Laboratory Astrophysics: from Observations to Interpretation
Proceedings IAU Symposium No. 350, 2019
F. Salama & H. Linnartz, eds.
doi:10.1017/S1743921319008354

Characterization of large carbonaceous molecules in cosmic dust analogues and meteorites

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Abstract. We present a new experimental setup called AROMA (The Aromatic Research of Organics with Molecular Analyzer) based on the use of laser mass spectrometry techniques. We demonstrate the potential of AROMA for the analysis of meteoritic samples and cosmic dust analogues. Tens of peaks are identified in the mass spectra with notable discrepancies across the different samples. These discrepancies provide clues on the chemical history of each sample and are not a bias of our analysis. A double bound-equivalent (DBE) method is applied to sort the detected carbonaceous molecules into families of compounds. It reveals in addition of polycyclic aromatic hydrocarbons, the presence of other populations such as mixed aromatic-aliphatic species and carbon clusters.

Keywords. Astrochemistry, dust, solar system: formation, methods: laboratory, methods: analytical

1. Introduction

Most of our knowledge on the chemical composition and evolution of carbonaceous cosmic matter is based on astronomical observations. Still, Solar System objects such as meteorites, interplanetary dust particles (IDPs) and samples from return missions can provide direct information on this matter. Meteorites are the most available type of extraterrestrial material on Earth and are representative of the early Solar System. Analysis of Murchison, the most studied carbonaceous chondrite, shows the extensive variety of organics (up of tens of thousands of different molecular species) in meteorites amongst which heterocycle compounds and aromatic hydrocarbons (Schmitt-Kopplin *et al.* 2010). Other studies have shown the capability of laser mass spectrometric techniques to specifically target the aromatic species in extraterrestrial materials, including meteorites and IDPs as well as cometary coma dust (Spencer *et al.* 2008).

2. The AROMA setup

AROMA (Sabbah *et al.* 2017), is an experimental set-up developed in the framework of the Nanocosmos ERC synergy project. Its main purpose is to analyze the carbonaceous molecular content of cosmic dust analogues and meteoritic samples. The experimental set-up consists of a laser desorption ionization (LDI) source and an ion trap connected to an orthogonal time of flight mass spectrometer. The ion source offers the possibility to study large carbonaceous molecules such as polycyclic aromatic hydrocarbons (PAHs) that are embedded in a variety of solid samples by performing LDI in a single or/and double steps. The trap allows studying the structure of desired species by collision induced dissociation (CID) and UV photodissociation studies. Finally the ion signal is monitored using an

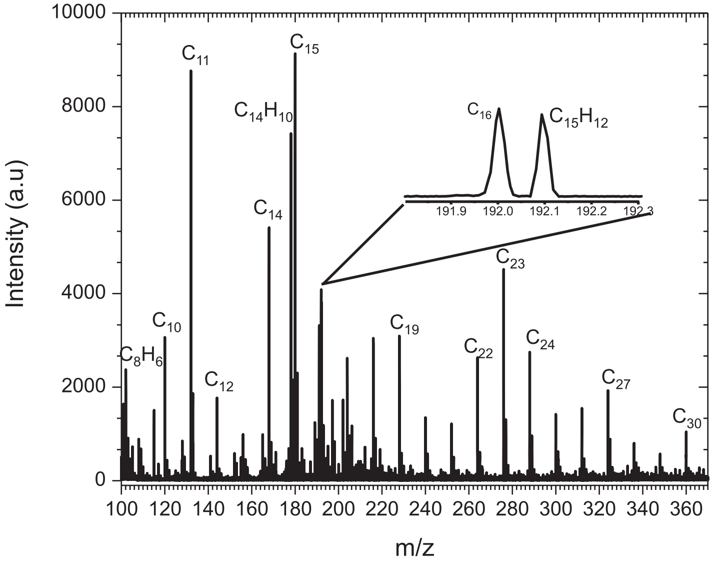

Figure 1. Mass spectrum of Almahata Sitta meteorite recorded using AROMA. A distribution of aromatic species and carbon clusters has been detected. Some peaks assignments are presented.

orthogonal time-of-flight mass analyzer equipped with a two-stage reflectron and a fast microchannel plate (MCP) detector, thus providing high mass resolution ($m/\Delta m{=}10^4$).

We have previously reported (Sabbah *et al.* 2017) the capabilities of the apparatus and its high sensitivity to aromatic species (100 of femtograms). We also detected the PAH distribution in the Murchison meteorite, which is made of a complex mixture of extraterrestrial organic compounds. A key molecule in the PAH family is m/z=202.08. In order to identify the dominant isomeric structure at this position, we investigated the fragmentation pattern of this molecule employing the CID technique. We firmly identified the main peak at m/z=202 as due to pyrene. Combining CID experiments and double bound-equivalent (DBE) plot representation, we identified a series of methylated pyrene species.

3. From mass spectrum to DBE

In order to explore the diversity of carbonaceous molecules in meteorites, a fragment of a few milligrams of the Almahata Sitta meteorite (Jenniskens *et al.* 2009) was powdered and introduced in AROMA. Figure 1 shows the mass spectrum recorded for this sample in the same mass range as for the Murchison analysis. Peaks are annotated with their corresponding chemical formula. We found a distribution of carbonaceous species ranging from m/z=100 to 360. The mass spectrum reveals the co-existence of aromatic species with carbon clusters. In order to investigate the chemical diversity in both meteorites we applied the DBE method.

An elemental formula was associated to each detected mass peak with a signal-to-noise ratio (S/N) greater than 10. This is achieved employing the mMass software (Strohalm *et al.* 2008), an open source mass spectrometry tool. The DBE is then calculated using the following equation:

$$\text{Double bond equivalent } (C_cH_hN_nO_oS_s) = c - h/2 + n/2 + 1$$

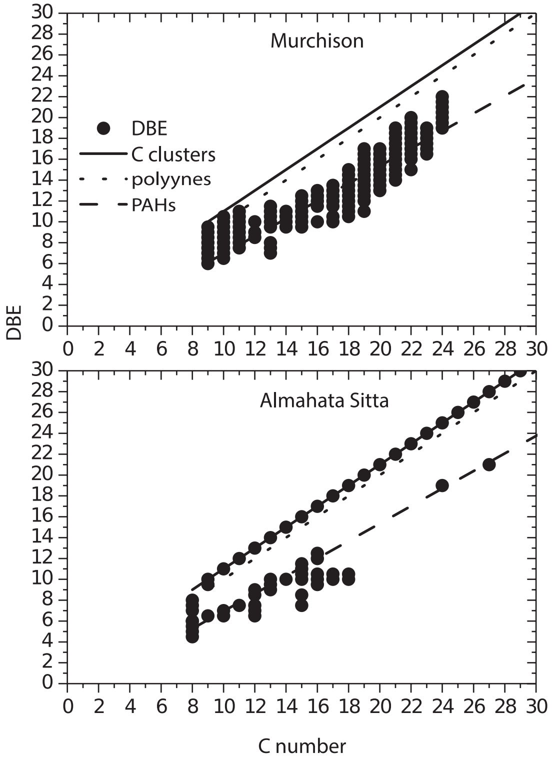

Figure 2. DBE vs. carbon number plots for the Murchison meteorite (top) and Almahata Sitta (bottom) meteorites. PAHs are present in both meteorites whereas carbon clusters are only observed in Almahata Sitta. Species having the same DBE and differing by one carbon number include substitutions by methyl group (-H $+CH_3$).

The DBE is representative of the unsaturation level of the molecules and thus corresponds to a direct measure of their aromaticity. Its value is equal to the number of rings plus double bonds involving carbon atoms (because each ring or double bond results in a loss of two hydrogen atoms). In Figure 2 we represent the DBE versus carbon number for both meteorites, Murchison (top) and Almahata Sitta (down). Three linear curves are inserted in the graphs corresponding to carbon clusters (DBE(C clusters)= C+1), polyynes (DBE(polynnes)= C) and PAHs (DBE(PAHs)= 0.84×C - 1.45). Species aligned horizontally and separated by one carbon number are indicative of substitutions by methyl group (-H $+CH_3$).

The DBE plots are clearly very different. Murchison contains a large variety of aromatic species and mixed aromatic-aliphatic species whereas Almahata Sitta contains a specific PAH family aligned on the dashed line (Figure 2 bottom) and going up to $C_{27}H_{14}$. This observation is similar to previous work on this meteorite (Sabbah *et al.* 2010). Almahata Sitta contains also a series of carbon clusters spanning size from C=9 to 30 and even larger species (not shown here).

4. Conclusion and prospectives

In this work, we investigated the aromatic content of two different meteorites, Murchison and Almahata Sitta, with the AROMA setup. We have been able to detect aromatic species in both samples in agreement with previous work (Callahan *et al.* 2008; Sabbah *et al.* 2010). Moreover, we report for the first time the co-existence of carbon clusters along with PAHs in the Almahata Sitta meteorite. Applying the DBE method we have been able to clearly identify chemical families. This observation has motivated us to undertake a systematic analysis of multiple Almahata Sitta samples to confirm the presence of carbon clusters and explore the chemical diversity across the different samples (Sabbah *et al.* in prep.). Enlarging the scope of this study to a larger collection of meteorites will also allow us building a database in order to compare populations of carbonaceous materials within different types of meteorites and cosmic dust analogues.

Acknowledgment

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Program (FP/2007-2013) ERC-2013-SyG, Grant agreement n. 610256 NANOCOSMOS. We acknowledge support from La Region Occitanie, Grant N° 15066466.

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