COORDINATED TEM, ISOTOPIC AND HEATING ANALYSES OF DISTINCTIVE CARBONACEOUS PHASES IN IDPS. G. Matrajt[1], S. Messenger[2], D. Brownlee[1], and. D. Joswiak[1]. [1]University of Washington, Department of Astronomy, Box 351580 Seattle WA 98195, USA (matrajt@astro.washington.edu), [2] Robert M. Walker Laboratory for Space Science, ARES, NASA Johnson Space Center 2101 NASA Pkwy Houston TX, 77058

Introduction: Interplanetary dust particles (IDPs) are very rich in carbon and the carbon is usually present in several distinct morphologies [1]. Here we present data on three IDPs: W1754-I1 (called Plin), an anhydrous porous particle; W7259A-6C (called Nayeli), a hydrated smooth particle; and two fragments of giant cluster particle U2-20GCA (called Tetouille and Cielo). All the particles were investigated using a TEM, followed by NanoSIMS analyses. For one of the particles heating experiments using a tube furnace were performed in order to investigate the fate of the carbonaceous phases when exposed to high (> 600 ºC) temperatures. Our study has several goals: first to characterize the different types of morphologies observed among the carbonaceous phases found. Second, to determine the ^{15}N and ^{13}C isotopic compositions of each of the different morphologies found in the particles, and finally, to investigate whether these morphologies are the result of flash heating at high temperatures during the atmospheric entry or are primary.

Materials and methods: All particles were embedded in acrylic, microtomed and sections were placed on TEM grids. Acrylic was removed from grids using condensed chloroform vapors. All samples were analyzed with a 200 kV Tecnai F20 FEG STEM equipped with an energy dispersive X-ray (EDX) detector and a Gatan Imaging Filter (GIF) detector, used to locate and map the carbon with Electron Energy Loss Spectroscopy (EELS). An Orius CCD camera, was used to obtain high resolution images of the carbonaceous areas and to accurately determine the type of morphology. Then, samples were subjected to C and N isotopic imaging with the JSC NanoSIMS 50L ion microprobe. Images of $^{12}C^-$, $^{13}C^-$, $^{16}O^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, and $^{28}Si^-$ were acquired simultaneously in multidetection with electron multipliers and by rastering a 16 keV, 1 pA Cs^+ ion beam focused to 100 nm. We acquired 20-30 images of each sample over periods of 5-8 hours. Sample charging was mitigated by use of an electron flood gun during the analysis. Nearby grains of 1-hydroxyl benzotriazole hydrate were measured as C and N isotopic standards. In addition, the amorphous C film substrate served as a secondary isotopic standard, providing an isotopic reference during the sample analysis. A microtomed section of particle Cielo placed on a Cu grid was heated for 10 sec at 620 ºC, 660 ºC, 750 ºC and 850 ºC inside a tube-shaped ceramic furnace with a N_2 flow passing through to avoid oxidation. To accurately monitor the temperature, a thermocouple was placed inside the furnace at the time of the experiment. Time was chosen in order to mimic the flash heating time to which IDPs are exposed when entering the atmosphere. The grid was observed in the TEM to monitor the fate of the different morphologies after each heating sequence and before raising the temperature to the next level up.

Results: The TEM-EELS studies showed that all the particles analyzed contain carbon. Carbon was imaged using a high resolution camera at different magnifications and this procedure revealed, as was already found in past studies [1], that carbon is present in several different types of morphologies. In the present study we found five different morphologies: globular, spongy, vesicular, smooth, and dirty, defined as carbon containing embedded mineral grains (Fig. 1).

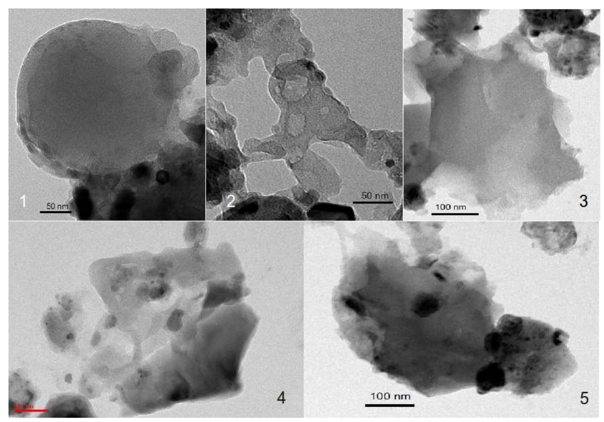

Fig.1. Carbon morphologies. 1) globular; 2) spongy; 3) smooth; 4)vesicular; and 5) dirty.

All particles have at least three of these morphologies. Carbonaceous areas range in size from ~100-300 nm and are typically found spread within the particle in discreet, individual regions rather than concentrated in one bigger/unique area. The NanoSIMS analyses revealed two main things: first, because this technique can map both C and N when bonded together, we could see that all the carbonaceous morphologies contain N and that the N concentrations vary within different morphologies. Second, although not all the morphologies have δ^{13}C anomalies (Table 1), all of them have δ^{15}N enrichments to some extent, with the presence of hot spots in all the particles studied. In general, δ^{15}N enrichments varied from 200 to more than 1000‰, and δ^{13}C was normal for almost all particles. In particle Tetouille we found several small δ^{15}N hotspots that exceed 1000 ‰, but most areas are in the 600-700‰ range.

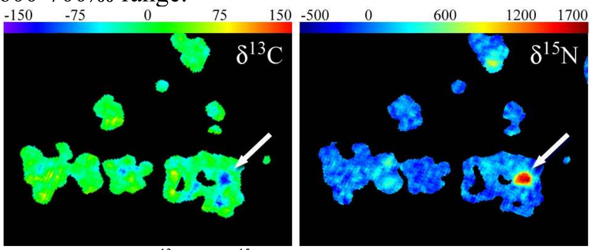

Fig. 3. $\delta^{13}C$ and $\delta^{15}N$ isotopic maps of Tetouille.

One spot in particle Tetouille showed simultaneously a $\delta^{15}N$ enrichment of 1440 ±100‰ and a $\delta^{13}C$ depletion of -122±26 (Fig. 3). This spot corresponds to a dirty morphology (Fig. 4).

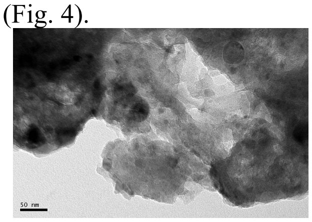

Fig. 4. Carbonaceous area with dirty morphology in particle Tetouille which showed simultaneously $\delta^{13}C$depletion and $\delta^{15}N$ enrichment.

The heating experiments of particle Cielo did not show obvious changes/modifications/alterations in the carbonaceous morphologies (Fig. 5).

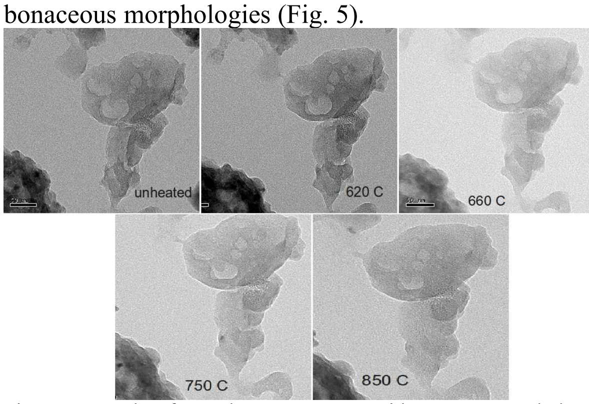

Fig. 5. Example of a carbonaceous area with spongy morphology that was heated at several temperatures.

For example, we did not observe an increase/decrease in the amount of vesicles, globules, spongy areas, etc. Smooth areas remained smooth. Dirty areas remained dirty and perhaps became smoother but in no case new bubbles/vesicles or globules were observed. This suggests that the carbonaceous phases are refractory. It is still unknown whether they are pristine refractory phases or they became refractory after being strongly heated upon atmospheric entry. Further heating experiments on smaller, less heated IDPs are in progress to address this question.

Discussion: The morphologies observed in these particles were also observed in past studies [1]. In particular the globular morphology [2, 3 and ref therein] which has been associated with some of the highest H and N anomalies [4]. N isotopic anomalies are commonly observed in primitive meteorites, IDPs, and Stardust samples [5-7]. The most anomalous material we identified is isotopically similar to an IDP hotspot reported by Floss et al. [8] ($\delta^{15}N$=1270‰, $\delta^{13}C$=-70‰), but in our study the hot spot is more anomalous in both isotopes ($\delta^{15}N$=1440‰, $\delta^{13}C$=-122‰). It is believed that these isotopic anomalies probably originated from low temperature chemical fractionation in the outer solar system or cold molecular cloud [6], suggesting that the carbonaceous grains in our particles likely formed at very low temperatures, either in a pre-solar cold molecular cloud or in very cold regions of the Solar System before they aggregated into the parent body. The different morphologies studied do not show consistently the same isotopic compositions, i.e. they show a wide range of values, suggesting that they either have different origins or have gone through different histories before they aggregated in the parent body. Given that we did not observe significant/obvious changes in the carbon morphology when exposed to high temperatures and that these morphologies are next to each other (within just a few nm) meaning that they must have had the same thermal history during entry, we suggest that the different morphologies found in these particles are primary, i.e. they formed in the parent body (or before they aggregated) and not during the process of atmospheric entry. In addition, some of these morphologies (i.e. globules) have also been found in meteorites [2,3] supporting the argument that they are primordial phases. Comparison of these carbonaceous morphologies to similar carbonaceous phases in Stardust particle Isis are in progress.

Particle	Morphology	$\delta^{15}N \pm 1\sigma$(‰)	$\delta^{13}C \pm 1\sigma$(‰)
Nayeli	globular	210±20	Normal
Plin	globular/smooth	335±95	-41.6±55
Plin	spongy+globular	495±87	17.5±39
Tetouille	globular	765±18	-25±12
Tetouille	smooth	675±52	30±19
Tetouille	vesicular	431±30	-32±11
Tetouille	spongy	469±35	-19±15
Tetouille	dirty	1440±100	-122±26

Table 1.

References: [1] Matrajt G. et al. (2010) *LPS XLI,* Abstract #1564; [2] Nakamura-Messenger K. et al. (2006) *Science* 314, 1439. [3] Garvie L. et al. (2008) *Meteoritics & Planet. Sci.* 43, 1-5. [4] Messenger S. et al (2008) *LPS XXXIX*, Abstract #2391.[5] Busemann H. et al. (2006), *Science* 312, 727. [6] Messenger S. (2000) *Nature* 404, 968. [7] Matrajt G. et al. (2008) *Meteoritics & Planet. Sci.*, 43, 315-334. [8] Floss C. et al. (2004) *Science* 303, 1355.