

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/227120193>

# Natural C<sub>60</sub> and Large Fullerenes: A Matter of Detection and Astrophysical Implications

CHAPTER · JANUARY 1970

DOI: 10.1007/1-4020-4135-7\_5

---

CITATIONS

3

---

READS

41

3 AUTHORS, INCLUDING:



[Alessandra Rotundi](#)

Parthenope University of Naples

157 PUBLICATIONS 1,772 CITATIONS

SEE PROFILE

## Chapter 5

# NATURAL C<sub>60</sub> AND LARGE FULLERENES: A MATTER OF DETECTION AND ASTROPHYSICAL IMPLICATIONS

ALESSANDRA ROTUNDI

*Dipartimento di Scienze e Applicazioni, Università "Parthenope" di Napoli, Via A. De Gasperi 5, 80133 Napoli, Italy*

FRANS J.M. RIETMEIJER

*Department of Earth and Planetary Sciences, MSC03-2040, 1-University of New Mexico, Albuquerque, NM 87131-0001, USA*

JANET BORG

*Institut d'Astrophysique Spatiale, Bâtiment 121, Campus 91405 Orsay Cedex, France*

**Abstract:** Fullerene was theoretically predicted and experimentally discovered, but its detection in laboratory studies is still underrepresented with respect to its theoretical abundance. Recent High Resolution Transmission Electron Microscopy (HRTEM) studies of soot samples, however, lead to single fullerene molecule detection in higher amounts than was previously established. HRTEM is able to identify fullerenes even if they are only present in small quantities that would be below the detection limit of chemical techniques. Fullerenes will probably remain largely undetected until higher signal to noise ratio measurements are used to search for them. Such studies could yield different conclusions on fullerene abundances both in terrestrial and in extraterrestrial samples. For the latter, important astrophysical implications have to be considered.

**Key words:** Carbon chain molecules; carbon monocyclic ring molecules; carbon vapor condensation; carbonaceous chondrites; cosmic dust; fullerenes; high-resolution transmission electron microscopy (HRTEM); interplanetary dust particles; meteorites; polycyclic aromatic hydrocarbons (PAHs); PAH molecules; Raman microspectroscopy; soot

## 1. INTRODUCTION

The prediction by Kroto et al. (1985) that fullerene molecules, including C<sub>60</sub>, ought to be abundant seems not yet to be borne out by the analyses of natural soot samples but, more importantly, they are apparently also not seen in soot that was produced in the laboratory under carefully controlled conditions that should have led to fullerene formation. In fact, while [Krätschmer et al. \(1990\)](#) synthesized macroscopic amounts of C<sub>60</sub>, this molecule remains under-represented in natural samples and it seems that experimental conditions for its production are either too peculiar to prove its theoretical pervasiveness (Taylor et al., 1991), or some other factors control the existence of natural fullerenes. Fullerene searches included circumstellar and interstellar environments, Interplanetary Dust Particles (IDPs), meteorites, lunar rocks, terrestrial hard-rocks, coal, and sedimentary rocks (Heymann et al., 2003). The only diagnostic tool available for fullerene detection in astronomical environments (e.g. Snow and Seab, 1989; Foing and Ehrenfreund, 1994, 1997; Webster, 1997; Sassara et al., 2001) relies on the analysis of electromagnetic radiation, which requires a synergy between laboratory and theoretical studies. Because of the prediction that fullerenes should exist and their subsequent detection in astronomical environments, the search for fullerenes in meteorites was a next logical step. In particular, carbonaceous chondrites rich in presolar grains, and being more carbon-rich than any other meteorites, were considered the most likely to contain fullerenes. Some chemical analyses of carbon-rich residues extracted from these meteorites gave positive results (e.g. Becker and Bunch, 1997; Becker et al., 1994, 1999) while others did not find fullerenes in other allocations of these same meteorites (e.g. Ash et al., 1993; DeVries et al., 1993; Gilmour et al., 1993; Heymann, 1997).

Chondritic aggregate IDPs and cluster IDPs from ca. 2  $\mu\text{m}$  to ca. 1 mm in size are considered the least-modified debris from the solar nebula because they were not processed in small protoplanets such as the meteorite parent bodies (Rietmeijer, 2002). The carbonaceous phases in these IDPs contain D/H “hot spots” of interstellar origin that were incorporated during solar nebula dust accretion (Keller et al., 2000; Messenger, 2000) and these particles should be good candidates to contain astronomical fullerene. Carbon XANES (X-ray Absorption Near Edge Spectroscopy) spectra of carbon-rich IDP L2008F4 show a notable similarity to the C-XANES spectrum of C<sub>60</sub>, but the search for

fullerenes was inconclusive (Bajt et al., 1996). [Flynn et al. \(2003\)](#) later concluded that the C-XANES signals, which were initially interpreted as possibly C<sub>60</sub>, could be due to C=O of organic carbon, result from the C-H, carboxyl, or carbonyl functional group, or could be due to an oxidized C<sub>60</sub>O fullerane.

Using High-Resolution Transmission Electron Microscopy (HRTEM), [Wang and Buseck \(1991\)](#) were the first to directly view the stacking of C<sub>60</sub> molecules forming close-packed arrays in a synthetic sample of crystalline fullerite that was known to contain C<sub>60</sub> and C<sub>70</sub> fullerenes. [Buseck et al. \(1992\)](#) were also first to identify C<sub>60</sub> and C<sub>70</sub> fullerenes by HRTEM in naturally occurring shungite that is compositionally a coal of meta-anthracite rank albeit the origin of this unusual geological rock remains uncertain. The HRTEM results obtained on carbon films in the shungite sample were confirmed by Fourier transform mass spectroscopy and by both laser desorption and thermal desorption/electron-capture methods (Buseck et al., 1992; Buseck, 2002). Recently, using transmission electron microscopy, [Rietmeijer et al. \(2004\)](#) successfully identified C<sub>60</sub> and higher ('giant') fullerene molecules in amorphous soot particles produced by the arc discharge technique. The presence of fullerenes in soot particles, which were predicted by Taylor et al. (1991) but that was heretofore not identified in soot, was subsequently confirmed by mass spectroscopy and HPLC chromatography analyses (Rietmeijer et al., 2004). Subsequently C<sub>60</sub> and smaller fullerene molecules were identified by HRTEM analyses of flame-produced soot (Goel et al., 2004) confirming that amorphous soot is an agglomeration of fullerenes, but not of uniformly C<sub>60</sub> fullerene, as both smaller (Goel et al., 2004) and larger ([Rietmeijer et al., 2004](#)) fullerenes can be present.

These studies on soot evidenced that HRTEM is able to detect and identify fullerenes when present in minute quantities that might be below the detection limits of conventional bulk chemical analyses. For example, circular objects approximately the size of C<sub>60</sub> and C<sub>70</sub> fullerenes can be seen in HRTEM images of soot not only from low-pressure benzene/oxygen flames well-known to contain fullerenes but also in soot produced in atmospheric-pressure ethylene/air flames ([Grieco et al., 2000](#)). The corollary being that C<sub>60</sub> and other fullerenes exist in both synthetic and natural carbon samples wherein they went undetected by the particular analytical tools used in those soot studies.

Even though the Raman signature of the various elemental carbons, including C<sub>60</sub> and C<sub>70</sub>, is well known, apart from the pioneering work

by Wopenka (1988), Raman microspectroscopy has not been commonly used to identify the presence of fullerenes in laboratory-produced and extraterrestrial carbon-containing samples. In part this situation might exist because small amounts of  $C_{60}$  and other fullerenes could not be confirmed previously by independent chemical techniques. This situation has changed after the successful HRTEM fullerene identifications by Rietmeijer et al. (2004) and Goel et al. (2004), which justifies the re-assessment of some of the published Raman carbon identifications, as was the case for published HRTEM soot images.

## 2. FULLERENE DETECTION

After the HRTEM identification of  $C_{60}$  and other, both smaller and larger, fullerenes in amorphous soot (Goel et al., 2004; Rietmeijer et al., 2004) we revisited the published record on HRTEM soot observations. We noticed that the same characteristic fullerene fingerprints, i.e. densely packed single-walled rings, are present in HRTEM images of soot particles produced by quenching a supersaturated vapor obtained by evaporation of a bulk elemental carbon sample using different techniques (e.g. Curl and Smalley, 1988; Ugarte, 1992; Bethune et al., 1993; De Heer and Ugarte, 1993; Wang and Kang, 1996; Jäger et al., 1999; Richter and Howard, 2000; Reynaud et al., 2001; Henning et al., 2004). With HRTEM analyses, capable of identifying fullerenes by their diameter, it is now possible to locate fullerene molecules in samples wherein they are present below the detection limits of chemical and spectroscopic techniques (e.g. Heymann et al., 2003). It seems warranted to conduct Raman micro-spectroscopy of elemental carbons on samples known to contain  $C_{60}$  and other fullerenes using a wider spectral range and a higher signal to noise ratio to resolve the  $1470\text{ cm}^{-1}$   $C_{60}$  peak in between the 'D' and 'G' peaks of graphitic carbon.

### 2.1 High Resolution Transmission Electron Microscopy

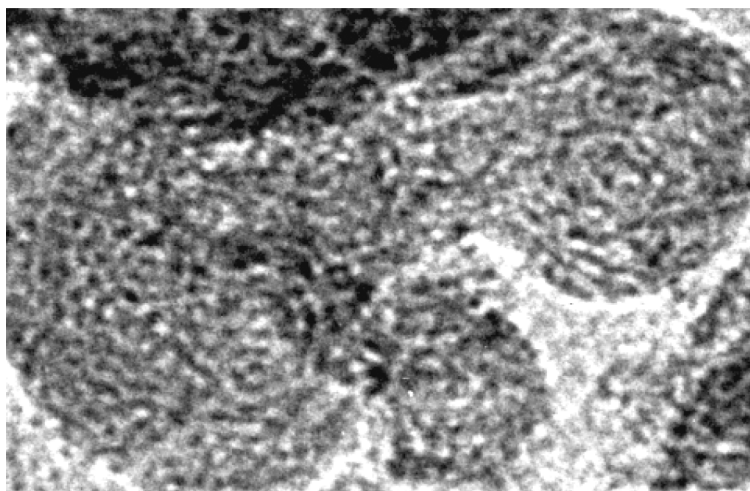
When searching for fullerene in a carbon-rich material wherein fullerene is present among many different carbon forms, it is important to consider its unique signature in HRTEM images (Wang and Buseck, 1991). This signature was not noticed previously as a unique carbon-vapor condensed texture, but it now appears that many

of the amorphous soot particles in the peer-reviewed literature could actually be agglomerations of fullerene molecules that went undetected. The very nature of HRTEM analysis requires only a small amount of sample mass to identify nanometer-sized structures and as such the detection of the characteristic single-walled fullerene rings was just a matter of time.

### 2.1.1 Laboratory-Condensed Fullerene Identification

Soot is a form of solid carbon that is easy to make in the laboratory (Ugarte, 1992; De Heer and Ugarte, 1993; Mennella et al., 1995; Wang and Kang, 1996; Rotundi et al., 1998; Jäger et al., 1999; Reynaud et al., 2001) and found in natural environments such as in the remote marine troposphere (Pósfai et al., 1999), and it has industrial applications such as in traditional Chinese ink sticks (Osawa et al., 1997a, 1997b) and for its structural reinforcement properties (Baccaro et al., 2003). Although it is not our focus, soot and fullerenes are considered a potential health hazard from combustion processes used in transportation, manufacturing and power generation (Richter and Howard, 2000). It is thus important that the presence and lifetime of fullerene molecules in soot can be assessed properly. The first HRTEM detection of fullerenes in soot is an example of serendipity.

The study by Rotundi et al. (1998), using electron microbeam techniques to characterize the carbon phases in samples produced by arc discharge was originally intended to identify the carrier phase or phases of the astronomical 217.5-nm ‘carbon’ feature. These condensed samples contained many different carbon forms, viz. (1) chain-like aggregates of amorphous soot grains 7 to 70 nm in diameter, (2) multi-walled onions (10 - 40 nm in diameter) and hollow tubes (up to about 100 x 10 nm) (i.e. fullerenic carbons), (3) amorphous carbon, and (4) poorly graphitized and graphitic carbons. The individual amorphous soot grains are dense agglomerations of single-walled rings (Fig. 1) with average diameters corresponding to C<sub>60</sub> fullerene and ‘giant’ fullerenes (Rietmeijer et al., 2004). Goel et al. (2004) also used ring diameter as the defining fullerene property and their C<sub>60</sub> diameter is well matched to the one reported by Rietmeijer et al. (2004) (Table 1).



*Figure 1.* HRTEM image of a dense cluster of individual soot grains (20 to 38.5 nm in diameter) with a mostly random packing of the single-walled open rings of the condensed fullerenes in a typical soot grain produced by arc-discharge (applied voltage = 100 V, current = 10 Amp) between two amorphous carbon electrodes in a controlled atmosphere of argon and hydrogen at 10mbar pressure (Rietmeijer et al., 2004; unpublished image)

**Table 1.** Diameters of single-walled rings in soot grains from two different studies and the corresponding number of carbon atoms for the fullerene molecules

Fullerene Diameter (nm)		Carbon Atoms
Rietmeijer et al. (2004)	Goel et al. (2004)	
	0.52	36
0.70	0.685	60
	0.86	
1.1	1.03	
	1.2	176
3.0		540
5.5		960
8.2		1500

The soot-containing samples studied by Rotundi et al. (1998) were produced by condensation of a carbon vapor inside a chamber wherein the heat dissipation rate and efficiency may have contributed to a transient phase of autoannealing of the condensed carbons. The linear and curvi-linear structures, referred to as proto-fringes, seen inside many soot grains could be due to such post-condensation structural ordering of individually condensed fullerenes (see section 3).

### 2.1.2 Natural Fullerenes in Meteorites

Elemental carbon can be found in two of the three major classes of meteorites, i.e. iron meteorites and both differentiated and undifferentiated stony meteorites (see for reviews the chapters in Papike, 1998). Searches for fullerenes were directed towards the undifferentiated, carbonaceous chondrite meteorites of the stony class because they are carbon-rich meteorites with high abundances of accreted pre-solar grains that survived post-accretion thermal processing. From what we learn from laboratory work fullerene is an “easy to come and easy to go” molecule, i.e. will most likely be formed in any carbon condensation process and sensitive to solid-state evolution due to even modest thermal processing. Thus, the more pristine a sample, the higher is the probability of finding C<sub>60</sub> molecules not yet evolved into giant fullerenes either in fully disordered solids or locally ordered in proto- fringes.

The presence of disordered fullerenes in extraterrestrial environments sampled by these primitive carbonaceous chondrites is supported by HRTEM images of meteoritic soot. For example, a HRTEM image of the Orgueil meteorite (Fig. 1 in Derenne et al., 2002) that is a very primitive meteorite shows a preponderance of single-walled ring structures. A HRTEM image of the Allende meteorite (Fig. 3 in Henning et al., 2004) shows circular and elongated single-walled ring structures, as well as curvilinear concentric features that we consider being evolved fullerene molecules.

To date no such single-walled ring structures or curvi-linear features (i.e. proto-fringes) were reported in amorphous carbons from carbon-rich cometary aggregate IDPs despite the fact these primitive particles would be quite likely candidates of solar system material to contain fullerenes, assuming these molecules were present in the solar nebula. However, when IDPs enter the Earth’s atmosphere at velocities ranging from ca. 10 km/s to ca. 25 km/s they are decelerated by collisions with air molecules and experience a brief period (5-15s) of flash heating to temperatures between ca. 300 °C and ca. 1000 °C



(Nier and Schlutter, 1993; Rietmeijer, 1998; Flynn, 2002). It seems possible that under these conditions all traces of fullerenes could be erased. This is not the case for meteorites where the kinetic energy goes towards surface ablation that protects the interior of the meteorite against flash heating. In fact, the meteorite temperature below ca. 3mm from its ablation surface (i.e. the fusion crust) is much less than its temperature in space of ca. 500 °C (Ramdohr, 1967; Rietmeijer and Mackinnon, 1984). From these examples we conclude that condensed C<sub>60</sub> and other fullerenes in carbonaceous chondrite meteorites would survive atmospheric entry with a much higher probability than those in chondritic aggregate IDPs.

## 2.2 Raman Microspectroscopy

Among the various analytical techniques used to characterize carbonaceous material of terrestrial and extraterrestrial origins, Raman micro-spectroscopy has been widely used to study the degree of order of polyaromatic materials (Ferrari and Robertson, 2000). However, its application to samples of astrophysical interest, e.g. IDPs (Wopenka, 1988; Raynal, 2003) and carbons in meteorites, remains quite limited. The latter include interstellar graphite grains extracted from the Murchison meteorite (Zinner et al., 1995) and carbon inclusions associated with Fe,Ni-grains in chondrites (Mostefaoui et al., 1999). A typical spectrum of such material exhibits several bands, the most intense being the first order bands, namely the G-band (peaking at ca. 1580 cm<sup>-1</sup>) and the D-band (peaking at ca. 1350 cm<sup>-1</sup>). These bands were intensively studied, as they are sensitive to the degree of order/disorder in the aromatic plane. The degree of structural order of the carbonaceous material modifies the parameters of these bands, i.e. their position, width or intensity in manner that is directly linked to the length of the coherent domain L<sub>a</sub>.

Raman microspectroscopy is a relatively fast, non-destructive method that can be applied in situ on samples a few microns in size. Meteorites and 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 Raman spectra of carbon-rich material obtained in the laboratory by carbon-vapor condensation experiments wherein fullerene is present among many different carbon forms in such analog samples.

In the late 80's, a survey of 20 chondritic IDPs showed that 75% of these particles contained "poorly crystallized carbonaceous material" with a Raman signature consistent with variable degrees of "disorder".

The mean crystallite size in the most ‘ordered’ of these IDP materials was estimated at ca. 3 nm but <6 nm assuming the material resembled activated charcoal or glassy carbon with a “turbostratic structure” (Wopenka, 1988). Since this pioneering work, searches for  $C_{60}$  and other fullerenes in these materials were so far neglected, even in recent studies of the organic matter in meteorites and IDPs (Quirico et al., 2003, 2005). The Raman spectra from two different areas in a sample from the same condensed carbon study with fullerenic carbons,  $C_{60}$  and larger fullerenes containing soot (Rietmeijer et al., 2004) show peaks at 396, ca. 500, 680, 1358 and 1594  $\text{cm}^{-1}$  (Fig. 2). In the spectrum the separation of the ‘D’ and ‘G’ peaks at ca. 1350 and ca. 1580  $\text{cm}^{-1}$ , respectively, is poorly defined with regard to this separation in a typical Raman spectrum of disordered, pre-graphitic carbons, and the intensity ratio of the D/G peaks is  $\geq 1$ , i.e. the D/G ratio expected for pre-graphitic mature carbons (Raynal, 2003).

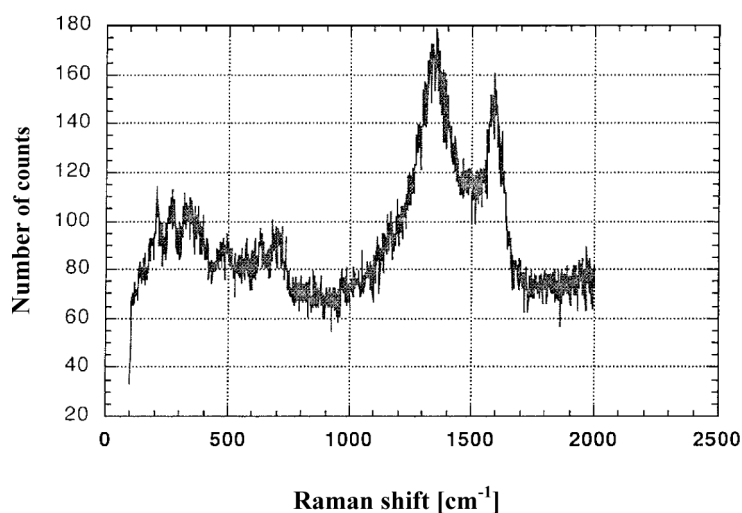


Figure 2. Raman spectrum from sample ACH<sub>2</sub>800 (Rotundi et al., 1998) obtained in the 200 – 3000  $\text{cm}^{-1}$  region showing signatures that could be due to the presence of fullerene and/or fullerenic carbons

This particular peak configuration could suggest an additional Raman carbon signal such as from C<sub>60</sub>+C<sub>70</sub> fullerene or fullerenic-carbon nanotubes present in the sample. The latter have additional peaks at <1100 cm<sup>-1</sup> and >2600 cm<sup>-1</sup>; the fullerenes have a major peak at 1470 cm<sup>-1</sup>. Thus, we hypothesize that this particular peak configuration (Fig. 2) in this condensed carbon analog sample (Rotundi et al., 1998) is due to the presence of either one, or both, of these carbon forms.

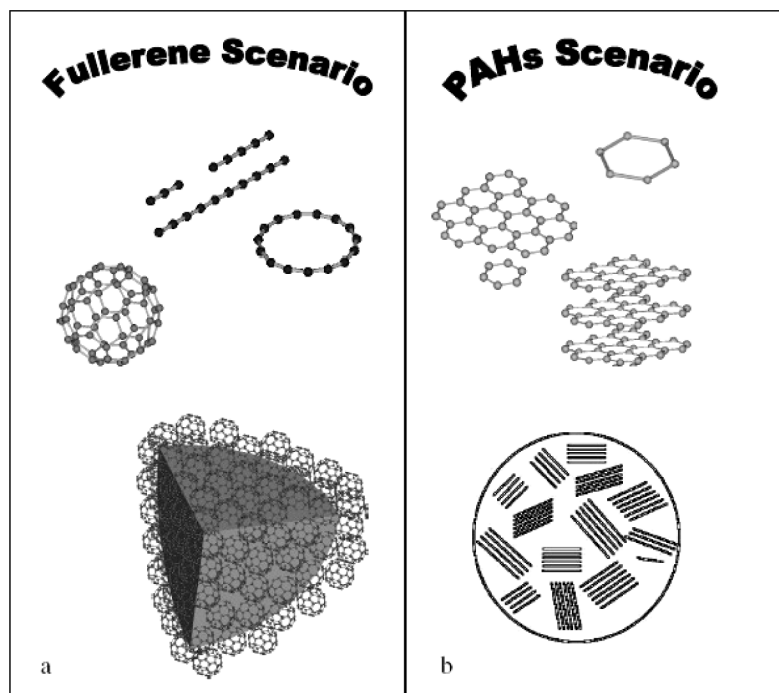
A wider spectral range and a stronger signal to noise ratio between 300-1100 cm<sup>-1</sup> and in the 'D' and 'G' regions, would allow detection of fullerene and fullerenic carbons in various extraterrestrial samples. The clear implication being that these carbon forms went undetected by previous Raman micro-spectroscopic analyses. We note that the Raman spectra of the "most 'ordered' material" in IDPs (Wopenka, 1988) show a similar 'D' and 'G' peak configuration as those shown in Fig. 2. Whereas Jelička et al. (2005) concluded that Raman microspectroscopy could not detect dispersed, low (ppb to ppm levels), fullerene concentrations in carbon-rich geological materials, the situation is much more favorable for synthetic and natural soot samples.

### **3. THE KEY ROLE OF C<sub>60</sub> IN CARBON CONDENSATION AND SOOT EVOLUTION INFERRED FROM HRTEM IMAGES**

The results of a comparative study of soot condensed in an arc discharge experiment (Rietmeijer et al., 2004), and of pure carbon black, carbon-black-toluene solution and soot material collected from a pre-mixed benzene/oxygen/argon flame (Goel et al., 2004), provided a reason to revisit published HRTEM images of soot produced by different techniques (e.g. Curl and Smalley, 1988; Ugarte, 1992; Bethune et al., 1993; De Heer and Ugarte, 1993; Wang and Kang, 1996; Jäger et al., 1999; Richter and Howard, 2000; Reynaud et al., 2001; Henning et al., 2004). We find that the common occurrence of single-wall rings in soot could support the hypothesis that metastable C<sub>60</sub> is the primary condensed form of carbon. Many important details of carbon condensation still remain poorly understood.

The commonly accepted scenario of soot formation (e.g. Richter and Howard, 2000) starts from small molecules such as benzene and then proceeds to larger and larger polycyclic aromatic hydrocarbon (PAH) growth, involves both the addition of C<sub>2</sub>, C<sub>3</sub> or other small

units, among which acetylene has received much attention, to PAH radicals, and reactions among the growing aromatic species, such as PAH–PAH radical recombination and addition reactions. This process is followed by the nucleation or inception of small soot particles whereby mass is converted from the molecular to particulate systems, i.e. heavy PAH molecules form nascent soot particles with a molecular mass of approximately 2000 amu and an effective diameter of about 1.5 nm (Fig. 3).



*Figure 3.* Carbon condensation. The initial seeds that agglomerate to form carbon grains in the “**Fullerene scenario**” (a) are molecules with different geometry depending on the number of C atoms (chains, rings, cages) and in the “**PAHs scenario**” (b) they are small molecules, e.g. benzene, that grow to larger and larger polycyclic aromatic hydrocarbons (PAHs) that can either form extended graphene layers or small aromatic nanocrystalline stacks called ‘Basic Structural Units’

A slightly different condensation scenario (Henning et al., 2004) is based on the presence of small graphene sheets of few aromatic rings stacked (sub) parallel to each other, i.e. aromatic nanocrystalline stacks referred to as Basic Structural Units (*BSUs*) (Oberlin et al., 1984). *BSUs* can be differently organized depending on the experimental conditions during soot formation (Henning et al., 2004) (see Fig. 3).

It is important to mention that flat aromatic structures in a carbon vapor would have numerous dangling bonds and they would have little reason to remain flat. The physical tendency to reach the lowest energy level available would induce the sheets to eliminate the dangling bonds by curling up (Robertson et al., 1992).

Therefore we propose a new carbon condensation scenario wherein  $C_{60}$  molecules are the “seeds” for soot grain growth; not PAHs. Consequently  $C_{60}$  carbon cages are the original building blocks that upon agglomeration will yield amorphous soot grains (Fig. 3). Carbon atoms in the vapor will form short chains that assume a monocyclic ring geometry for a number of carbon atoms larger than 10 (Weltner and Van Zee, 1989). In the  $C_{30}$ - $C_{40}$  region closed structures become more stable than linear chains and planar ring structures (von Helden et al., 1993). Even when small fullerenes appeared around  $C_{30}$  they will grow by sequential addition of  $C_2$  units, eventually stopping at  $C_{60}$  when further  $C_2$  additions become improbable in the gas phase (Heat, 1991). The  $C_{60}$  scenario is substantiated by arguments of

1. Symmetry (Kroto et al., 1985),
2. Electronic structure calculations (Newton and Stanton, 1986), and
3. Laboratory experiments (von Helden et al., 1993).

For all fullerenes the strain of closure tends to concentrate at the vertices of the pentagons; only for  $C_{20}$  and  $C_{60}$  this strain is distributed uniformly over all atoms (Curl and Smalley, 1988).  $C_{60}$  is favored with respect to  $C_{20}$  as the strain of closure is independent of the fullerene molecule size but the average strain per carbon atom increases for smaller clusters (Schmaltz et al., 1988).

When separating *proper* carbon condensation features from secondary, evolved features due to variable quench rates and post-condensation heat dissipation, Rotundi et al. (1988) and Rietmeijer et al. (2004) found that  $C_{60}$  fullerene was the original carbon condensate that had agglomerated in soot grains. The  $C_{60}$  molecule has a key role

in solid-state modification of soot, that is, concentric structures in soot grains represent re-adjustments of condensed metastable  $C_{60}$  molecules that had coalesced into higher fullerenes (Yeretzian et al., 1992; Zhao et al., 2002a, 2002b; Kim et al., 2003; Rietmeijer et al., 2004) (Fig. 4).

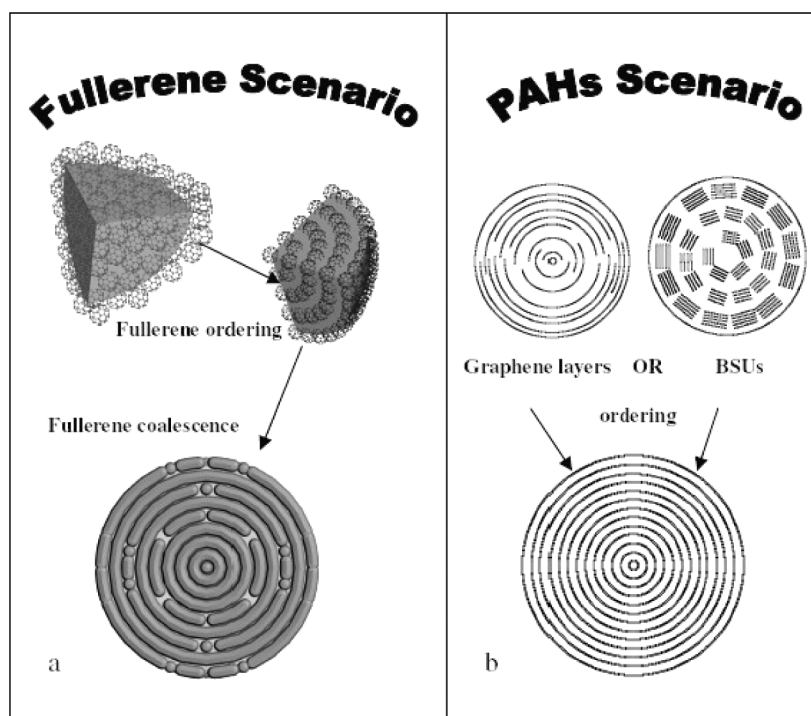
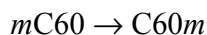
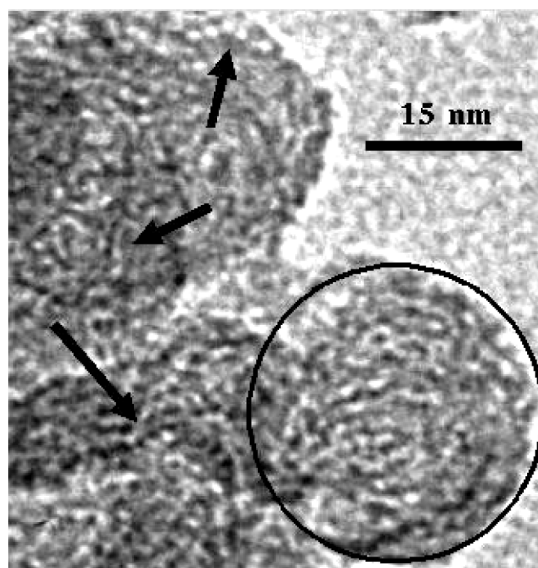


Figure 4. Ordering processes of the original molecules drives graphitization and in the “**Fullerene condensation scenario**” (a) it will be driven by the coalescence of closed carbon cages in ever-larger fullerenes finally forming the oft-seen concentric graphitized structure. Graphitization in the “**PAHs condensation scenario**” (b) will be caused by the arrangement of PAH molecules on ever-larger curved planes (i.e. graphene layers) or by enlargement of *BSUs*

Fullerene coalescence is kinetically controlled and depends on the combination of the reigning thermal regime and vapor density. Larger fullerenes are formed by a reaction of the type,



which would yield an orderly sequence of fullerenes. Giant fullerene growth can occur within the vapor or during post-condensation auto-annealing by uncontrolled endogenic thermal annealing. The latter process was responsible for incipient fullerene ordering forming proto-fringes (Fig. 5): short and straight, or longer and curved features composed of aligned single-wall spheres in either a single layer or a small stack of two to five layers.



*Figure 5.* High magnification TEM image showing aligned (arrows) and densely packed single-walled rings of individual fullerene molecules in a soot sample. The encircled grain shows concentric proto-fringes that could evolve towards the typically concentric circular onion structure. (Rietmeijer et al., 2004; unpublished image)

We depicted a scenario of continuous ordering from amorphous soot formed by agglomerated fullerenes that coalesced into ever-larger fullerenes that finally formed the often-seen concentric graphitized structure (Fig. 4). Giant fullerenes may have properties of a single graphitic sheet (Yeretzian et al., 1992). For comparison with the new proposed soot ordering process based on fullerenes growth (Fig. 4) we show the classical carbon graphitization processes led by the arrangement of PAH molecules on curved and wide planes (i.e. graphene layers) or by the enlargement of *BSUs* (Reynaud et al., 2001; Henning et al., 2004).

In support of the fullerene coalescence scenario we mention the studies of electron-beam irradiation (Luzzi and Smith, 2000) and heat treatment (Bandow et al., 2001) on carbon composites that induced coalescence of fullerenes into a single-wall nanotube, 0.71 nm in diameter. Bandow et al. (2001) found that coalescence started at 800 °C and the transformation to a single-wall nanotube was completed at 1200 °C.

Confirmation for the post-condensation secondary nature of curvilinear features, that represent very small-scale structural ordering of individual fullerene molecules, comes from HRTEM images of soot samples subjected to post-condensation heat-treatment, ion bombardment or prolonged electron-beam irradiation. These images show

1. Dense agglomerations of single-wall rings in the pre-treated soot, and
2. Linear, curvilinear and concentric circular features that were invariably present in thermally processed soot (see, Fig. 4 in Ugarte, 1992; Figs. 1 and 2 in De Heer and Ugarte, 1993; Fig. 3 in Reynaud et al., 2001).

In addition, Grieco et al. (2000) found that the formation of highly ordered carbon nanostructures, such as nanotubes and onion structures, requires long residence times, seconds or minutes depending on the temperature, in the flame environment, while the formation of amorphous and fullerenic carbon occurs in milliseconds. Internal rearrangement processes are required for more ordered structures to form rather than gas-phase molecular-weight growth pathways as occur at flame temperatures (Grieco et al., 2000). These observations support the hypothesis that autoannealing could induce better-ordered structural forms of carbon in condensed soot.



Such evolved carbon features may well form in natural environments as a result of interactions between fullerene-laden amorphous soot with some type of natural processes that could induce heat treatment of the material, e.g. energetic particles, UV irradiation, or atmospheric entry. Proto-fringe textures are seen in extraterrestrial samples, e.g. the Allende meteorite (e.g. Fig. 3 in Henning et al., 2004). Different stages in the evolution of secondary features are visible in this published figure ranging from single-wall rings, to elongated fullerenes and long curvilinear structures.

#### 4. ASTROPHYSICAL IMPLICATION

Astronomical observations from the far-UV to the millimeter spectral region indicate the presence of carbon-based materials in space. Amorphous carbon, hydrogenated amorphous carbon, coal-like matter, soot, quenched-carbonaceous condensates, nanodiamonds, and fullerenes were all proposed as possible candidates for interstellar carbon dust (Thaddeus, 1994; Mennella et al., 1995; Papoular et al., 1996; Cherchneff et al., 2000; Ehrenfreund and Charnley, 2000; Henning et al., 2004). The origin of the interstellar UV absorption spectrum with the most prominent feature at 217.5 nm, although it is commonly assigned to carbonaceous material, does not yet have a definitive explanation. Similarities between experimental and observed absorption spectra indicated that carbon onions are very strong candidates for the origin of this interstellar UV absorption peak (Chhowalla et al., 2003).

Iglesis-Groth (2004) showed that photoabsorption by fullerenes and bucky-onions (i.e. multi-shell fullerenes) could explain the shape, width, and peak energy of the UV absorption feature. Comparing theoretical photoabsorption cross-sections of individual and multi-shell fullerenes and astronomical data, Iglesias-Groth (2004) estimated a density of fullerenes and bucky-onions in the diffuse interstellar medium of 0.1-0.2 ppm. In particular, for a mixture based on single fullerenes she estimated that about 80 carbon atoms per million hydrogen atoms would be locked in these molecules. If as expected the cosmic carbon abundance is close to the solar atmosphere value, individual fullerenes may lock up 20% to 25% of the total carbon in diffuse interstellar space. When bucky-onions are also considered in the mixture, carbon in fullerene-based molecules could reach 50% of the cosmic carbon abundance. That is, fullerene-based molecules appear to be a major carbon reservoir in the interstellar medium.

Carbon vapor condensation experiments are conducted for the purpose of constraining the composition, morphology and structure of dust formed around C-type stars residing in the diffuse and dense regions of the interstellar medium (De Heer and Ugarte, 1993; Mennella et al., 1995; Papoular et al., 1996; Rotundi et al., 1998; Jäger et al., 1999; Ehrenfreud and Charnley, 2000; Reynaud et al., 2001; Henning et al., 2004).

Circumstellar regions range from the stellar outflow winds of very young stars to dust envelopes around highly evolved stars. Within the dense circumstellar envelopes around carbon-rich stars interesting chemistry involving a plethora of carbon molecules and dust formation occur. Carbon grains form in the vicinity of the star, but one of the major open problems in circumstellar dust studies remains to define the chemical pathways from small radical clusters towards carbon grain formation. It was proposed that the route to carbon grains passes through PAH molecules (e.g. Léger and Puget, 1984; Herbst, 1991). Other circumstellar condensation scenarios took the path to grain formation from linear chains, to rings and to fullerenes depending on the number of carbon atoms (Cherchneff et al., 2000). These carbon molecules could coexist in various proportions and pass from one geometry to another in the ambient radiation field because of small energetic separations (less than 1–2 eV) (Thaddeus, 1994; Pascoli and Polleux, 2000).

If C<sub>60</sub> fullerene molecules are shown to be the primary carbon condensates available for agglomeration and structural evolution, there will be a number of implications for astrophysics:

1. The scenario of carbon chains, rings and cages will be more plausible than the one starting with PAHs.
2. While it is almost impossible to avoid metastable C<sub>60</sub> formation, once formed it may be short-lived as an isolated molecule whose existence in astrophysical environments depends on competition between the efficiency of the condensation process and the destruction rate due to cosmic radiation, among others. The experimental data show that C<sub>60</sub> has a very high formation rate and the degree of C<sub>60</sub> decomposition due to prolonged  $\gamma$ -irradiation was shown to be less than 15%, which actually demonstrates extreme stability (Basiuk et al., 2004).
3. Once agglomerated in amorphous soot grains, C<sub>60</sub> will be shielded from interacting with the environment. The C<sub>60</sub> molecules near the soot grain surface would evolve prior to the inner part and evolved

larger fullerenes and other secondary features from solid-state processing will be preferentially found in the soot near-surface zone.

4. Graphitization of carbon grains in astrophysical environments (Papoular et al., 1996; Mennella et al., 1997; Henning et al., 2004) will be driven by structural evolution of condensed  $C_{60}$  molecules once closely-packed inside a soot grain. Progressive fullerene ordering would lead to proto-fringes concentrically arranged within the soot grain. Once the original fullerenes so arranged had unfolded the new arrangement could eventually lead to the formation of nested fullerenes that could ultimately evolve into well-ordered carbon onions.

## 5. CONCLUSIONS

Although  $C_{60}$  appears to be the dominant condensate in laboratory experiments wherein carbon had agglomerated into soot grains, the published literature consistently reported an overall dearth of this and other fullerene molecules among laboratory-condensed carbon samples. Fullerenes appear also to be missing from carbon-rich extraterrestrial samples, as the collected primitive meteorite and IDP samples that should contain the products of carbon condensation in astrophysical environments. These samples were analyzed using mostly chemical techniques that may not have been sensitive enough to detect very small quantities of  $C_{60}$  and other fullerenes. A positive result means that fullerenes are present in the sample but a negative result cannot be interpreted as proof of absence of fullerenes. In such ‘negative outcome’ samples HRTEM analyses would be able to detect individual fullerene molecules and fullerene clusters in an amorphous carbon matrix. Recent Raman microspectroscopy analyses of condensed soot showed that fullerenes are detectable when the “traditional” experimental conditions are modified to enhance the signal in the region between the ‘D’ and ‘G’ carbon region. Recent HRTEM studies of condensed carbons found that soot grains were agglomerations of  $C_{60}$  and other fullerenes ranging from  $C_{36}$  to  $C_{1500}$  that were recognizable as distinctive single-wall rings with variable diameters between 0.52 nm and 8.2 nm. The very nature of such TEM analyses allows for the detection of individual nanostructures without constraints of abundance.

The apparent dearth of fullerenes in natural and synthetic carbon samples may just be a matter of detection. Finding a technique able to

detect small quantities of fullerenes was only a matter of time. Some studies searching for fullerenes among meteoritic carbons were positive while others were negative. Such studies did not analyze the same sample allocations and the possibility remains that sample heterogeneity might be a contributing factor, in particular when fullerene concentrations were low.

The recognition that C<sub>60</sub> was the major primary carbon condensate has implications for the interpretation of secondary carbon textures of fullerene and soot evolution in synthetic samples used to identify the carbon phase most likely to be responsible for the 217.5-nm astronomical absorption feature. Fullerene molecules as primary condensates prior to carbon ageing, instead of the scenarios involving PAHs or *BSUs*, might offer an alternative to assess the physical conditions for carbon-condensation within the dense circumstellar envelopes around carbon-rich stars and an opportunity to re-assess the presence of low fullerene abundances in primitive amorphous meteoritic carbons. Such low abundances would not rule out the possibility that C<sub>60</sub> and other fullerene molecules might be the dominant condensed carbon in circumstellar environments and in the interstellar medium. It will require additional laboratory analyses of carbons from carbonaceous chondrite meteorites and interplanetary dust particles and of in situ collected asteroid and comet nucleus samples before the anticipated pervasiveness of natural extraterrestrial fullerenes will be a firmly established fact.

**Acknowledgements.** We thank Dr. Nuth for constructive suggestions. We are grateful to Dr. V. Della Corte for kind help in drawing Figs. 3 and 4. This work was supported by ASI and MURST research contracts (AR). One author (J.B.) is grateful to G. Montagnac of the *Laboratoire des Sciences de la Terre* (ENS-Lyon, France) who helped in performing the Raman measurements, using a LabRaman Jobin-Yvon confocal micro-spectrometer. FJMR was supported by NAG5-11762 from the National Aeronautics and Space Administration.

## 6. REFERENCES

- Ash, R.D., Russell, S.S., Wright, I.P. and Pillinger, C.T. (1993) Minor high temperature components confirmed in carbonaceous chondrites by stepped combustion using a new sensitive static mass spectrometer (abstract). *Lunar Planet. Sci.*, 22, 35-36, Lunar and Planetary Institute, Houston, Texas, USA.
- Baccaro, S., Cataldo, F., Cecilia, A., Cemmi, A., Padella, F and Santini, A. (2003) Interaction between reinforce carbon black and polymeric matrix for industrial applications. *Nuclear Instr. Methods Phys. Res. B*, 208, 191-194.

- Bandow, S., Takizawa, M., Hirahara, K., Yudasaka, M. and Iijima, S. (2001) Raman scattering study of double-wall carbon nanotubes derived from the chains of fullerenes in single-wall carbon nanotubes. *Chem. Phys. Lett.*, 337, 48-54.
- Bajt, S., Chapman, H.N., Flynn, G.J. and Keller, L.P. (1996) Carbon characterization in interplanetary dust particles with a scanning transmission X-ray microscope (abstract). *Lunar Planet. Sci.*, 27, 57-58, Lunar and Planetary Institute, Houston, Texas, USA.
- Basiuk, V.A., Albarrána, G., Basiuk, E.V. and Saniger, J.-M. (2004) Stability of interstellar fullerenes under high-dose  $\gamma$ -irradiation: New data. *Adv. Space Res.*, 33, 72-75.
- Becker, L. and Bunch, T.E. (1997) Fullerenes, fulleranes and polycyclic aromatic hydrocarbons in the Allende meteorite. *Meteorit. Planet. Sci.*, 32, 479-487.
- Becker, L., Bada, J.L., Winas, R.E. and Bunch, T.E. (1994) Fullerenes in the Allende meteorite. *Nature*, 372, 507-507.
- Becker, L., Bunch, T.E. and Allamandola, L.J. (1999) Higher fullerenes in the Allende meteorite. *Nature*, 400, 227-228.
- Bethune, D.S., Kiang, C.H., de Vries, M.S., Gorman, G., Savoy, R., Vazquez, J. and Beyers, R. (1993) Cobalt-catalyzed growth of carbon nanotubes with single-atomic-layer walls. *Nature*, 363, 605-607.
- Buseck, P.R. (2002) Geological fullerenes: review and analysis. *Earth Planet. Sci. Lett.*, 203, 781-792.
- Buseck, P.R., Tsipurski, S.J. and Hettich, R. (1992) Fullerenes from the geological environment. *Nature*, 247, 215-217.
- Cherchneff, I., Le Teuff, Y.H., Williams, P.M. and Tielens, A.G.G.M. (2000) Dust formation in carbon-rich Wolf-Rayet stars? I. Chemistry of small carbon clusters and silicon species. *Astron. Astrophys.*, 357, 572-580.
- Chhowalla, M., Wang, H., Sano, N., Teo, K.B.K. and Amaratunga, G.A.J. (2003) Carbon onions: Carriers of the 217.5-nm interstellar absorption feature. *Phys. Rev. Lett.*, 90, 155504-1-155504-4.
- Curl, R.C. and Smalley, R.E. (1988) Probing  $C_{60}$ . *Science*, 242, 1017-1022.
- De Heer, W.A. and Ugarte, D. (1993) Carbon onions produced by heat treatment of carbon soot and their relation to the 217.5 nm interstellar absorption feature. *Chem. Phys. Lett.*, 207, 480-486.
- DeVries, M.S., Reihs, K., Wendt, H.R., Golden, W.G., Hunziker, H.E., Fleming, R., Peterson, E. and Chang, S. (1993) A search for  $C_{60}$  in carbonaceous chondrites. *Geochim. Cosmochim. Acta*, 57, 933-935.
- Derenne, S., Robert, F., Binet, L., Gourier, D., Rouzaud, J.-N. and Largeau, C. (2002) Use of combined spectroscopic and microscopic tools for deciphering the chemical structure and origin of the insoluble organic matter in the Orgueil and Murchison meteorites. *Lunar Planet. Sci.*, 33, abstract #1182, Lunar and Planetary Institute, Houston, Texas, USA, CD-ROM.
- Ehrenfreund, P. and Charnley, S.B. (2000) Organic molecules in the interstellar medium, comets, and meteorites: a voyage from dark clouds to the early Earth. *Ann. Rev. Astron. Astrophys.*, 38, 427-483.
- Ferrari, A.C. and Robertson, J. (2000) Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B*, 61, 14095-14107.
- Flynn, G.J. (2002) Extraterrestrial dust in the near-Earth environment. In *Meteors in the Earth's Atmosphere*, E. Murad and I.P. Williams, Eds., 77-94, Cambridge University Press, Cambridge, United Kingdom.
- Flynn, G.J., Keller, L.P., Feser, M., Wirick, S. and Jacobsen, C. (2003) The origin of organic matter in the solar system: Evidence from the interplanetary dust particles. *Geochim. Cosmochim. Acta*, 67, 4791-4806.

- Foing, B.H. and Ehrenfreund, P. (1994) Detection of two interstellar absorption bands coincident with spectral features of  $C_{60}^+$ . *Nature*, 369, 296-298.
- Foing, B.H. and Ehrenfreund, P. (1997) New evidence for interstellar  $C_{60}^+$ . *Astron. Astrophys.*, 317, L59-L62.
- Gilmour, I., Russell, S.S., Newton, J., Pillinger, C.T., Arden, J.W., Dennis, T.J., Hare, J.P., Kroto, H.W., Taylor, R. and Walton, D.R.M. (1993) A search for the presence of  $C_{60}$  as an interstellar grain in meteorites (abstract). *Lunar Planet. Sci.*, 22, 445-446, Lunar and Planetary Institute, Houston, Texas, USA.
- Goel, A., Howard, J.B. and Vander Sande, J.B. (2004) Size analysis of single fullerene molecules by electron microscopy. *Carbon*, 42, 1907-1915.
- Grieco, W.J., Howard, J.B., Rainey, L.C. and Vander Sande, J.B. (2000) Fullerenic Carbon in combustion-generated soot. *Carbon*, 38, 597-614.
- Heat, J.R. (1991) Synthesis of  $C_{60}$  from small carbon clusters: a model based on experiment and theory. In *Fullerenes, Synthesis, Properties and Chemistry of Large Carbon Clusters*, G.S. Hammond and V.J. Kuck, Eds., *Am. Chem. Soc. Symp. Series*, 481, 1-27.
- Henning, T., Jäger, C. and Mutschke, H. (2004) Laboratory studies of carbonaceous dust analogs. In *Astrophysics of Dust*, A.N. Witt, G.C. Clayton and B.T. Draine, Eds., *ASP Conf. Series*, 309, 603-628, Astronomical Society of the Pacific, San Francisco, California, USA.
- Herbst, E. (1991) In situ formation of large molecules in dense interstellar clouds. *Astrophys. J.*, 366, 133-140.
- Heymann, D. (1997) Fullerenes and fulleranes in meteorites revisited. *Astrophys. J.*, 489, L111-L114.
- Heymann, D., Jenneskens, L.W., Jehlička, J., Koper, C. and Vlietstra, E. (2003) Terrestrial and extraterrestrial fullerenes. *Fullerenes, Nanotubes, and Carbon Nanostructures*, 11, 333-370.
- Iglesias-Groth, S. (2004) Fullerenes and buckyonions in the interstellar medium., *Astrophys. J.*, 608, L37-L40.
- Jäger, C., Henning, Th., Schlögl, R. and Spillecke, O. (1999) Spectral properties of carbon black. *J. Crystal Growth*, 258, 161-179.
- Jelička, J., Frank, O., Pokorný, J. and Rouzaud, J.-N. (2005) Evaluation of Raman spectroscopy to detect fullerenes in geological materials. *Spectrochim. Acta, A*, in press.
- Keller, L.P., Messenger, S. and Bradley, J.P. (2000) Analysis of a deuterium-rich interplanetary dust particle and implications for presolar materials in IDPs. *J. Geophys. Res. Space Phys.*, 105, 10397-10402.
- Kim, Y.-H., Lee, I.-H., Chang, K.J. and Lee, S. (2003) Dynamics of fullerene coalescence. *Phys. Rev. Lett.*, 90, 065501-065501.
- Krätschmer, W., Lamb, L.D., Fostiropoulos, K. and Huffman, D. (1990) Solid  $C_{60}$ : a new form of carbon. *Nature*, 347, 354-358.
- Kroto, H.W., Heat, J.R., O'Brien, S.C., Curl, R.F. and Smalley, R.E. (1985)  $C_{60}$ : Buckminsterfullerene. *Nature*, 318, 162-163.
- Léger, A. and Puget, J.L (1984) Identification of the 'unidentified' IR emission features of interstellar dust? *Astron. Astrophys.*, 137, L5-L8.
- Luzzi D.E. and Smith B.W. (2000) Carbon cage structures in single wall carbon nanotubes: a new class of materials. *Carbon*, 38, 1751-1756.
- Mennella, V., Colangeli, L., Bussoletti, E., Monaco, G., Palumbo, P. and Rotundi, A. (1995) On the electronic structure of small carbon grains of astrophysical interest. *Astrophys. J. Suppl.*, 100, 149-157.

- Mennella, V., Baratta, G., Colangeli, P., Palumbo, P., Rotundi, A. and Bussoletti, E. (1997) Ultraviolet spectral changes in amorphous carbon grains induced by ion irradiation. *Astrophys. J.*, 481, 545-549.
- Messenger, S. (2000) Identification of molecular-cloud material in interplanetary dust particles. *Nature*, 404, 968-971.
- Mostefaoui, S., Perron, C., Zinner, E. and Sagon, G. (1999) Metal-associated carbon in primitive chondrites: structure, isotopic composition and origin. *Geochim. Cosmochim. Acta*, 64, 1945-1964.
- Newton, M.D. and Stanton, R.E. (1986) Stability of buckminsterfullerene and related carbon clusters. *J. Am. Chem. Soc.*, 108, 2469-2470.
- Nier, A.O. and Schlutter, D.J. (1993) The thermal history of interplanetary dust particles collected in the Earth's stratosphere. *Meteoritics*, 28, 675-681.
- Oberlin, A., Goma, J. and Rouzaud, J.N. (1984) Techniques d'étude des structures et textures (microtextures) des matériaux carbonés (in French). *J. Chimie Physique*, 81, 701-710.
- Osawa, E., Hirose, Y., Kimura, A., Shibuya, M., Gu, Z. and Li, F.M. (1997a) Fullerenes in Chinese ink. A correction. *Fullerene Sci. Techn.*, 5, 177-194.
- Osawa, E., Hirose, Y., Kimura, A., Shibuya, M., Kato, M. and Takezawa, H. (1997b) Seminal occurrence of fullerenes. *Fullerene Sci. Techn.*, 5, 1045-1055.
- Papike, J.J., (Ed.) (1998) *Planetary Materials, Revs. Mineral.*, 36, 1052p., The Mineralogical Society of America, Washington, D.C., USA.
- Papoulet, R., Conard, J., Guillois, O., Nenner, I., Reynaud, C. and Rouzaud, J.N. (1996) A comparison of solid-state carbonaceous models of cosmic dust. *Astron. Astrophys.*, 315, 222-236.
- Pascoli, G. and Polleux, A. (2000) Condensation and growth of hydrogenated carbon clusters in carbon-rich stars. *Astron. Astrophys.*, 359, 799-810.
- Pósfai, M., Anderson, J.R., Buseck, P.R. and Sievering, H. (1999) Soot and sulfate aerosol particles in the remote marine troposphere. *J. Geophys. Res.*, 104(D17), 21685-21693.
- Quirico, E., Raynal, P.I. and Bourot-Denise, M. (2003) Metamorphic grade of organic matter in six unequilibrated ordinary chondrites. *Meteorit. Planet. Sci.*, 38, 795-812.
- Quirico, E., Borg, J., Raynal, P.I., Montagnac, G. and d'Hendecourt, L. (2005) A micro-Raman survey of 10 IDPs and 6 carbonaceous chondrites. *Planet. Space Sci.*, in press.
- Ramdohr, P. (1967) Die Schmelzkrüste der Meteoriten (in German). *Earth. Planet. Sci. Lett.*, 2, 197-209.
- Raynal, P.I. (2003) Étude en laboratoire de matière extraterrestre: implications pour la physico-chimie du Système Solaire primitif (in French). PhD thesis, Université Paris 6, France.
- Reynaud, C., Guillois, O., Herlin-Boime, N., Rouzaud, J.-N., Galvez, A., Clinard, C., Balanzat, E. and Ramillon, J.-M. (2001) Optical properties of synthetic carbon nanoparticles as model of cosmic dust. *Spectrochim. Acta, A*, 57, 797-814.
- Richter, H. and Howard, J.B. (2000) Formation of polycyclic aromatic hydrocarbons and their growth to soot - a review of chemical reaction pathways. *Progr. Energy Comb. Sci.*, 26, 565-608.
- Rietmeijer, F.J.M. (1998) Interplanetary Dust Particles. In *Planetary Materials*, J.J. Papike, Ed., *Revs. Mineral.*, 36, 2-1-2-95, The Mineralogical Society of America, Washington, D.C., USA.
- Rietmeijer, F.J.M. (2002) The earliest chemical dust evolution in the solar nebula. *Chemie der Erde*, 62, 1-45.
- Rietmeijer, F.J.M. and Mackinnon, I.D.R. (1984) Melting, ablation and vapor phase condensation during atmospheric passage of the Bjurböle meteorite. *J. Geophys. Res.*, 87, Suppl., B597-B604.

- Rietmeijer, F.J.M. and Nuth, J.A. (1991) Tridymite and magh mite formation in a Fe-SiO smoke. *Proc. Lunar Planet. Sci.*, 21, 591-599.
- Rietmeijer, F.J.M., Nuth III, J.A., Karner, J.M. and Hallenbeck S.L. (2002) Gas to solid condensation in a Mg-SiO-H<sub>2</sub>-O<sub>2</sub> vapor: Metastable eutectics in the MgO-SiO<sub>2</sub> phase diagram. *Phys. Chem. Chem. Phys.*, 4, 546-551.
- Rietmeijer, F.J.M., Rotundi, A. and Heymann, D. (2004)  $C_{60}$  and giant fullerenes in soot condensed in vapors with variable C/H<sub>2</sub> ratio. *Fullerenes, Nanotubes, and Carbon Nanostructures*, 12, 659-680.
- Robertson, D.H., Brenner, D.W. and White, C.T. (1992) On the way to fullerenes: molecular dynamics study of the curling and closure of graphitic ribbons. *J. Phys. Chem.*, 96, 6133-6135.
- Rotundi, A., Rietmeijer, F.J.M., Colangeli, L., Mennella, V., Palumbo, P. and Bussolletti, E. (1998) Identification of carbon forms in soot materials of astrophysical interest. *Astron. Astrophys.*, 329, 1087-1096.
- Sassara, A., Zerza, G., Chergui, M. and Leach, S. (2001) Absorption wavelengths and bandwidths for interstellar searches of  $C_{60}$  in the 2400-4100 Å region. *Astrophys. J. Suppl.*, 135, 263-273.
- Schmaltz, T.G., Seitz, W.A. and Hite, G.E. (1988) Elemental carbon cages. *J. Am. Chem. Soc.*, 110, 1113-1127.
- Snow, T.P. and Seab, C.G. (1989) A search for interstellar and circumstellar  $C_{60}$ . *Astron. Astrophys.*, 213, 291-294.
- Stephan, O., Bando, Y., Dussarrat, C., Kurashima, K., Sasaki, T., Tamiya, T. and Akaishi, M. (1997) Onionlike structures and small nested fullerenes formation under electron irradiation of turbostratic BC<sub>2</sub>N. *Appl. Phys. Lett.*, 70, 2383-2385.
- Taylor, R., Parsons, J.P., Avent, A.G., Rannard, S.P., Dennis, T.J., Hare, J.P., Kroto, H.W. and Walton, D.R.M. (1991) Degeneration of  $C_{60}$  by light. *Nature*, 351, 277.
- Thaddeus, P. (1994) On the large organic molecules in the interstellar gas. In *Molecules and Grains in Space*, I. Nenner, Ed., *AIP Conf. Proc.*, 312, 711-728, The American Institute of Physics Press, Woodbury, New York, USA..
- Ugarte, D. (1992) Curling and closure of graphitic networks under electron-beam irradiation. *Nature*, 359, 707-709.
- von Helden, G., Gotts, N.G. and Bowers, M.T. (1993) Experimental evidence for the formation of fullerenes by collisional heating of carbon rings in the gas phase. *Nature*, 363, 60-63.
- Wang, S. and Buseck, P.R. (1991) Packing of  $C_{60}$  molecules and related fullerenes in crystals: a direct view. *Chem. Phys. Lett.*, 182, 1-3.
- Wang, Z.L. and Kang, Z.L. (1996) Pairing of pentagonal and heptagonal carbon rings in the growth of nanosize carbon spheres synthesized by a mixed-valent oxide-catalytic carbonization process. *J. Phys. Chem.*, 100, 17725-17731.
- Webster, A.S. (1997) The interstellar extinction curve and the absorption spectra of two fullerenes. *Mon. Not. R. Astron. Soc.*, 288, 221-224.
- Weltner, W. and Van Zee, R.J. (1989) Carbon molecules, ions, and clusters. *Chem. Rev.*, 89, 1713-1747.
- Wopenka, B. (1988) Raman observations on individual interplanetary dust particles. *Earth Planet. Sci. Lett.*, 88, 221-231.
- Yeretzian, C., Hansen, K., Diederich, F. and Whetten, R.L. (1992) Coalescence reactions of fullerenes. *Nature*, 359, 44-47.
- Zhao, Y., Smalley, R.E. and Yakobson, B.I. (2002a) Coalescence of fullerene cages: Topology, energetics, and molecular dynamics simulation. *Phys. Rev. B*, 66, 195409-1-195409-9.



- Zhao, Y., Yakobson, B.I. and Smalley, R.E. (2002b) Dynamic topology of fullerene coalescence. *Phys. Rev. Lett.*, 88, 185501-1-185501-4.
- Zinner, E., Amari, S., Wopenka, B. and Lewis, R.S. (1995) Interstellar graphite in meteorites: isotopic compositions and structural properties of single grains from Murchison. *Meteoritics*, 30, 209-226.