ATMOSPHERIC ENTRY HEATING EFFECTS ON ORGANIC CARBONACEOUS PHASES OF IDPS AND POLAR MICROMETEORITES: AN EELS STUDY. G. Matrajt, *Department of Astronomy, University of Washington, Seattle WA, 98195 (matrajt@astro.washington.edu)*, D. Brownlee, D. Joswiak, *Department of Astronomy, University of Washington, Seattle WA, 98195*, S. Taylor, *U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, 03766*.

Introduction:

Electron Energy Loss Spectroscopy (EELS) is a technique currently used to study carbonaceous phases in small particles such as IDPs [1]. Very ordered carbon such as graphite presents a particular EELS spectrum, which is different from the EELS spectrum of poorly ordered carbon such as amorphous or organic carbon [2,3]. Among the differences that exist between these two types of EELS spectra, the two most visible are the presence or absence of a well defined σ peak with a maximum between 292-293 eV, and the presence or absence of a small peak near 6 eV (that we called γ peak) in the loss region [4], between the ZLP (zero loss peak) and the plasmon peak (see Figs. 1 and 2). Heated carbon presents some order in its structure that is usually distinguished in the EELS spectrum by the presence of a small σ peak [4]. IDPs and micrometeorites contain pristine and thermally processed carbonaceous phases. To distinguish these two different phases we combined EELS with high resolution imaging methods to study the carbonaceous phases of 3 IDPs and one polar micrometeorite. To determine the nature and temperature at which the thermally processed phases were formed we studied a range of different carbonaceous materials that we pulse-heated to different temperatures.

Samples and Methods:

Two of the IDPs studied are pieces from giant cluster particles. The polar micrometeorite is a scoriaceous particle that appears to have been heated above 1000 $^{\circ}$C due to the presence of vesicles. Several carbonaceous materials were used as standards: a PAH (coronene), an aliphatic (oxalic acid), graphite, kerogen (acid residue of Orgueil), coal and a fullerene (C_{60}). These were crushed and dispersed on Quant-foil holey-carbon grids. One cluster IDP fragment was crushed into tiny grains before embedding. The other IDPs and the micrometeorite were embedded directly without crushing. The purpose of crushing was to investigate carbonaceous phases that could be surrounded and hidden by silicates and other mineral phases. The embedded samples were then microtomed. To avoid carbon interference from the embedding media we used a new embedding medium (Weldon 40 acrylic) which is fully removed from sections by vapor condensed chloroform, a technique we developed. Some sections were placed on Quant-foil holey-carbon grids while others were placed on SiO film grids. EELS spectra were obtained using a 200 kV Tecnai F20 FEG STEM equipped with a Gatan parallel spectrometer. The energy resolution typically obtained was 0.8-0.9 eV. The acquisition times were typically between 10-15 sec to avoid beam damage and contamination. Pulse-heating experiments were performed using a small volume cylindrical tube furnace under a constant N_2 flow to avoid oxidation by air. The samples were placed in Pt foils and heated for 5 sec at 450, 550, 645, 930 and 1030 ^{o}C.

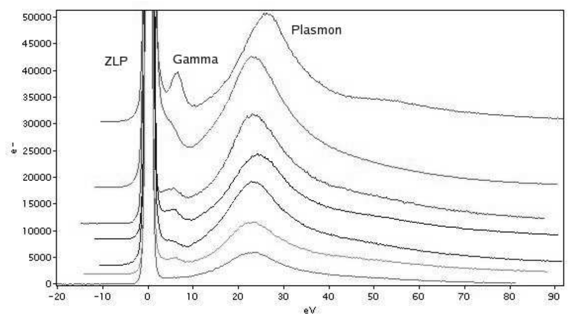

Figure 1: EELS spectra (low-loss region) of some of the samples studied. From top to bottom: graphite, Orgueil residue heated at 1030 ^{o}C, PAH (coronene), micrometeorite, IDP, PAH (coronene) heated and amorphous carbon (film of grid).

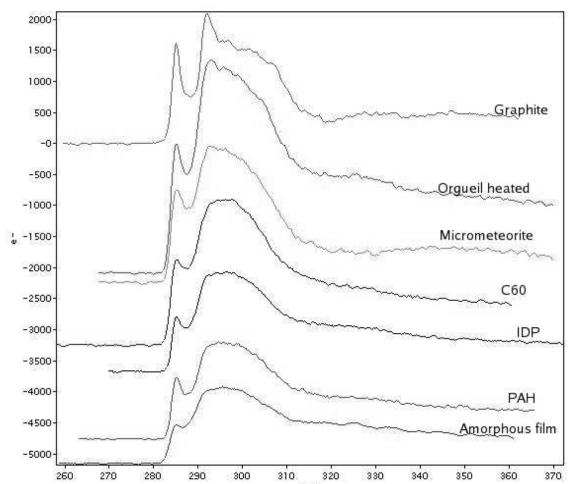

Figure 2: EELS spectra (core-loss region) of some of the samples studied. From top to bottom: graphite, Orgueil residue heated at 1030 ^{o}C, micrometeorite, C_{60}, IDP, PAH (coronene) and amorphous carbon (film of grid).

Results:

Spectroscopy: The low loss region (see Fig. 1): Completely amorphous carbon such as the one found on the film of the grid does not have a γ peak. Graphite, on the other hand, has a very well separated and distinguished γ peak whose position is typically found at 5.5-6.0 eV. The organic and kerogen standards have a barely distinguishable γ peak that appears as a shoulder of the ZLP. Its position varies from one material to the other. In graphite, this peak is usually found between 25-27 eV, whereas in the other samples its position falls between 22-24 eV.

The core loss region (see Fig. 2): all the unheated standards except graphite present a similar core-loss EELs spectrum, typical of amorphous carbon. These spectra typically have a π peak at 285 eV and a broad σ feature. The center of this broad feature is typically found between 295-300 eV. In graphite, the core-loss has also a π peak at the same position and the σ peak presents structure with a maximum between 292-293 eV.

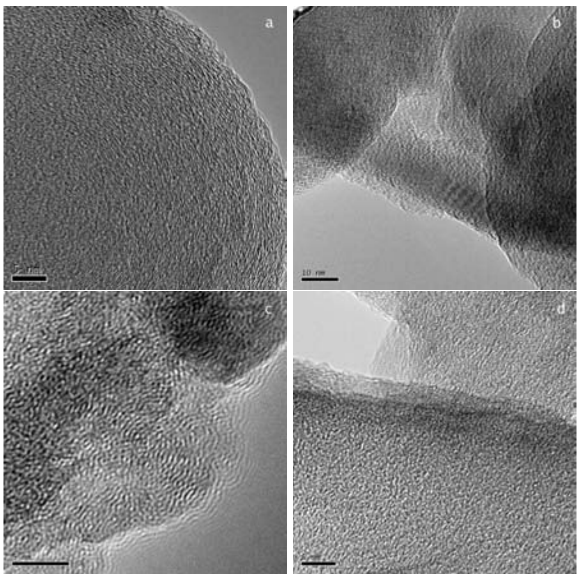

Figure 3: High resolution images of a) circular onion-like fringes in micrometeorite; b) circular onion-like and graphite-like fringes in micrometeorite; c) circular onion-like fringes in Orgueil heated and d) amorphous carbon (no fringes) in IDP.

Imaging: The high resolution images of all the unheated standards, except graphite, show a structure typical of amorphous carbon *i.e.* no order. Graphite presents the typical fringes with 3.4 Å spacing.

Pulse-heating experiments: Only the kerogen extracted from Orgueil heated at 1030 ^{o}C and the coronene (organic) heated at 645 ^{o}C showed a different core loss EELs spectrum compared to their unheated counterparts (see Fig. 2). In particular, one can start distinguishing a tiny σ peak with a maximum between 292-293 eV. However, this σ peak can only be clearly distinguished at some spots because, as for graphite, the core-loss shape and intensity varies in function of the orientation of the sample relative to the incident beam [2]. In these same samples one can observe (see Fig. 3) circular onion-like fringes typical of poorly ordered carbon [5]. The heating at the other temperatures of the other standards did not show any differences in the EELs spectra compared to their unheated counterparts. Their high resolution images appear to be amorphous carbon with no order at all. The PAH heated at temperatures higher than 645 ^{o}C did not survive.

Discussion:

The two cluster IDPs that were analyzed showed, in all the areas surveyed, an amorphous carbonaceous material. Neither the structure observed with HR imaging nor the EELs spectra obtained revealed any sign of heating. Because the structure of the amorphous non-organic carbon (film of grid, C_{60}, ...) and its EELs spectrum is identical to the organic materials used as standards (PAH, oxalic acid, kerogen from Orgueil, ...), we cannot determine whether the observed amorphous carbonaceous material in IDPs is organic or not. However, the absence of fringes, circular onion-like structures, well-defined γ and σ peaks, suggest that these two particles could not have been heated during their atmospheric entry to more than 645 ^{o}C (if this carbon is indeed a PAH-like organic) or more than 1030 ^{o}C (if this carbon is kerogen-like). The other IDP and the polar micrometeorite have a combination of structures in their carbonaceous phases: poorly organized graphitic layers [5] with 3.4 Å spacings, circular onion-like structures with discontinous fringes, and amorphous carbon (see Fig. 3). In general, the amorphous phases dominate the other phases, which seem to be "embedded" in the surrounding amorphous carbon. In most cases the fringes are found in little regions or "islands", only observed at very high magnifications (> 940,000 X). The EELs spectra very often look like an amorphous carbon, but at some spots a σ peak is present, typically between 292.2-293.6 eV (see Fig. 2). These observations suggest that these two particles were heated above 645 ^{o}C or 1030 ^{o}C, depending on the nature of the precursor carbon. It is worth noting that for the IDP, the heated carbonaceous regions were only observed in the very first microtomed slice (50 nm thick). None of the other slices (up to 10 surveyed so far) presented any structure typical of a heated carbon. This observation suggests that this particle could have been submitted to a temperature gradient during its atmospheric entry. Further studies are needed to investigate this possibility.

Conclusions:

This work has shown that high resolution imaging combined with EELS spectroscopy can distinguish strongly heated from less heated and pristine carbon in IDPs. However, the edge structure (σ peak) observed in the EELS spectra only occurs in carbonaceous phases that have been heated above 700 ^{o}C.

References: [1] Keller et al (2004) *GCA*, **68**, 2577-2589. [2] Egerton, R.F. (1986) in *Electron energy-loss spectroscopy in the electron microscope*, 410 p. [3] Garvie L.A.J. and Craven A.J. (1994) *Am. Mineral.*, **79**, 411-425. [4] Jeanne-Rose V. et al. (2003),*J. Microscopy*, **210**, 53-59. [5] Buseck P. and Bo-Jun H. (1985), *GCA*, **49**, 2003-2016.