

# Interstellar and interplanetary solids in the laboratory

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## Abstract:

The composition of the interstellar matter is driven by environmental parameters (e.g. elemental abundance, density, reactant nature, radiations, temperature, time scales) and results also from extreme interstellar medium physico-chemical conditions. Astrochemists must rely on remote observations to monitor and analyze the composition of interstellar solids. These observations give essentially access to the molecular functionality of the solids, rarely elemental composition constraints and isotopic fractionation only in the gas phase. Astrochemists bring additional information from the study of analogues produced in the laboratory, placed in simulated space environments. Planetologists and cosmochemists can have access and spectroscopically examine collected extraterrestrial material directly in the laboratory. Observations of the diffuse interstellar medium (DISM) and molecular clouds (MC) set constraints on the composition of organic solids and large molecules, that can then be compared with collected extraterrestrial materials analyses, to shed light on their possible links.

## 1 Introduction

Astrochemists investigations of the interstellar medium depend on remote astronomical observations, to follow and study the physical and chemical composition of interstellar solids (e.g. Spoon et al., 2007; Dartois & Muñoz Caro, 2007; Van Diedenhoven et al., 2004; Chiar et al., 2002; Pendleton et al., 1994). Cosmochemists and planetologists possess the advantage of the availability of any collected extraterrestrial material, like (micro-)meteorites, they can spectroscopically examine in the laboratory

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(e.g. Orthous-Daunay et al., 2013; Dartois et al., 2013; Brunetto et al., 2011; Kebukawa et al., 2011; Sandford et al., 2006; Flynn et al., 2003). To constrain the interstellar solids molecular functionalities, astrochemists rely principally on the dust infrared observed absorption and emission, emanating from stellar winds, young stars, the diffuse interstellar medium and dense clouds. Such observations are complemented by the information gained from the production and study of laboratory interstellar dust analogues, placed in experimentally simulated space environments. The dust observed is the superposition and mixing of different galactic phases that participate to a dust life cycle. The dust production rates, when looking at the galactic scale, are fed principally by old stars stellar masses, as well as debated contributions from supernova (that inject but also destroy a large fraction) and young star jets (e.g. Jones 2001; Dartois 2005b; Tielens et al. 2005; Robitaille & Whitney 2010; Matsuura et al. 2011). The interstellar solids include minerals (such as silicates and oxides) and carbonaceous matter (among which aromatic hydrocarbons and various observed structural forms such as amorphous carbons, diamond, hydrogenated amorphous carbons and other materials with aromatic/aliphatic mixed structures). In the dense molecular clouds and protoplanetary disks, more volatile solids, such as interstellar ice mantles, are observed. These solids experiences physical and chemical processes that will modify their structure and/or composition. The focus will here be made on the carbonaceous components.

## **2 The different carbonaceous solids observed**

The interstellar medium is populated by different forms of carbonaceous solids (polyaromatic hydrocarbons, amorphous carbons, hydrogenated amorphous carbons, diamonds, fullerenes, and ices, precursors for organic residues). The Aromatic Infrared Bands (AIBs), observed in the ISM, trace a polyaromatic material giving rise to emission bands, notably at 3.3, 6.2, 7.7, 8.6, and 11.3 microns. Still unidentified with a definite carrier, they are associated with the Polycyclic Aromatic Hydrocarbons (PAHs) hypothesis. The observed bands result from the infrared fluorescence of large PAH-like entities, upon absorption and relaxation of energetic UV photons (Léger & Puget 1984; Allamandola et al. 1985). The increasing number of telescopic survey of many emitting sources pointed out variabilities in the AIB band profiles. A first classification based on the decomposition of these profiles into three classes A,B and C emerged (Peeters et al. 2002; van Diedenhoven et al. 2004). By number, the most observed ones are the class A, then class B and a smaller number of class C. The profiles variations are related to the chemical composition variation among the carriers, and the number of observed sources is weighted by the modifying environments and efficiency of the emitting mechanisms among the different classes. It is commonly thought that the more aromatic carriers are the class A, and the class C display additional features attributed to an aliphatic character, based on the outcome of observations (Sloan et al. 2007; Boersma et al. 2008; Keller et al. 2008; Acke et al. 2010) and experiments (Pino et al. 2008; Carpentier et al. 2012; Gadallah et al. 2013). Among the carbon solids, important amounts of carbon under an amorphous form are injected by the so-called late-type carbon stars. This solid phase is difficult to observe remotely, as no specific features are associated with them, and traced by a blackbody emission from the amorphous carbon particles in equilibrium with the stellar radiation field (Volk et al. 2001; Gauba & Parthasarathy 2004; Chen et al. 2010). This interstellar dust component is very difficult to detect elsewhere, as it possesses neither specific nor strong infrared features. However, it probably contributes to the extinction in the UV-visible part of the DISM spectrum. Amorphous solids made of C and H, the hydrogenated amorphous carbons (HAC or a-C:H), constitute another important interstellar dust component. They were observed at 3.4  $\mu\text{m}$  in absorption against background infrared sources (Allen & Wickramasinghe, 1981). Since then, a large number of observations confirmed its ubiquitous presence in the DISM. This absorption can be decomposed in various sub bands, pertaining to the  $\text{sp}^3$   $\text{CH}_3$  and  $\text{CH}_2$  stretching modes

(Duley & Williams, 1983). The cosmic carbon abundance required to explain these absorptions varies depending on the carrier network adopted and the lines of sight, from a few percents up to 35% (e.g. Sandford et al. 1991; 1995; Pendleton et al. 1994; Duley 1994; Duley et al. 1998; Dartois & Muñoz Caro 2007). Two specific infrared emission bands observed at 3.43 and 3.53 microns around young stars are the sign of the hydrogen-terminated surfaces of nanodiamonds. The observed profiles and ratios imply diamonds a few nanometers in size, containing hundreds of C atoms (Chang et al. 1995; Guillois et al. 1999; Pirali et al. 2007). Only a handful of sources with these characteristics are known, with the nano diamonds observed close to the stars (Habart et al. 2004; Acke et al. 2006; Goto et al. 2009). Fullerenes have been searched for and given upper limits since a long time (e.g. Foing & Ehrenfreund 1994; Fulara et al. 1993; Moutou et al. 1999; Herbig 2000; Misawa 2009). The observation of a reflexion nebula (NGC7023, Sellgren et al. 2007; 2009; 2010), spatially resolved, allowed to point out the presence of two mid-infrared (17.4 and 18.9  $\mu\text{m}$ ), then another (7.04  $\mu\text{m}$ ) emission bands coinciding with the expected  $\text{C}_{60}$  transitions, allowing its first space detection.  $\text{C}_{60}$  and  $\text{C}_{70}$  infrared transitions were also detected in a hydrogen deficient planetary nebula (Cami et al. 2010). The fullerenes observed require locally  $\text{C}_{60}/\text{C}$  ratios typically a few 0.1%, a low percentage of the available cosmic carbon.  $\text{C}_{60}$  mid infrared transitions are reported in the surroundings of many objects with different physical conditions such as Asymptotic Giant Branch, Post-AGB, Proto-planetary Nebulae, and Herbig Ae/Be stars (Garcia-Hernandez et al 2012; Roberts et al 2012). The observations of fullerenes to constrain their presence in various sources is still a recent going process. Interstellar dust grains entering the dense and cold cloud phases of the ISM are coated by ice mantles at low temperature (about 10K, Bottinelli et al. 2010, Boogert et al. 2008; Pontoppidan et al. 2008; Oberg et al. 2008; Bergin et al 2005; Dartois et al. 2005a; Van Dishoeck 2004; Boogert & Ehrenfreund 2004; Gibb et al. 2000). These interstellar ice mantles are subjected to cosmic rays and secondary UV photons. Another form of carbonaceous dust can be produced as a consequence of the recombination of the photolysis and radiolysis products, leaving behind stable macromolecular residues long after the ice sublimation (e.g., Muñoz Caro & Schutte 2003; Nuevo et al. 2006). Such solids could be incorporated into later stages of dust evolution.

### **3 From ISM observations to analogues and meteorites**

Besides the high diversity of carbonaceous dust observed and discussed above, most of the interstellar and circumstellar carbonaceous dust incorporated in a protoplanetary disk, in terms of abundance, should be found among the ice mantles evolution organic residues, the so-called PAHs polyaromatic solids or (hydrogenated-)amorphous carbons.

Comparisons between extraterrestrial carbonaceous matter, extracted from primitive meteorites, that consists of a mixture of insoluble and soluble organic matter (IOM and SOM) were performed via infrared spectroscopy on the IOM fraction (e.g. Ehrenfreund et al. 1991). This was limited to the 3.4  $\mu\text{m}$  spectral window and led to conclude that the relative good match suggested that the chemical composition of the observed interstellar matter was similar to the meteorite organic extract. The extension to the full infrared spectral domain, covered by satellites later, in particular in the atmosphere free mid-infrared region showed that the spectroscopic comparison with the IOM in the 5 to 10  $\mu\text{m}$  was no longer compatible with the ISM hydrogenated carbons contributing at 3.4  $\mu\text{m}$ . A spectroscopic discrepancy also existed between macromolecular organics expected to be formed from ice mantles processed in the laboratory under simulated dense cloud conditions. More than ten years ago, the diffuse interstellar medium a-C:H organic matter structural unit was understood as a highly polyaromatic, hydrogenated at the periphery of aromatic platelets, with few aliphatic bridges (Pendleton & Allamandola 2002). The IOM structure in Orgueil meteorite and the labile fraction in CM chondrites (Kitajima et al. 2002, Remusat et al. 2007, right structure Fig1; Derenne & Robert

2010) have definitely another chemical network. The possibility to observe the infrared spectrum of the ISM of other galaxies (middle spectrum displayed in Fig1) has brought additional information to constrain the a-C:H organic matter structure. In particular, the aromatic versus aliphatic content of the DISM a-C:H shows that the aromatic CH stretching modes are less prominent than those suggested by the proposed former structure (Dartois & Muñoz Caro, 2007, upper structure Fig1). The structure is then pointing toward a material with a lower aromatic CH contribution, such as hydrogenated amorphous carbon (the upper trace of Fig1 corresponds to a laboratory produced analogue spectrum) or hydrogen rich soot like analogues. This suggests a greater similarity of the a-C:H structure with the IOM structure. However, many absorptions in the mid-infrared spectral fingerprint region (Kebukawa et al. 2011; Orthous-Daunay et al. 2013, lower spectrum in Fig1) for the IOM does not allow to provide a correct spectral match. These IOM absorption are mainly related to the presence of oxygen heteroatoms. In the ISM dust, there are no evidence for a large amount of incorporation of such oxygen heteroatoms, nor nitrogen ones. This does not precludes the ISM dust to be a precursor modified during the meteorites formation process. The question is then what are the observed evidence of the solids evolution from the diffuse to dense medium. The DISM a-C:H signatures disappear at the interface of molecular clouds. Deeper, the onset conditions are met for interstellar ice mantles. In the laboratory, a-C:H analogues have been shown to be dehydrogenated in the dense phase and/or at the interface between diffuse and dense clouds (Mennella et al. 2003; Godard et al. 2011), thus, before being incorporated into a protosolar nebula. In the dense phase preceding the protosolar nebula formation, interstellar ice mantles experience the cosmic ray radiolysis and secondary UV photolysis, leading to the formation of a macromolecular organic residue. The replication in the laboratory of the space energetic environments impinging on ices is possible and produces analogues residues, measured after sublimation of the ice. Both room temperature (e.g. Muñoz Caro et al. 2004; Nuevo et al. 2006), and the space-exposed laboratory residues (e.g. EURECA experiment, Greenberg 1995) do not match with the IOM. Again, such residues can be seen as a potential starting or precursor material (Muñoz Caro & Dartois, 2013), provided that the subsequent evolutionary pathways can lead to some kind of IOM.

## **4 Potential outer solar system organic matter**

In the past years, most comparisons between extraterrestrial collected organic matter and the interstellar medium dust observations have been focused on meteorites arising from the asteroid belt region. We have at our disposal carbonaceous component for Interplanetary Dust Particles (IDPs) and micrometeorites coming from larger distances and thus potentially preserved. The small sizes of collected IDPs, generally of a few to tens of microns are such that their organic content, at most a few percents in mass, cannot be easily separated using the same techniques as for the meteorites. The measurement of their organic infrared spectra is therefore difficult. In the  $3\mu\text{m}$  spectral region, many of the IDPs infrared spectra display a stretching mode absorption profile different from the Galactic center lines of sight, that display the a-C:H dust components (e.g. Keller et al., 2004; Matrajt et al., 2005; Bradley, 2005; Muñoz Caro et al. 2008; Brunetto et al. 2011). Some micrometeorites collected at the poles offer a size distribution that is sometimes more suitable for these techniques to be applied, thus allowing for a more direct comparison with astronomical spectra. Of particular interest are the rare and very specific ultracarbonaceous micrometeorites (UCAMMs), which seem to provide a sampling of another form of organic matter from our Solar System. These UCAMMs were discovered as a small fraction in various Antarctic micrometeorites collections. These micrometeorites were reported by Nakamura et al. (2005) from the Dome Fuji collection and more recently by Yabuta et al. (2012), and were found also in the Concordia micrometeorites collection of the CSNSM, from the French-Italian Dome C station (Duprat et al. 2007). Combined with Nano-SIMS measurements,

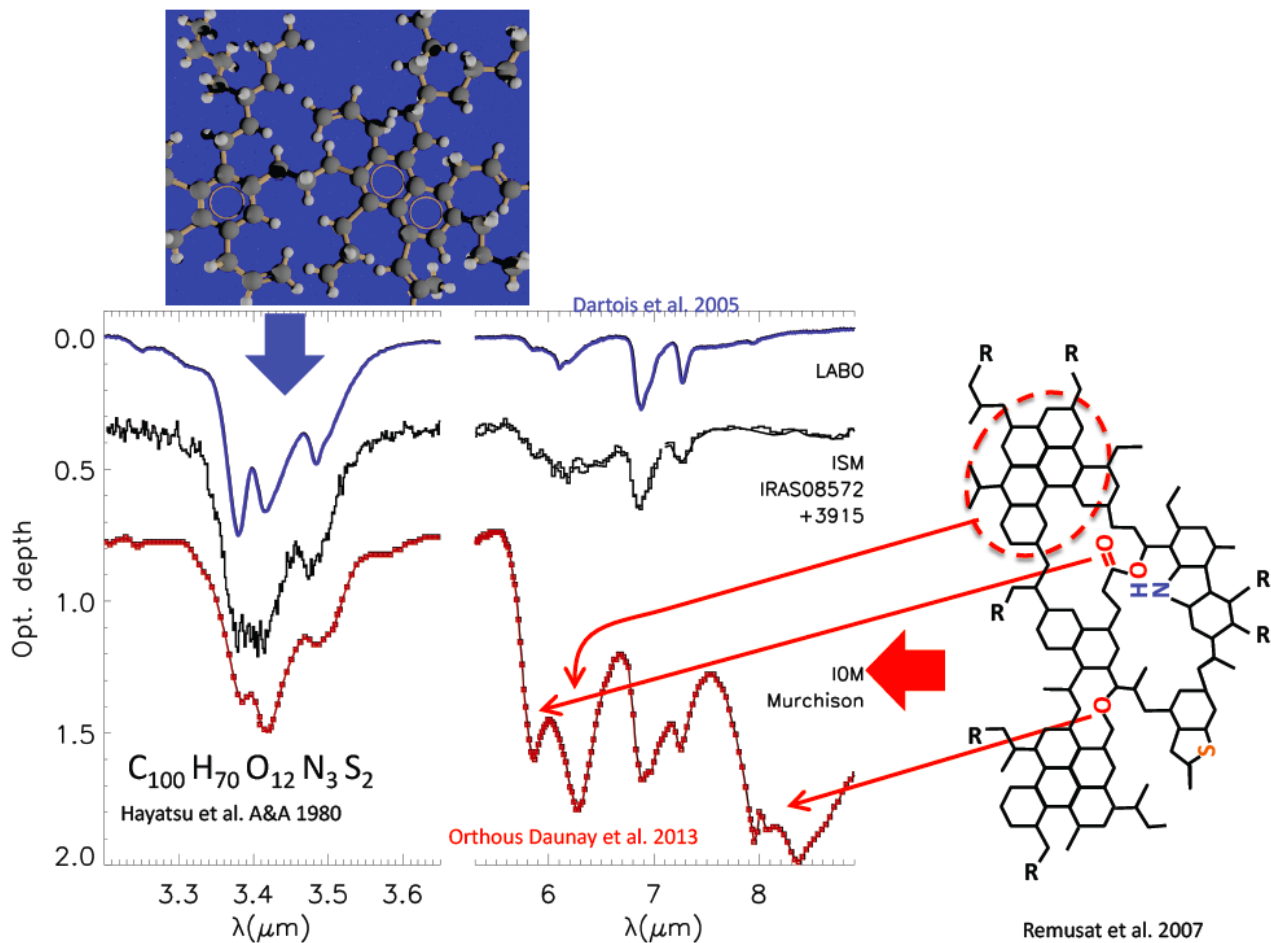


Figure 1: Comparison between infrared spectra and expected chemical structural units. Upper structure and spectrum: laboratory produced hydrogenated amorphous carbon. Middle trace: observed extragalactic ISM hydrogenated amorphous carbons infrared signature. Lower spectrum and right side structural unit: Murchison IOM extract. See text for detailed discussion.

scanning electron micrographs and X-ray maps measurements of two UCAMMs show that they are very rich in organic content (more than 50% and up to 95% of the whole UCAMM atoms being organic matter). They also possess a high deuterium enrichment, often associated with a formation in cold environment. Their organic matter presents infrared (Dartois et al. 2013) and Raman spectra (Dobrica et al. 2011) similar to laboratory analogues of polyaromatic hydrogenated carbon nitrides, and display a nitrogen concentration characterized by bulk atomic N/C ratios of 0.05 and 0.12 (locally exceeding 0.15). Such nitrogen rich solids are not observed in the interstellar medium. In the solar system N-rich materials are seldom encountered. In addition, experimentally, the inclusion of such high amounts of nitrogen (10-20%) in a (oxygen poor) carbon nitride requires a carbon rich precursor and energetic processes in an N-dominated environment (i.e. H<sub>2</sub>O ice depleted). The UV photolysis or cosmic ray radiolysis of N- and C-rich ices may lead to these nitrogen-rich carbonaceous materials. Beyond the trans-Neptunian region, in the cold outer regions of our solar system, the surface of small icy bodies can meet these conditions. Even closer to us, for large bodies such as Pluto, N<sub>2</sub> rich ices are observed (e.g. Doute et al. 1999; Protopapa et al. 2008; Grundy et al. 2013). The UCAMMs potentially provide a unique collected extraterrestrial material to get insight into the evolution of matter incorporated from the protosolar nebula. Comparisons and differences between UCAMMs and many of the solar system collected materials and ISM spectra are provided in a summary figure in a similar

review in Dartois et al. (2014). UCAMMS would result from the physico-chemical processes that occurred beyond a nitrogen snow-line, revealing organic material from the extreme outer regions of the Solar System. The remote observations cannot investigate actually surface reflectance spectra for the many small icy bodies at such distances.

## 5 Potential implications

The comparisons discussed in the previous sections show the difficulty to directly assign any observed interstellar solids to solar system collected material. It appears not probable that such ISM dust has been incorporated at a large scale in the solar system without any significant modifications. The interstellar dust should therefore be seen at most as a precursor. Laboratory studies guidance is essential to simulate the pathways for the modification and evolution of these solids observed in the previous phases of the ISM cycle. Genuine preserved ISM material, apart from dust particles such as found in presolar grains and/or highly refractory and resilient solid phases are probably exceptions in terms of volume fraction, and the observed, collected and analysed dust grains in the solar system are often probing nebular processes or specific physical and chemical mechanisms acting inside the very young or actual solar system.

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