Interstellar and interplanetary carbonaceous solids in the laboratory

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INTRODUCTION

While cosmochemists interested in studying (micro-)meteorites chemical composition can spectroscopically examine any collected extraterrestrial material in the laboratory (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, and references therein), astrochemists must rely on interstellar medium (ISM) investigations based on remote observations to monitor and analyze the physico-chemical composition of interstellar solids (Spoon et al., 2007; Dartois and Muñoz-Caro, 2007; Van Diedenhoven et al., 2004; Chiar et al., 2002; Pendleton et al., 1994; and reference therein). The composition of solid state matter can be deduced by observing infrared dust absorption and emission from stellar winds, recently born stars, diffuse interstellar medium (DISM), and molecular clouds (MC). These observations give essential access to the molecular functionality of these solids, rarely strong constraints related to their elemental composition, and their isotopic fractionation, mostly in the gas phase. Astrochemists can bring in additional information from the study of analogues produced in the laboratory and placed in simulated space environments.

In the interstellar dust lifecycle, interstellar matter bounces back and forth between various phases. During this process, stellar mass loss by old stars contributes significantly to dust production and injection in the diffuse medium, adding to the mass fraction injected by supernova and young star jets, which is debated (Jones, 2001; Dartois, 2005b; Tielens et al., 2005; Robitaille and Whitney, 2010; Matsuura et al., 2011). The solid interstellar materials observed between these phases are typically divided in three main categories, including minerals (among which the silicates play an important role); “carbonaceous matter,” comprising almost any organic matter; and ices, which are encountered in the densest...
places such as molecular clouds and protoplanetary disks. The first two compose the so-called “refractory solids,” whereas the ice mantles are the volatile solids.

Although this article concentrates on carbonaceous dust, the observations of silicates in the interstellar dust cycle are considered instructive, as they possess sharp crystalline phases that provide well-identified spectral features, raising important questions. Silicates have been observed in emission during the late phases of stellar evolution, like the stars in the Asymptotic Giant Branch and Red Giant phases, when copious amount of matter is ejected by stellar winds. The observed silicates in these environments are significantly crystalline. By contrast, the silicates injected in the diffuse interstellar medium are observed to be fully amorphous (e.g., Kemper et al., 2001). The amorphization of the silicates occurs due to the processing by energetic cosmic rays, as demonstrated in the laboratory (Carrez et al., 2002; Demyk et al., 2008; Bringa et al., 2007). In a later evolutionary stage, these silicates, present into dense clouds, are incorporated in the eventual formation of protostellar objects. The spectra of disks around T Tauri stars harbor large fractions of crystalline silicates. The observations in these disks lead to a so-called “crystallinity paradox” (e.g., Olofsson et al., 2009), as more crystalline silicates are observed in regions that are colder, rather than warmer, and closer to the star, and therefore far from their presumed (trans-)formation regions.

Careful investigations are still needed to conclude about the origin of crystalline silicate in the cold regions of T Tauri stars, as alternative silicates crystallization mechanisms have been invoked at temperatures lower than the classical condensation temperatures (Molster and Kemper, 2005), such as by intense electron bombardment (Carrez et al., 2001; Kimura et al., 2008) and exothermic reactions (Tanaka et al., 2010). This implies that silicate crystallization occurs under a wider range of astrophysical conditions. However, the radial distributions observed in these crystalline silicates are still associated with efficient outward radial transport mechanisms in the disks around T Tauri stars, with the silicates incorporated from the protostellar phase being amorphous. The constraints suggested through the observation of these minerals raises similar questions on our understanding of the interstellar organic matter.

**The Carbonaceous “Allotropes” of the Interstellar Medium**

Several forms of carbonaceous solids are observed in the Galaxy’s ISM: nanodiamonds, fullerenes, polyaromatic hydrocarbons, amorphous carbons, hydro-genated amorphous carbons, and ices that can form organic residues. Nanodiamonds are best observed around young stars through two specific infrared emission bands at 3.43 and 3.53 microns. They are attributed to vibrational modes of hydrogen-terminated nanodiamonds, typically a few nanometers in size, and containing hundreds of C atoms (Chang et al., 1995; Guillois et al., 1999; Pirali et al., 2007) in equilibrium with the stellar radiation field. They are observed around very few objects and are close to stars (Habart et al., 2004; Acke et al., 2006; Goto et al., 2009).

Space fullerenes have been observed more recently, after long searches of upper limits (e.g., Foing and Ehrenfreund, 1994; Fulara et al., 1993; Moutou et al., 1999; Herbig, 2000). C60 was first spatially resolved in a reflection nebula by Sellgren et al. (2009, 2010), and then C60 and C70 in a planetary nebula (Cami et al., 2010). The fullerenes observed occurs due to a low percentage of the available carbonic carbon, with C60/C ratios typically <0.1%. However, recent observations report the presence of mid-infrared features that are expected to arise from C60 in the surroundings of many objects with different physical conditions such as Asymptotic Giant Branch, Post-AGB, Protoplanetary Nebulae, and Herbig Ae/Be stars (Garcia-Hernandez et al., 2012; Roberts et al., 2012).

Aromatic Infrared Bands (AIB), with emission bands observed at around 3.3, 6.2, 7.7, 8.6, and 11.3 microns, are characteristic of a polyaromatic material and are observed ubiquitously in the ISM. They have led to the so-called “Polyyclic Aromatic Hydrocarbons” (PAHs) hypothesis. Under this hypothesis, AIB bands are associated with the infrared fluorescence of large PAHs molecules upon absorption of energetic UV photons (Leger and Puget, 1984; Allamandola et al., 1985). AIB astrophysical spectra are variable in their band profiles, and the observed sources are classified as A, B or C, based on the phenomenological decomposition of the bands’ positions (Peeters et al., 2002; Van Diedenhoven et al., 2004). The class A spectra are observed the most in terms of numbers, followed by class B, and class C. The evolution among the profiles is primarily linked to differences in the chemical composition of the emitting molecules or particles. The ones in class A are probably the most aromatic ones. The ones in class B show an evolution of the band that can be attributed to several factors, including the possible presence of heteroatoms or structural changes at the nanoscale in the carbonaceous network. And the ones in class C display additional features attributed to a more aliphatic character, both observationally (Sloan et al., 2007; Boersma et al., 2008; Keller et al., 2008; Acke et al., 2010) and experimentally (Pino et al., 2008; Carpentier et al., 2012; Gadallah et al., 2013).

Amorphous carbon dust is also observed around carbon (C)-rich stars, mainly through a blackbody emission from the amorphous carbon particles (Volk et al., 2001; Gauba and 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.

Hydrogenated amorphous carbons (HAC), also called by physicists a-C:H after amorphous material made of C and H, are another major component of interstellar dust. Observed for the first time in an absorption band at 3.4 µm against a Galactic center source (Allen and Wickramasinghe, 1981), the features contributing to this absorption band are associated with sp3 CH3 and CH2 stretching modes (Duley and Williams, 1983). Numerous experiments and observations have been performed to identify its origin. The a-C:H Galactic abundance has been estimated from the observed CH stretching modes in many lines of sight (e.g., Sandford et al., 1991, 1995; Pendleton et al., 1994; Duley, 1994; Duley et al., 1998; Dartois and Muñoz-Caro, 2007), and varies from a few percent up to 35% (laboratory HAC) of the cosmic C abundance.

In the densest phases of the interstellar dust cycle, or molecular clouds, the dust grains are covered by volatile molecules that are frozen at low temperature (about 10 K, Bottinelli et al., 2010; Boogert et al., 2008; Pontoppidan et al., 2008; Öberg et al., 2008; Bergin et al., 2005; Dartois, 2005a; van Dishoeck, 2004; Boogert and Ehrenfreund, 2004; Gibb et al., 2000). These simple ice mantles may act as chemical sites for surface processes (e.g., Hama and Watanabe, 2013; and reference therein) and are simultaneously processed in bulk by cosmic rays and UV photons. The radiolysis and photolysis products recombine, leading to the formation of macromolecular residues that are stable upon sublimation of the ice mantles (e.g., Muñoz Caro and Schutte, 2003; Nuevo et al., 2006) and could be incorporated into later stages of dust evolution.

Comparisons between ISM Observations/Laboratory Analogues and Solar System Matter

From the point of view of expected abundance, and among the observed carbonaceous solids, the formation of a protosolar nebula would mainly incorporate PAHs, a-C:H, and/or organic residues. Early comparisons between the ISM a-C:H features and meteorite Insoluble Organic Matter (IOM) have been performed (e.g., Ehrenfreund et al., 1991; and citations therein). The relatively good match between both infrared spectra around 3.4 microns led to the conclusion that the chemical composition of interstellar matter was similar to the meteorite organic extract (Ehrenfreund et al., 1991). The observational astronomical constraint came later, when satellites gave access to the mid-infrared spectral fingerprint region (inaccessible for ground telescopes because of atmospheric absorption), showing that the 5 to 9 microns spectral region in IOM was neither compatible with DISM a-C:H nor were organics expected from ice mantles processed in dense clouds.

The underlying structure proposed more than ten years ago for a-C:H diffuse organic matter was highly polyaromatic, fully hydrogenated at the edges of the aromatic planes, with few aliphatic bridges (Pendleton and Allamandola, 2002), and very different from the inferred IOM structure in Orgueil (Remusat et al., 2007; Deenne and Robert, 2010) and the labile fraction in CM chondrites (Kitajima et al., 2002). Recent extragalactic specific lines of sight that cover a larger astronomical scale give us additional information about the a-C:H structure by probing the diffuse medium at galactic scales (Dartois and Muñoz-Caro, 2007). Galaxies are receding from us and distant ones bring the a-C:H absorption to a more favorable atmospheric transmission window, giving access to the aromatic CH absorption (Dartois et al., 2007). The background reference source is now an entire galactic nucleus with a large parsec probe beam. Apart from the strong amorphous silicate absorption, other absorptions in some lines of sight are dominated by a-C:H, while the aromatic versus aliphatic content of DISM a-C:H shows that the aromatic CH stretching modes are less prominent than those suggested by the proposed former structure.

The evolution of the schematic basic structural unit of diffuse ISM analogues resembles more the IOM structure, but the meteoritic organics still display too many absorptions in the mid-infrared spectral fingerprint region (Kebukawa et al., 2011; Orthous-Daunay et al., 2013). Comparing the interstellar a-C:H spectra to the IOM spectra in more detail, we see that the former spectra do not display the strong infrared signatures of oxygen heteroatoms, nor there is evidence of a large amount of incorporated nitrogen atoms. However, this ISM dust could be a precursor that could evolve when incorporated into dense clouds.

Following observations of the transition from diffuse to dense ISM when MC are formed, the a-C:H infrared signatures disappear, while ice mantles begin to form. This raises the question of whether the ISM hydrogenated carbonaceous dust is destroyed or transformed. Several experiments have investigated this modification and show that the a-C:H are dehydrogenated either in the dense phase (Mennella et al., 2003) and/or in the interface between diffuse and dense clouds (Godard et al., 2011), thus, before being incorporated into a protosolar nebula.

In this dense cloud phase, an alternative organic material can be produced by the photolysis and radiolysis of ice mantles covering the dust grains. However, the laboratory-produced residues, which are measured at room temperature (e.g., Muñoz Caro et al., 2004; Nuevo et al., 2006), and the space-exposed laboratory residues
(e.g., EURECA experiment, Greenberg et al., 1995) do not match. The same applies to the entire infrared spectra of IOM. Therefore, they can only be seen as a potential starting or precursor material (Muñoz Caro and Dartois, 2013), provided that the subsequent evolutionary pathways can lead to some kind of IOM.

We have previously compared ISM dust with meteorite organic matter originating from the asteroid belt region. Now it is important to discuss the carbonaceous component for Interplanetary Dust Particles (IDPs) and micrometeorites from larger distances. IR spectra are difficult to measure for IDPs, and their organic content cannot be easily separated using techniques similar to the ones used for meteorites given their small sizes. Many of the IDPs infrared spectra display a stretching mode region different from the Galactic center lines of sights that display the a-C:H dust components (e.g., Keller et al., 2004; Matrajt et al., 2005; Bradley, 2005; Muñoz Caro et al., 2005; Brunetto et al., 2011). Micrometeorites collected at the poles offer a size distribution that is more suitable for these techniques to be applied, thus allowing for a more direct comparison with astronomical spectra.

The remaining part of this article focuses on rare, specific, and very interesting ultracarbonaceous micrometeorites (UCAMMs), which provide a sample of another form of organic matter from the Solar System. These UCAMMs were discovered as a small fraction in various Antarctic micrometeorites collections, such as those reported by Nakamura et al. (2005) and Yabuta et al. (2012) from the Dome Fuji collection, and those present in the Concordia collection of the CSNSM, from the French-Italian Dome C station (Duprat et al., 2011).

Scanning electron micrograph and X-ray maps of two UCAMMs, combined with Nano-SIMS measurements, show that these are very rich in organic content, with more than 50% and up to 95% of the whole UCAMM atoms being organic matter, and have a high D enrichment (D/H = 1.0 ± 0.3 × 10^{-3} and D/H = 7.2 ± 3.2 × 10^{-4}, respectively).

**Fig. 1.** Comparison of the infrared spectra of some ISM, Solar System, and laboratory-produced solids. From bottom to top: emission spectrum of the class A emission line star IRAS23133+6050 displaying the characteristic PAH features (ISO database); laboratory-produced interstellar a-C:H analogue and diffuse interstellar absorption from interstellar a-C:H in the extragalactic source IRAS08572+3915 (Dartois et al., 2007); OR1 (Muñoz Caro and Schutte, 2003) and OR2 (Muñoz Caro et al., 2004) are organic residues obtained by laboratory UV irradiation of interstellar ices analogues; IOM extracted from PCA91008 and Murchison (Orthous-Daunay et al., 2013); laboratory-produced hydrogenated amorphous carbon nitride (Ong et al., 1996); UCAMMsDCC060565 and DCC060594 infrared spectra (Dartois et al., 2013). The top right spectra (i) and (ii) represent possible forsterite and enstatite silicates contributions to the UCAMMS (see Dartois et al., 2013 for details).
tively), suggesting formation in a low T environment (Dartois et al., 2013). Their organic matter presents an infrared spectrum 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).

N-rich materials in the Solar System are rare and no such materials are observed in ISM. Incorporating 10-20% of N in a carbon nitride requires a C-precursor and energetic processes in an N-dominated environment (i.e., H₂O ice depleted). Such nitrogen-rich carbonaceous material could possibly be formed by irradiation of N- and C-rich ices by UV photons and/or cosmic rays in very low temperature regions of the Solar System. These conditions are encountered at the surface of small objects beyond the trans-Neptunian region. UCAMMs could therefore provide unique insights into the material incorporated from the protosolar nebula and the physico-chemical processes that occurred beyond the nitrogen snow-line, revealing organic material from the extreme outer regions of the Solar System that cannot be investigated by remote sensing methods. To summarize the comparison and emphasize the differences between many of the above-discussed materials, their infrared spectra are displayed in Fig. 1.

CONCLUSION

In view of the comparisons made above, there seems to be no strong evidence for interstellar materials being directly imported and incorporated at a large scale in the Solar System. When incorporated, the interstellar dust provides at most a precursor, and laboratory studies are important to decipher the future evolution of these solids as observed in the previous phases of the ISM cycle. Apart from very specific particles, such as the extremely resistant presolar grains (highly refractory SiC, Diamonds), the materials observed, collected, and analyzed are more often probing nebular processes or physico-chemical mechanisms occurring inside the Solar System during its youth rather than genuine fully preserved ISM material.

Acknowledgments—The Goldschmidt conference fees and part of the work presented here were supported by the ANR projects COSMISME (Grant ANR-2010-BLAN-0502) and OGRESS (Grant ANR2011-BS56-026-01) of the French Agence Nationale de la Recherche. We thank Dr. Shogo Tachibana, Dr. Itsuki Sakon and an anonymous reviewer for thoroughly reviewing and providing comments, as well as a language editor, that helped improve the manuscript.

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516 E. Dartois et al.


