brook, NY 11794 USA, [3]NASA Johnson Space Center, Houston TX 77058 USA, [4]NASA Ames Research Center, Moffett Field, CA 94035 USA.

Introduction: Chondritic, porous interplanetary dust particles (CP IDPs) are the most primitive samples of extraterrestrial material available for laboratory analysis [1]. These CP IDPs are unequilibrated aggregates of mostly submicron, anhydrous grains of a diverse variety, including olivine, pyroxene, glass, and sulfide. The CP IDPs contain a significant amount of organic matter that was not produced by parent body aqueous processing [2], some carrying H and N isotopic anomalies consistent with molecular cloud or outer Solar System material [3]. However, we were not able to tightly constrain the time or mechanism of its production. Detailed analyses of organic coatings on the individual mineral grains in CP IDPs now allows comparison to models for production of pre-biotic organic matter and examination of the role of this organic matter in the assembly of grains into dust particles.

The CP IDPs, typically ~5 to 20 µm dust from asteroids and comets, are collected by NASA from the Earth's stratosphere after relatively gentle deceleration in the upper atmosphere. Typical ~10 µm CP IDPs are aggregates of $>10^4$ anhydrous grains, mostly submicron in size. The individual grains in CP IDPs are not in direct contact with each other. Most grains are coated by alayer of carbonaceous material ~50 to 200 nm thick [4]. This structure indicates the carbonaceous material must have been added to the surface of each grain before aggregation of the dust particles.

This structure implies a three-step sequence for the formation of primitive dust from the Solar Nebula. First, individual grains condensed from the cooling nebular gas. Then complex, refractory organic molecules covered the surfaces of the grains either by deposition, formation in-situ, or a combination of both processes. Finally, the grains collided and stuck together forming the first dust-size material in the Solar System, these CP IDPs. Thus, the grains that acquired this organic coating are likely to be the earliest grains from the Solar Nebula, preceeding the assembly of the primitive CP IDP dust particles.

Samples and Measurement Techniques: Ultramicrotome sections, ~70 to 100 nm thick were cut from several CP IDPs that were embedded in elemental S [2]. Some sections were deposited on TEM grids with SiO substrates for carbon analyses, while other sections of the same IDP were deposited on TEM grids with conducting substrates for mineralogical characterization in a transmission electron microscope (TEM).

We analyzed the carbonaceous grain coatings using a scanning transmission x-ray microscope (STXM) on Beamline X1A1 of the National Synchrotron Light Source (Brookhaven National Laboratory). This STXM has a monochromatic x-ray beam focused to an ~35 nm spot using a zone plate (see Flynn et al. [2]. By rastering the sample through the fixed beam, we obtain x-ray absorption maps of each sample at the selected energy. We collect a sequence of absorption maps by stepping the monochrometer over the range from 280 to 310 eV, typically in 0.1 eV steps over the critical range from 294 to 300 eV, where the distinctive molecular features occur. The maps in this image stack are then aligned, and x-ray absorption near-edge structure (XANES) spectra are derived by comparing the absorption at a pixel in the image with the absorption in a reference area located on the substrate.

In XANES spectroscopy x-rays induce electron transitions from the ground state to unoccupied, higher-energy molecular orbitals, which have transition energies characteristic of specific functional groups. This probes the molecular structure. Carbon-XANES spectroscopy is particularly useful in distinguishing elemental carbon, such as graphite, amorphous carbon, and fullerenes, from organic carbon by detecting the carbon to H, N, or O bonding characteristic of organic matter.

Results: "Cluster analysis" was used to compare the C-XANES spectra from each of the pixels in an image stack and identify groups exhibiting similar spectra [5]. When applied to a CP IDP, the cluster analysis technique identifies most of the carbonaceous grain coatings in a particle as material having similar C-XANES spectra (see Figure 1). In each case, the grain coating is organic, rather than elemental amorphous carbon. The typical C-XANES spectrum shows two strong pre-edge absorption peaks, one near 285 eV, which results from the C=C functional group, most likely C-rings, and a second near 288.6 eV, which results from the C=O functional group. The weaker absorption near 286.5 eV is in an energy range where several functional groups, including C-N and O bonded to an aromatic C-ring, have absorption features.

Implications for the Production Mechanism: Two processes are commonly suggested in the literature for production of organic coatings on mineral grains: catalysis of gas phase species on grain surfaces [6] or condensation of C-bearing ices that are then altered by UV or ionizing radiation [7]. The similarity in thickness and in C-XANES spectra of the coatings on different minerals in the same IDP indicates that mineral specific catalysis, like the Fischer-Tropsch process, was not the process that produced these organic rims. Further, since catalysts are poisoned by even a monolayer of product, the ~100 nm thickness of these rims is inconsistent with mineral specific catalysis. An alternative catalysis process, in which the carbonaceous grain coatings themselves serve as catalysts for further organic production [8] cannot be ruled out by our measurements. Noneteless, our results are consistent with this primitive organic matter being produced by condensation of C-bearing ices onto the grain surfaces and production of refractory organic matter by UV or other ionizing radiation bombardment of the ices.

Implications for Grain Aggregation in the Early Solar System: The processes by which primitive grains aggregate to form the first dust of our Solar System are not well understood. After condensing from the Solar Nebula these grains are believed to have orbited the Sun in nearly circular orbits, resulting in relatively low speed collisions. A number of theoretical studies have examined the possible processes resulting in grain sticking [9]. But collision experiments indicate that bare rocky particles bounce apart at collision speeds less than 30 to 50 m/s and shatter each other at larger speeds [10]. It appears to require a coating of shock absorbing material to allow collisions to result in aggregation and growth of dust particles [10].

The organic rims we observe on these primitive grains may have been critical for aggregation. Kudo et al. [11] performed collision experiments on laboratory analogs of interstellar organics and found they stuck together quite easily, even at collision speeds up to 5 m/s – an order of magnitude higher than the speed at which silicate- or ice-based grains accrete [11].

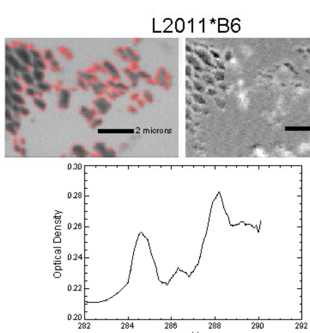

Figure 1: X-ray absorption image of an ultramicrotome section of the CP IDP L2011*B6, with the red overlay showing the pixels selected by "cluster analysis" as having a common C-XANES spectrum (top). The C-XANES spectrum of the pixels highlighted in red is shown below the image.

While we have not directly measured the strength of the organic matter that coats the grains in the CP IDPs, we have two indirect indications of the strength. First, the ~10 µm CP IDPs remain intact upon impact with the aircraft-borne collector, indicating significant strength. A more compelling inference of the adhesive strength of this organic matter comes from the survival of these particles in space. The photoelectric effect, driven by Solar photons, causes small grains, like the CP IDPs, to be charged to a potential of ~10 volts in space near 1 AU. Since the CP IDPs are aggregates of $>10^4$ individual grains, they would be blown apart by the electrostatic forces resulting from this charging unless there were an even greater force holding them together. For a surface potential of 10 volts, a 10 µm particle is estimated to require a minimum tensile strength of 10^3 N/m^2 to remain intact [12], which is comparable to the strength inferred for cometary meteors based on fragmentation in the atmosphere [13].

Conclusions: The individual grains in CP IDPs are rimmed by a thin coating of organic matter. These organic rims may have been critical to grain aggregation in the Solar Nebula, and certainly provide an adhesive force that holds the grains in CP IDPs together today. These organic coatings have properties inconsistent with their formation by mineral specific catalysis, such as the Fischer-Tropsch process, but consistent with formation by condensation of carbon-bearing ices on grain surfaces and production of more refractory organic matter by UV or charged particle irradiation.

References: [1] Ishii, H. et al. *Science* 2009. [2] Flynn, G. J. et al. (2003) *Geochim. Cosmochim. Acta*, **67**, 4791-4806. [3] Keller L. P. et al. GCA (2004) *Geochim. Cosmochim. Acta*, **68**, 2577-2589. [4] Thomas, K. L. et al. (1996) *ASP Conference Series*, **104**, 295-298 [5] Lerotic, M. et al. (2005) *J. Electron Spectroscopy and RelatedPhenomena,* **144--147**, 1137-1143. [6] Hayatsu, R. and Anders, E. (1981) *Topics Curr. Chem.* **99**, 1–37. [7] Bernstein, M. P. et al. (1995) *Astrophys. J.,* **454**, 327-344. [8] Nuth, J. et al. (2008) *Proceedings of IAU Symposium 251* (eds. S. Kwok and S. A. Sandford), 403-408. [9] Dominik, C. and A. G. G. M. Tielens (1997) *Astrophys. J.,* **480**, 647-673. [10] Hartmann, W. K. (1978) *Icarus*, **33**, 50-61. [11] Kudo, T. et al. (2002) *Meteoritics & Planet. Sci.*, **37**, 1975-1983. [12] Graps, A. and Grun, E. (2000) www.mpi-hd.mpg.de/dustgroup/~graps/debris/graps-gruen_630.pdf [13] Trigo-Rodriguez, J. M. and J. llorca (2006) *Month. Not. Royal Astron. Soc.*, **372**, 655-660.