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► **To cite this version:**

Hassan Sabbah, Christine Joblin. PAHs, carbon clusters and fullerenes in cosmic dust analogues and meteorites. European Conference on Laboratory Astrophysics ECLA2020 The Interplay of Dust, Ice, and Gas in Space, Vito Mennella; Christine Joblin, Sep 2021, Anacapri - Capri Island, Italy. pp.119, 10.1007/978-3-031-29003-9_14 . hal-04259792

HAL Id: hal-04259792

<https://hal.science/hal-04259792v1>

Submitted on 26 Oct 2023

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PAHs, carbon clusters and fullerenes in cosmic dust analogues and meteorites

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Abstract. Large carbonaceous molecules such as polycyclic aromatic hydrocarbons (PAHs) and fullerenes are abundant species in astrophysical environments but only a few specific molecules, mainly C_{60} and some two-ring aromatics, have been identified so far. Targeting specific species of these families raises the question of their formation, particularly in the hot and dense envelopes of evolved stars. This has motivated a number of research groups to produce cosmic dust analogues using a variety of techniques. Laboratory analysis of extraterrestrial matter such as meteorites can also provide additional clues regarding the origin of these molecules and their physical and chemical evolution. In this work, we present a new experimental setup, the Astrochemistry Research of Organics with Molecular Analyzer (AROMA) and demonstrate its potential to probe PAHs, carbon clusters, and fullerenes in cosmic dust analogues and meteorite samples. We have analyzed Murchison and Allende, the two most studied carbonaceous chondrites, as well as the Almahata Sitta ureilite. The same technique is used to analyze cosmic dust analogues such as those produced by the Stardust machine. Hundreds of peaks are identified in the mass spectra with notable discrepancies between the different types of samples. Here we present our ability to use these discrepancies to better understand the chemical history of each sample. Ultimately, our approach can help elucidate the role of these species in the formation and evolution of carbonaceous cosmic grains.

Keywords: Large carbonaceous molecules · Meteorites · Dust.

1 Introduction

The aromatic emission bands (AIBs) in the mid-infrared (3.3, 6.2, 7.7, 8.6, 11.2, and $12.7\ \mu\text{m}$) are well observed in photodissociation regions associated with evolved stars (post-asymptotic giant branch stars and planetary nebulae), as well as in star- and planet-forming regions ([1], A.G.G.M. Tielens in this volume). They have been attributed to PAH molecules that relax radiatively following the absorption of ultraviolet (UV) photons. The observation of infrared (IR) emission bands attributed to C_{60} and C_{60}^+ in the reflection nebula NGC 7023 confirmed the validity of the emission mechanism [2, 3]. Cami et al. reported

that in addition of C_{60} , another fullerene C_{70} could also be present in the planetary nebula Tc 1.[4]. AIBs are well fit by distribution of PAHs molecules/ions. However it is difficult to identify specific molecules/ions in the mid IR. For this reason none of the species carrying the classical AIBs could be identified so far. Recently, a major milestone in the identification of small aromatic species has been achieved with the detection of indene (C_9H_8) ([5], J. Cernicharo et al. in this volume) and cyanonaphthalene ($C_{10}H_7CN$) [6] in the cold pre-stellar core TMC-1. These aromatic species are the product of cold chemistry (e.g., McCabe et al. in this volume) active in molecular clouds that are the birthplace of new stars and planets [5].

To explore the chemical pathways of PAH and fullerene formation and to understand their role in stardust formation, several laboratory techniques and reactors have been used to produce and characterize cosmic dust analogues [7–12]. In addition, chemical analysis of pristine material in the Solar System such as comets, interplanetary dust particles (IDPs), and meteorites, offers us the opportunity to access presolar molecules and dust. In this context, meteorites are the most available type of cosmic samples on Earth.

Establishing the molecular chemical composition of these astromaterials can shed light on interstellar chemical processes and conditions in the early solar system. To this end and as part of the Nanocosmos ERC synergy project¹ we have developed an experimental setup called Astrochemistry Research of Organics with Molecular Analyzer (AROMA). As part of the Nanocosmos objective to understand the physical and chemical processes leading to the formation of stardust, AROMA was tasked with analyzing the molecular content of stardust analogues and meteorites. Here we briefly review the results obtained.

2 Experimental Techniques

2.1 AROMA

AROMA is an experimental setup developed in collaboration with Fasmatech (Greece), to probe with high sensitivity the carbonaceous molecular composition associated with dust samples, such as cosmic dust analogues and meteorites [13]. The setup consists of a microprobe laser desorption ionization (LDI) source and a segmented linear quadrupole ion trap (LQIT) connected to an orthogonal time-of-flight (oTOF) mass spectrometer. The low pressure (10^{-6} mbar) ion source provides the ability to study large carbonaceous molecules such as PAHs and fullerenes that are embedded in a variety of solid samples by performing LDI in a single or double steps (L2MS). A pulsed (5 ns) infrared (IR) laser (Nd:YAG at 1064 nm) is used for desorption and a pulsed (5 ns) ultraviolet (UV) laser (fourth harmonic of an Nd:YAG at 266 nm) is used for ionization. The separation of desorption and ionization in time and space allows us better control to produce ions with minimal fragmentation and higher sensitivity (tens of attomole per laser shot). The LQIT also allows us to trap and isolate desired species and

¹ Principal investigators: J. Cernicharo, J.A. Martín Gago, and C. Joblin

perform collision-induced dissociation experiments as well as photodissociation studies. Ions exiting the LQIT are mass separated using an oTOF equipped with a two-stage reflectron and a fast microchannel plate detector. The mass analyzer has a peak resolution power of 10^4 at $m/z=300$.

2.2 From Detected m/z to Family Analysis

The ion signal is processed using the mmass software, an open source mass spectrometry tool [14]. The accuracy of our assignments for the peaks approaches 0.01 on m/z , giving us high confidence in our analysis of pure hydrocarbons. Hydrocarbon molecules, identified by their chemical formula, can be classified into families according to their double bond equivalent (DBE). This is the number of unsaturations (double bond or ring system) present in the organic molecule and is a direct measure of aromaticity. The DBE is given by [15]:

$$DBE = C\# - H\#/2 + N\#/2 + 1, \quad (1)$$

where $C\#$, $H\#$ and $N\#$ are the number of carbon, hydrogen and nitrogen atoms. Pure carbon species are sorted into carbon clusters (CC for $C\# < 30$) and fullerenes ($C\# \geq 30$). Hydrocarbons are sorted into two categories, aromatics and hydrogenated carbon clusters (HC) clusters. This is done using empirical factors and DBE boundaries set for hydrocarbons to contain or not aromatic moieties in complex natural organic matter. Hydrocarbons with $(0.5 \leq DBE/C\# \leq 0.9)$ are considered to be aromatics. Others hydrocarbons with higher $DBE/C\#$ including polyynes are called HC clusters. Aliphatic species with $DBE/C\# < 0.5$ are not considered because the number of species detected is often very small (a few species per sample). Figure 1 illustrates this method. The upper part shows a mass spectrum of soot particles collected (at a height of $Z=14\text{mm}$ above the burner) from an ethylene/air laminar premixed flame stabilized on a McKenna burner. The lower part presents its projection in $DBE/C\#$ versus $C\#$ to have a clear view of the aromaticity and the nature of the chemical species composing the sample.

3 Results

3.1 Cosmic Dust

We have demonstrated that the L2MS technique in AROMA can track global changes in the molecular composition of dusty samples [16,12]. Figure 2 (a) shows the relative compositions of the molecular families for four samples, two from collected soot particles and two synthesized using the Stardust machine. The Stardust machine was developed to simulate the chemistry of carbon dust formation in evolved stars [12] in a highly controlled environment (see Sobrado et al. in this volume). It includes an atomic gas aggregation source but also several on-line characterization techniques. Molecular and dust compositions can thus be analyzed both by in-situ diagnosis and by ex-situ analysis notably with AROMA.

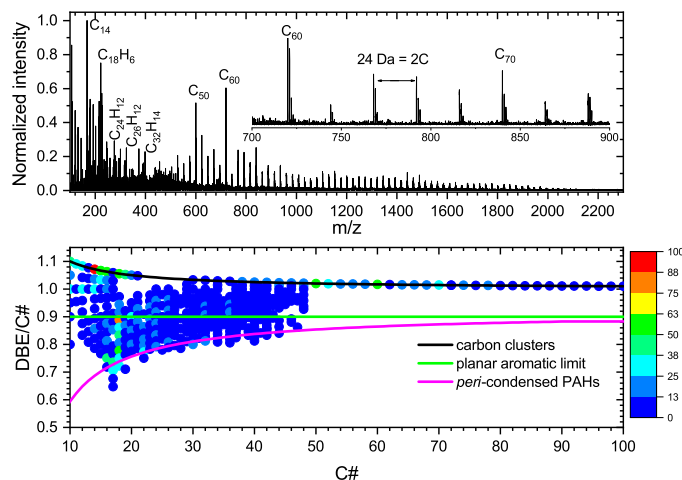


Fig. 1. From top, mass spectrum recorded for just-grown soot particles collected at $Z=14$ mm above the burner. Peak annotations are given for the corresponding neutral species. The spectrum highlights the detection of fullerenes. Colored map plots of $\text{DBE}/C\#$ vs $C\#$ constructed from the molecular formulas from the mass spectrum. The color scale is representative of the relative intensity (normalized to the highest peak in the spectrum) for each identified species. The black line corresponds to the CC and fullerenes ($\text{DBE} = C\# + 1$); the green line corresponds to the planar aromatic boundary ($\text{DBE} = 0.9 \times C\#$) and the magenta line corresponds to the purely *peri*-condensed PAHs (most compact structures made up of 6-member rings) with $\text{DBE} = -3.24 + 0.92 \times C\#$.

The molecular composition given by AROMA proved to be consistent with but much more sensitive than complementary analysis (in-situ mass spectrometry, STM imaging). For experiments using atomic C (and C_2) vapor and in the presence of H_2 gas, CC and HC Clusters were detected. These results led to the conclusion that PAHs may not be formed efficiently during the early gas phase growth in circumstellar environments. In the presence of C_2H_2 , CC, HC Clusters and PAHs with aliphatic sidegroups were detected. The results are used to strengthen the role of C_2H_2 in the formation of aromatic species and alkyl-substituted aromatic species in the outflow of asymptotic giant branch stars and in proto-planetary nebulae. Chemical pathways could be provided for the main observed species: polyacetylenic chains, carbon clusters with odd $C\#$, PAHs and alkylated-substituted aromatics. In these studies, no fullerenes were detected, probably due to the relatively low gas temperature (<1000 K) during aggregation in the Stardust machine ([12], Sobrado et al. in this volume).

The same approach was used to perform the analysis of the nascent soot particle samples. Soot particles produced in chemical reactor for combustion

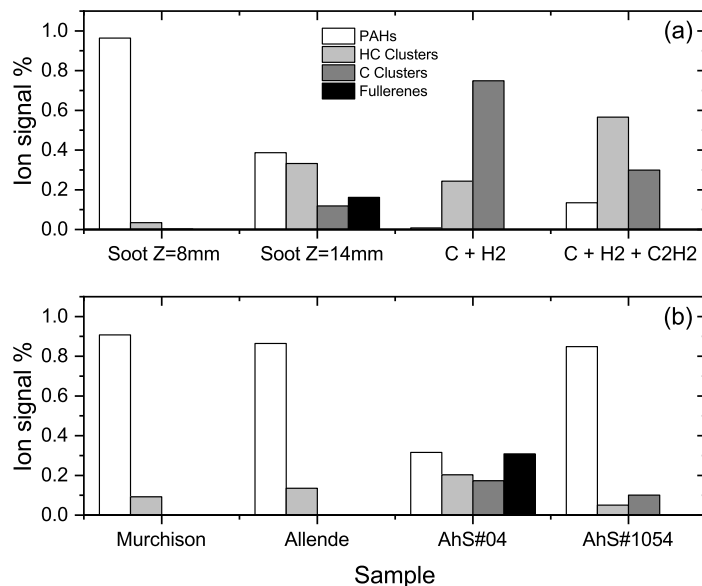


Fig. 2. Bar graph summarizing the relative family compositions obtained by DBE analysis on the full mass spectra. (a): case of two soot samples collected at different height above the burner ($Z=8$ and 14mm) and two Stardust samples synthesized using different atomic and molecular precursors. (b): case of Murchison and Allende carbonaceous chondrites, and of AhS #04 and AhS #1054 (LL3-4) ureilites.

studies was already shown to provide pertinent laboratory analogues of cosmic dust particles [10]. Clear changes in molecular composition are observed with distance from the burner. We do not detect fullerene species at $Z = 8\text{mm}$ but they are clearly observed at $Z = 14\text{mm}$ (see Fig. 2(a)). There is no doubt that these changes reflect changes in the flame chemistry, as shown by the evolution of the molecular composition with distance from the burner. The formation of fullerenes from large HC Clusters could be rationalized as being due to thermal processing in the flame. It could even be quantified somehow [16].

3.2 Meteorites

The validity of the AROMA technique for probing the distribution of PAHs in meteorites has been clearly demonstrated by the analysis of a Murchison meteorite sample [13]. Recently, we reported the first firm detection of fullerenes (C_{30} to C_{100}) in seven clasts of ureilites from the Almahata Sitta (AhS) polymict meteorite [17]. Figure 3 shows the mass spectrum of fullerenes detected in AhS #04 using L2MS on the bulk sample without extraction step. The detection

of fullerenes in meteorites has been a controversial topic during the last two decades. All searches [18] have failed to detect fullerenes in meteorites, with the exception of those by Becker and coworkers on several extracts from the Allende [19] and Murchison meteorites [20]. No fullerenes or carbon clusters were detected in our previous analysis of Murchison. To complete our investigations and the search for fullerenes in meteorites, we analyzed a powder from the interior of the Allende meteorite. The recorded mass spectrum does not show the signature of fullerenes, it is dominated by PAHs and shows some m/z peaks related to HC clusters and aliphatics.

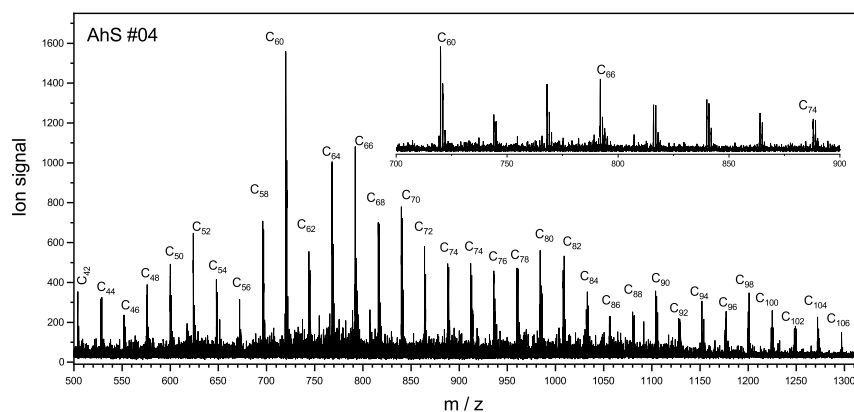


Fig. 3. Mass spectrum of AhS#04 recorded by L2MS with the AROMA setup. A distribution of fullerene species is detected ranging in size from $C\#= 42$ up to $C\#= 106$. The inset zoom graph shows some of the species detected in the m/z range of 700 to 900.

4 Conclusion

In this work, we presented our investigations using the AROMA setup of the carbonaceous molecular content of three different meteorites (Murchison, Allende and Almahata Sitta), and two types of possible stardust analogues. By applying the DBE method we were able to clearly identify chemical families and demonstrate our ability to track chemical changes in samples as a function of experimental parameters. Furthermore, we report for the first time a firm detection of fullerenes in a meteorite ending a long controversy about the existence of fullerenes in meteorites. However, the origin of these species still needs to be investigated. To this end, we demonstrated that the search for fullerenes in meteorites should be expanded beyond investigations of carbonaceous chondrites.

Extending this study to a larger collection of meteorites will also allow us to expand our mass spectrometry database (<http://aroma.irap.omp.eu>; also contains chemical analysis tools) to compare molecular populations within different types of meteorites and cosmic dust analogues.

Acknowledgements We acknowledge support from the European Research Council under the European Union’s Seventh Framework Programme (FP/2007-2013) ERC-2013-SyG, Grant agreement N°610256 NANOCOSMOS.

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