REVISITING C_{60} FULLERENE IN CARBONACEOUS CHONDRITES AND INTERPLANETARY DUST PARTICLES: HRTEM AND RAMAN MICROSPECTROSCOPY

Frans J. M. Rietmeijer[1], Janet Borg[2] and A. Rotundi[3]; [1]Department of Earth and Planetary Sciences, MSC03-2040, 1-University of New Mexico, Albuquerque, NM 87131-0001, USA; [2]Institut d'Astrophysique Spatiale, Bâtiment 121, Campus 91405 Orsay Cedex, France; [3]Ist. di Matematica, Fisica e Applicazioni, Università di Napoli "Parthenope", Via A. De Gasperi 5, 80133 Naples, Italy

Introduction: When getting ready for comet Wild-2 STARDUST samples the true nature of the carrier of the astronomical 217.5nm UV extinction feature is yet again of interest. Amorphous carbon, hydrogenated amorphous carbon, 'quenched carbonaceous condensates', nanodiamonds, fullerenes and soot are viable candidates [1,2] although fullerenic carbons such as the famous onions found in the Allende meteorite [3] are missing from this list. The returned dust from comet Wild-2 could finally show the true nature of the carbon carrier. Here, we assess the detection of minor amounts of C_{60} in natural and analog samples.

High-resolution transmission electron microscope (HRTEM) studies of carbons in the Allende, Leoville and Vigarano meteorites found multiple- and single-wall fullerenic (closed) carbons structures [4,5]. The single-wall ring structuresof *ca*. 2-5 nm in diameter in the Allende meteorite might be higher fullerenes, suggesting that C_{60} could also have been present [5]. Meteorites and interplanetary dust particles (IDPs) are complex samples and when searching for a minor constituent, *e.g*. fullerene, it would be expedient to know the unique fullerene signature in HRTEM images or in Raman spectra of carbon-rich material obtained by vapor-vapor condensation experiments wherein fullerene is present among many different carbon forms in such analog samples.

Fullerenic Carbons and C_{60}: An arc-discharge carbon-vapor condensation experiment, conducted to identify the carrier of the 217.5nm feature, yielded (1) soot grains, (2) fullerenic nanotubes and onions, and (3) amorphous, (4) poorly-graphitized, and (5) graphitic carbons [6]. The amorphous soot grains were the most likely carbon carrier of this feature [6]. A subsequent combined TEM/HPLC study identified the single-wall ring structures with average 0.7, 1.1, 3.0, 5.5 and 8.2 nm diameters in soot [7] as C_{60} and larger, C_{540}, C_{960}, C_{1500}, fullerene. Many soot grains show curvilinear 'protofringes' that are regular arrangements of individual fullerenes [7] (Fig. 1). Another HRTEM study identified similar single-wall ring structures in carbon black as fullerenes C_{36} to C_{176} [8].

Both studies show that HRTEM is capable to identify small quantities of fullerenes in amorphous soot that would be below the detection limit of chemical techniques. Now knowing what to look for in HRTEM images, were fullerenes overlooked in carbonaceous chondrites, IDPs and carbon analogs? Yes, probably.

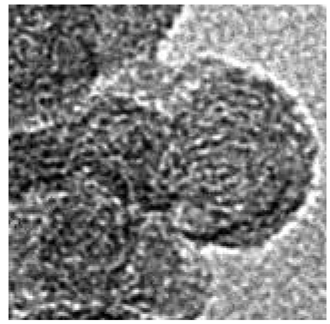

Fig. 1: Fullerene protofringes in condensed soot, the carrier of the 217.5 nm extinction feature [6]. [Modified after ref. 7]

For example, without pretending being complete, a few studies of condensed carbon analogs show single-wall ring structures in onion-type nanoparticles [9-11]. Similar structures were seen in insoluble organic matter of the Murchison and Orgueil meteorites [12], supporting the presence of fullerene in these meteorites.

C_{60} Fullerene in IDPs: C-XANES peaks at 284.8, 286.3 and 288.5eV energies for carbonaceous material in a C-rich, chondritic porous aggregate IDP were initially linked to C_{60} [13]. Re-assessment of these data, as part of a larger dataset of chondritic IDPs, no longer assigned these peaks to C_{60} [14]. Does it mean there is no C_{60} in aggregate IDPs? Could fullerene be oxidized during atmospheric entry flash heating with only vestiges surviving intact? The literature shows a surprising dearth of HRTEM images of carbon materials in C-rich IDPs for a proper assessment of fullerene presence.

Raman Microspectroscopy: A survey of 20 chondritic IDPs found that 75% contained "poorly crystallized carbonaceous material" with a Raman signature consistent with variable degrees of "disorder" [15]. The mean crystallite size in the most 'ordered' of these IDP materials was estimated at ~3 nm but <6 nm assuming the material resembled activated charcoal or glassy carbon with a "turbostratic structure" [15]. The calculated crystallite sizes closely resemble those of fullerene molecules in condensed soot [7].

Since this pioneering work [ref. 15] Raman microspectroscopy has been little used to identify the nature and crystallographic structure of elemental carbons in extraterrestrial materials. Raman searches for C_{60} and other fullerenes in these materials were so far neglected even in the recent work on characterizations of the organic matter in various meteorites and several IDPs

[16,17]. The Raman spectra from two different areas in a sample from the same condensed carbon study with fullerenic carbons and the C_{60} and larger fullerenes containing soot [6,7] show peaks at 396, 680, 1358 and 1594 cm^{-1} (Fig. 2; left) and at 1352, 1593, ~2700 and ~2900 cm^{-1} (Fig. 2; right). In both spectra, the separation of the 'D' and 'G' peaks (respectively ~1350 and ~1580 cm^{-1}) is poorly defined with regard to this separation in a typical Raman spectrum of disordered, pre-graphic carbons, and the intensity ratio of the D/G peaks is equal to or larger than unity, *i.e.* the D/G ratio expected for pre-graphitic mature carbons [18].

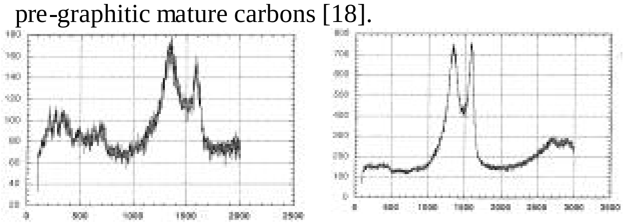

Fig. 2: Raman spectra for two areas in a sample [ACH_2800, ref.6] obtained in the 200-2000 cm^{-1} region (left) and the 200–3000 cm^{-1} region (right) be due to the presence of fullerene and/or fullerenic carbons.

This peak configuration (Fig. 2) could suggest an additional Raman carbon signal such as $C_{60}+C_{70}$ fullerene or fullerenic-carbon nanotubes. The latter have additional peaks at <1100 cm^{-1} and >2600 cm^{-1}; the fullerenes have a major peak at 1470 cm^{-1}. Thus, we hypothesize that the particular peak configuration in this condensed carbon analog sample [6] is due to the presence of either one, or both, of these carbon forms. We will test whether a wider spectral range and a stronger signal to noise ratio between 300-1100 cm^{-1} and in the 'D' and 'G' region, would allow detection of fullerene and fullerenic carbons in various extraterrestrial samples. The clear implication being that these carbon forms went undetected by previous Raman micro-spectroscopic analyses. We note that Raman spectra of the "most 'ordered' material" in IDPs [15] show a similar 'D' and 'G' peak configuration as in Fig. 2.

Discussion: Even a cursory literature search shows that natural C_{60} survival (and other fullerenes?) seems a matter of "easy come, easy go". There are apparently few environmental constraints on natural C_{60} formation but its survival is sensitive to environmental factors, e.g. ozone, UV radiation or hypervelocity impact that could cause a solid-state fullerene to nanodiamond transformation. In this regard the remarkable similarity between the range and modal dimension of fullerenes in soot [7] and carbon black [8] and those of nanodiamonds in IDPs [19] lends support for this fullerene transformation in the solar nebula or protoplanets. However, more mundane processes could destroy pre-existing C_{60} fullerene, *viz*. UV processing prior to, and during, nebular dust accretion or oxidation of IDPs during atmospheric entry flash heating. It is not too surprising when this carbon molecule is elusive in meteorite and IDPs, as its presence will be the remains of what was once a widespread original abundance.

We submit that *in situ* searches of carbonaceous matter by HRTEM and Raman microspectroscopy will locate fulllerene in quantities too small for other techniques, albeit without any prospect of quantification. It thus becomes imperative to prevent deterioration of extraterrestrial carbons in the terrestrial environment.

There are no curatorial precautions in place to prevent degradation of fullerene in C-rich meteorites (e.g. Tagish Lake) and C-rich chondritic aggregate IDPs. Not even against temperature and humidity that were found to cause the terrestrial redistribution of sulfate in CII chondrites [20]. Moisture in ambient air is also implicated in fullerene oxidation [21].

Conclusions: Within a year the STARDUST mission will deliver dust from comet Wild-2 that will be our best link yet to the presolar, molecular cloud, dust. HRTEM and Raman analyses could be used to detect C_{60} and other fullerenes in cometary dust. When the stability of these carbon molecules is limited by environmental conditions, it would be prudent to store and process STARDUST samples, and also IDPs, away from UV light in a nitrogen atmosphere to minimize fullerene degeneration and destruction.

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