COMPARISON OF THE RAMAN SPECTRA OF ION IRRADIATED SOOT AND COLLECTED EXTRATERRESTRIAL CARBON

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Submitted as Manuscript to Icarus
Submitted: October 6, 2008
Revised: November 18, 2008

Pages of manuscript: 46
Tables: 4
Figures: 9

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Abstract

We use a low pressure flame to produce soot by-products as possible analogues of the carbonaceous dust present in diverse astrophysical environments, such as circumstellar shells, diffuse interstellar medium, planetary disks, as well as in our own Solar System. Several soot samples, displaying an initial chemical diversity from aromatic to aliphatic dominated material, are irradiated with 200-400 keV H\(^+\), He\(^+\), and Ar\(^{++}\) ions, with fluences comprised between \(10^{14}\) and \(10^{16}\) ions/cm\(^2\), to simulate expected radiation induced modification on extraterrestrial carbon. The evolution of the samples is monitored using Raman spectroscopy, before, during, and after irradiation. A detailed analysis of the first and second-order Raman spectra is performed, using a fitting combination of Lorentzian and/or Gaussian-shaped bands. Upon irradiation, the samples evolve toward an amorphous carbon phase. The results suggest that the observed variations are more related to vacancy formation than ionization processes. A comparison with Raman spectra of extraterrestrial organic matter and other irradiation experiments of astrophysically relevant carbonaceous materials is presented. The results are consistent with previous experiments showing mostly amorphization of various carbonaceous materials. Irradiated soots have Raman spectra similar to those of some meteorites, IDPs, and comet Wild-2 grains collected by the Stardust mission. Since the early-Sun expected irradiation fluxes sufficient for amorphization are compatible with accretion timescales, our results support the idea that insoluble organic matter (IOM) observed in primitive meteorites has experienced irradiation-induced amorphization prior to the accretion of the parent bodies, emphasizing the important role played by early solar nebula processing.

Keywords: Spectroscopy, Experimental Techniques, Interplanetary Dust, Meteorites, Comet Wild-2
1. Introduction

Carbonaceous extraterrestrial matter is observed, with a wide range of compositions and structures, in the Solar System and in the interstellar medium of galaxies, illustrating the rich carbon chemistry that occurs in space. Experimental studies on extraterrestrial carbon and analogues play a fundamental role in understanding the reasons for this diversity: in the laboratory it is possible to analyze collected extraterrestrial carbon, in particular from meteorites, micro-meteorites, interplanetary dust particles (IDPs), and grains collected by sample return space missions (e.g. the Stardust mission); additionally, it is possible to synthesize, characterize, and process laboratory analogues of carbonaceous cosmic dust to get an insight into the formation, origin, and evolution of the natural samples, under carefully controlled experimental conditions.

Several laboratories have concentrated their efforts on the production and characterization of refractory carbonaceous materials of astrophysical interest, and in particular on the extensively studied amorphous carbons, with different degrees of hydrogenation. Different types of amorphous carbon can be produced by several techniques, such as laser pyrolysis, laser ablation or arc discharge (e.g. Blanco et al., 1988; Scott and Duley, 1996; Herlin et al., 1998; Mennella et al., 1999; Rotundi et al., 2000), and ion and photon irradiation of hydrocarbon-rich ices (e.g. Strazzulla and Baratta, 1991; Jenniskens et al., 1993; Dartois et al., 2005). Recent studies show that the infrared (IR) spectra of these materials can be used to interpret observations of the dust in the diffuse interstellar medium of galaxies, where an important fraction of the available carbon (up to 40%) is locked in the dust (Dartois et al., 2007; Dartois and Muñoz-Caro, 2007). Among carbonaceous materials, carbon soots are promising material (Schnaiter et al., 1996; Rotundi et al., 1998; Jäger et al., 2006), due to their possible connection with polycyclic aromatic hydrocarbons (PAHs), that are proposed since almost 25 years (Léger and Puget, 1984) to be present in many and diverse astrophysical environments. In particular, IR spectra of soot may help to interpret some characteristics (band positions in particular) of some of the ubiquitously observed aromatic IR bands (Pino et al., 2008). Soot may also contain fullerene-like structures, and it has been proposed that C60 molecules are in fact the “seeds” for soot grain growth (Rotundi et al., 2006, and references therein).

Laboratory studies of carbons are also fundamental for interpreting Solar System observations. Carbonaceous dust is present almost everywhere in the Solar System, in particular in comets, many asteroids, satellites, trans-neptunian objects, and in the interplanetary medium. Information on these carbon materials is up to now mostly accessible using mid-IR reflectance spectroscopy. Other complementary techniques are being developed to study extraterrestrial carbon, thanks to laboratory analysis of collected extraterrestrial grains and to instruments on board spacecrafts and landers. To this respect, Raman spectroscopy is a technique complementary to IR spectroscopy, being sensitive to the carbon backbone structure and to its degree of order. It has been used to characterize the organic matter of meteorites and IDPs (e.g. Wopenka, 1988; Matraj et al 2004; Quirico et al., 2005; Busemann et al., 2007), and recently to analyze organics captured from comet 81P/Wild 2 by the NASA Stardust spacecraft (Sandford et al., 2006; Rotundi et al., 2008; Muñoz-Caro et al., 2008).

Cosmic ions play an important role in the life-cycle of interstellar dust in general and the carbonaceous one in particular (see e.g. Mennella et al., 2003). Irradiation processes are also important in the Solar System, as they are related to the production of complex organics in the presolar nebula (Muñoz-Caro et al., 2006) and on minor bodies surfaces (Brunetto et al., 2006), as well as to the alteration of pre-existing carbon (Moroz et al., 2004; Baratta et al., 2008). Moreover, many studies point out that the early Sun was much more active than today, passing through an active T-Tauri phase before entering the main sequence (e.g. Feigelson and Montmerle, 1999; Montmerle, 2002; Wood et al., 2002; Feigelson et al., 2002; Ribas et al., 2005); such strong particle and photon radiation emissions could have had major influences on processing of material during the accretion phase, and more specifically on the carbon chemistry. Consequently, it is essential to study the effects of ion irradiation on laboratory produced carbonaceous dust analogues to better constrain their likely evolution when placed in relevant astronomical environments.

Solar wind and cosmic ion irradiation simulations can be carried out using ions with energies in
the 1-1000 keV range, exploring different regimes of energy loss and then scaling them to plausible astrophysical conditions. For instance, thanks to relatively low energy (keV) ion irradiation / implantation experiments (e.g. Demyk et al., 2001; Brucato et al., 2004), it has been shown that ions accelerated during the propagation of shock waves in the diffuse interstellar medium (ISM) can fully amorphize silicates, a result fully compatible with the observation of totally amorphized silicate grains in the diffuse ISM (Kemper et al., 2004). Reynaud et al. (2001) reported MeV ion irradiation experiments on carbon nanoparticles with IR properties similar to soot. They found that the structure changes progressively to become an hydrogenated aromatic carbon with an aliphatic component, with broad IR bands characteristic of a disordered material, using doses up to about 400 MGy corresponding to about 65 eV per 16 amu. 

In this work, we study the effects of ion irradiation to simulate solar wind and high velocity shock ion irradiation. Target materials are soot samples, prepared to span a wide range of chemical bonds and physical structures. Samples are monitored using Raman spectroscopy, to characterize and follow the evolution of the samples during irradiation. We compare our results with those obtained in the analysis of extraterrestrial organic matter (meteorites, IDPs, and comet Wild 2 grains collected by the Stardust mission) and other irradiation experiments of carbonaceous materials of astrophysical relevance.

2. Experimental techniques

Soot samples were produced at the Laboratoire de Photophysique Moléculaire in Orsay (France). In our setup, a low pressure flat burner provides flames of premixed hydrocarbon / oxygen gas mixtures (Cao et al., 2007; Pino et al 2008), closely following the model system used by the combustion community. The flame is a one-dimensional chemical reactor offering a broad range of combustion conditions and sampling. A similar system has been used by Schnaiter et al. (1996) to synthesize circumstellar dust analogues.

The source chamber contains a flat burner (McKenna model) of 60 mm diameter. The hydrocarbon was either acetylene or ethylene. It was premixed with oxygen before flowing through the burner at a given rate (3-6 L.min⁻¹) and the rich C/O ratio was typically set in the range 1-2. In the source chamber the pressure was maintained in the range 30-80 mbar by continuous pumping. Adjusting all these parameters gave combustion regimes that could be maintained for hours and could produce a wide variety of soots. The by-products were then extracted by a cone in quartz inserted into the flame at a controlled distance from the burner. The particles diffused through a thermalization chamber filled with He at a pressure of a few mbars, and expanded into vacuum (10⁻² mbar) through a 10 mm diameter nozzle. The soot was then deposited on Cd or KBr substrate windows directly inserted into the molecular jet. The obtained thickness was typically in the range 1-3 µm. Soot is generally composed of primary spherical particles having a diameter on the order of 10-30 nm; these spherules agglomerate together to form larger grains. Our samples have therefore effective densities of about 0.45±0.25 g/cm³, while the density of single primary particle is about 1.7±0.5 g/cm³ depending on its nature (Slowik et al., 2004; Maricq and Xu, 2004).

Several samples were produced with the aim to vary the aromatic to aliphatic bonds ratio, and thus explore different kinds of extraterrestrial carbon analogues. We monitor the aromatic character of the samples forming the stretching mode integrated absorbance ratio \( R_{arom} = \frac{aromatic \ C-H}{(aliphatic \ C-H + aromatic \ C-H)} \), using IR spectroscopy measurement performed at the Institut d’Astrophysique Spatiale. With our experimental setup, we can obtain soots whose \( R_{arom} \) ratio ranges from about 0.05 to 0.8 . This is discussed in more details by Pino et al. (2008). In this paper, we name “aromatic-rich soot” the samples with \( R_{arom} > 0.6 \), and “aliphatic-rich soot” the samples with \( R_{arom} < 0.3 \).

The soot samples were irradiated at the Laboratory of Experimental Astrophysics in Catania (Italy), using \( H^+ \), \( He^+ \), and \( Ar^{++} \) ion beams, with energy of 200-400 keV. The three different ion masses were chosen to explore different regimes of energy loss, elastic vs. inelastic (Ziegler et al.,
We used ion fluences in the range \(10^{14} - 10^{16}\) ions/cm\(^2\), corresponding to the minimum fluence required to observe some significant spectral variations, and to the saturation regime of the same spectral variations, respectively. Details of the vacuum chamber and ion gun can be found in Brunetto and Strazzulla (2005).

Samples were characterized and monitored using Raman spectroscopy. In the Catania laboratory, Raman spectra can be acquired in situ in the vacuum chamber, giving the opportunity to follow the evolution of the samples under irradiation, and allowing a direct comparison between the intensity of the Raman features before and after irradiation. In the Catania laboratory system, a continuous Ar ion laser beam (about 1 mm in diameter, 514.5 nm) is used as the exciting radiation. The laser is focused on a 50 µm wide spot, with laser power on the sample ranging from 5 to 15 mW (~ 5 W/mm\(^2\)) to avoid modification of the carbon structure due to laser-induced heating effects. This is indeed confirmed by the fact that collecting several Raman spectra of the same soot sample over a few hours does not yield any spectral modification. As a comparison, in the Raman analysis of comet Wild 2 grains performed also in the Catania laboratory, the laser power was about 0.03 mW, but focused on a much smaller surface (about 1 µm spot), producing about 40 W/mm\(^2\). The spectral resolution is about 3 cm\(^{-1}\) and the wavelength accuracy is about 1 cm\(^{-1}\). Details of the Raman in situ technique are given by Brunetto et al. (2004).

### 3. Results

#### 3.1 Raman spectra of soot as produced

Figure 1 shows two Raman spectra of soot samples (aromatic-rich and aliphatic-rich). First-order spectra clearly show the presence of the so-called D (disorder) and G (graphitic) bands, at about 1350 cm\(^{-1}\) and 1600 cm\(^{-1}\) respectively. D and G bands have been observed in a large number of carbonaceous materials, and their origin has been widely discussed in the literature (see e.g. Ferrari and Robertson, 2000). The relative peak sizes and full widths at half maximum (FWHMs) of D and G bands reflect the degree of disorder of the material (broader lines corresponding to more disordered materials). In particular, the G band FWHM is very sensitive to structural disorder arising from bond angle and bond length distortions (e.g. Casiraghi et al., 2005). Second-order Raman spectra present overtones and combinations of first-order bands. Aromatic-rich soots also show a fluorescence continuum in the whole spectrum which is absent in the aliphatic-rich samples. It is probably due to the lower and therefore more accessible \(\pi\) electronic excitation of the aromatic component at the excitation wavelength used here.

**Figure 1**

A detailed analysis of D and G bands reveals the presence of several bands, as represented in Fig. 2. Sadezky et al. (2005) collected Raman spectra of soot and using multi-wavelength excitation were able to identify five bands: the G band, centered at about 1580 cm\(^{-1}\), corresponds to the mode of the ideal graphitic lattice (E2g symmetry); the D1 band, centered at about 1350 cm\(^{-1}\), is attributed to the disordered graphitic lattice (graphene layer edges, A1g symmetry); the D2 band, centered at about 1620 cm\(^{-1}\), is related to disordered graphitic lattice (surface graphene layers, E2g symmetry); the D3 band, centered at about 1500 cm\(^{-1}\), is related to amorphous carbon; the D4 band, centered at about 1200 cm\(^{-1}\), is attributed to disordered graphitic lattice (A1g symmetry), polyenes and ionic impurities.

**Figure 2**

First-order spectra of our aromatic-rich and aliphatic-rich soots can be successfully fitted using a combination of four Lorentzian-shaped (G, D1, D2, D4) and one Gaussian-shaped (D3) bands, as in Sadezky et al. (2005). This deconvolution is clearly satisfying in the case of aliphatic-rich soot (lower panel of Fig. 2), whereas in the case of aromatic-rich soot a Gaussian line shape is more suited to fit the D4 band (upper panel of Fig. 2). This is probably due to the presence of several smaller and narrower structures in the 1050-1300 cm\(^{-1}\) range of aromatic-rich soot spectra, whose
position and profile cannot easily be constrained. Other minor features are observed at about 1370 cm$^{-1}$ and 1430 cm$^{-1}$, and they cannot be reproduced by the 5-bands fit curve used here. All these features are most probably due to aromatic C-C stretching due to the presence of PAH units in the samples (see e.g. the Raman spectra of PAHs reported by Colangeli et al., 1992). The presence of PAH units in our soot is suggested by preliminary laser desorption – time of flight mass spectrometry analysis (Brunetto et al., 2008). Recent laser desorption experiments (Jäger et al., 2006; Apicella et al., 2007) on similar soot samples point to a distribution dominated by small PAH units (up to 32 carbon atoms).

It is known since decades (Tuinstra and Koenig, 1970) that an empirical relationship of inverse proportionality exists between the average crystallite size $L_a$ measured by X-ray diffraction and the D band / G band intensity ratio ($I_D/I_G$). However, recently it has been shown that such linear relationship between $1/L_a$ and $I_D/I_G$ breaks down for crystallite sizes below 2 nm, and that experimental points scatter significantly for $L_a > 2$ nm (Zickler et al., 2006). Using areal intensity, we estimate the $I_D/I_G$ ratio to be about 1.4 ± 0.1 for aromatic-rich soot, and 1.8 ± 0.5 for aliphatic-rich soot. Using the calibration reported by Zickler et al. (2006), we deduce that $L_a < 4$ nm for aliphatic-rich soot, and that $L_a$ is between 3 and 4 nm in the case of aromatic-rich soot. However, considering the uncertainties of the Tuinstra and Koenig correlation (dominated by uncertainties in the deconvolution of the Raman bands), we cannot exclude higher values for $L_a$ up to about 8 nm.

The second-order spectra (2200-3700 cm$^{-1}$ range) are fitted by Lorentzian-shaped bands, following previous results by Sadezky et al. (2005), as displayed in Fig. 3. Five bands corresponding to overtones and combinations of first-order bands can be identified. Aliphatic C-H stretching modes are probably present in the 2800-3000 cm$^{-1}$ range for the aliphatic-rich soot studied here, counterparts of the C-H observed in the IR (Pino et al., 2008), but they are too weak to be clearly analyzed and identified with our signal to noise ratio.

In Table 1 we report peak positions and FWHM of the observed Raman bands. The band centers are obtained after fitting several soot spectra, and they take into account both variability of soot samples and error bars from fitting routines. A certain degree of variability is observed for aliphatic-rich samples, especially for the D3 band, as can be deduced from a simple visual inspection of spectra included in the lower panels of Figs. 1 and 2. A main difference between aromatic-rich and aliphatic-rich samples is found in the position of the D1 band, being about 20 cm$^{-1}$ higher for aromatic-rich than aliphatic-rich soot. In addition, aromatic-rich samples tend to have D1/G intensity ratios lower than aliphatic-rich ones. Other parameters tend to overlap or to have large error bars. The D3 band parameters, in the case of aromatic-rich samples, suffer from uncertainties in the choice of the spectral continuum used to remove fluorescence; uncertainties of the D4 parameters in the aromatic-rich soot spectra are due to the presence of minor features (mentioned above), while in the aliphatic-rich soot spectra they are due to the weak intensity of the D4 band.

Table 1

| 2nd order band parameters are affected by large errors. In the aliphatic-rich soot spectra the 2*D4 band could not be identified and separated from the 2*D1 band. In the aromatic-rich soot spectra, a non-identified large band is present at about 3400 cm$^{-1}$, absent in aliphatic-rich soot spectra.

Comparing with the band parameters in the Raman spectra of soot and related carbon found in previous works (e.g. Jawhari et al., 1995, Sadezky et al., 2005), we find that our aliphatic-rich soot samples exhibit band parameters very similar to those of commercial soot Printex XE2. Using X-ray diffraction, Sadezky et al. (2005) found that such carbon is characterized by an average size of the crystallites or graphite-like crystalline domains of about 4 nm; this is in reasonable agreement with what estimated above using band intensity ratios. The fitted Raman band parameters (in particular narrow D1 and G bands) are consistent with such degree of structural order with respect to all other types of soot investigated in their work. The band parameters of our aromatic-rich soot do not correspond to any specific soot among those analyzed by Sadezky et al. (2005).
3.2 Raman spectra of irradiated soot

It should be stressed that the spectral analysis reported above is strongly affected by signal to noise ratios. In particular, the deconvolution of the broad and partially overlapping bands into multiple bands by curve fitting is subject to high statistical uncertainty (Sadezky et al., 2005). The spectral deconvolution becomes more arbitrary when the structure of the sample approaches that of amorphous carbon. Consequently, Raman spectra of carbons are sometimes analyzed in the literature only in terms of D and G band, i.e. including the D1, D4, and part of the D3 bands in an unique D band, and the rest in an unique G band. This is especially true in the case of extraterrestrial carbon spectra (see e.g. Rotundi et al., 2008, and references therein). Since our goal is to compare irradiated soot with extraterrestrial carbon, in the following we will describe spectra only in terms of D and G bands.

In Fig. 4 we display the evolution under 400 keV Ar$^+$$^+$ ions of the in-situ Raman spectra of aliphatic-rich (lower panel) and aromatic-rich (upper panel) soot. In both cases one observes a progressive reduction of the Raman intensity with increasing ion fluence, accompanied by an increase in the D and G bands FWHM up to a merging of the two peaks. The resulting broad band is typical of highly disordered amorphous carbon. One also observes a clear shift of the G band peak position, moving toward lower Raman shifts with increasing ion fluence. The D band peak position is only marginally affected. Minor PAH structures in the aromatic-rich soot spectra are destroyed after the very first irradiation step. Ion irradiation causes a strong reduction of the fluorescence signal when initially present. It indicates a destruction of the aromatic units that were carrying the accessible $\pi$ electronic excitation at 514 nm.

**Figure 4**

A simple two-bands fit is used to evaluate the relevant parameters such as relative peak intensity, peak positions, and FWHMs of the D and G bands. In the literature, these parameters are obtained after continuum subtraction (baseline between about 950 and 1900 cm$^{-1}$), and using different combinations of fitting functions: Gaussian, Lorentzian, or Breit-Wigner-Fano (BWF) curves (i.e. asymmetric Lorentzian curves). We used the three different methods and compared them in terms of reduced chi-square. An example is given in Fig. 5, showing the case of aliphatic-rich soot before (upper panel) and after (lower panel) irradiation with $2 \times 10^{15}$ Ar$^+$$^+$ / cm$^2$, energy of 400 keV. As a general result, we find that in the case of unirradiated soot, BWF fit curves are able to reproduce the spectra quite well. In the case of irradiated soot, the fit results tend to privilege Gaussian profiles. This is consistent with spectral congestion and an inhomogeneous broadening of the bands.

**Figure 5**

In the Raman analysis of extraterrestrial carbon, the analytical procedure usually consists of fitting the D and G bands with two Lorentzian bands and a linear baseline (e.g. Baratta et al., 2004; Rotundi et al., 2008). It has been shown that results of such fitting procedures may vary according to the different curves and continuum subtraction used (Busemann et al., 2007; Rotundi et al., 2008). The upper panel of Fig. 5 shows that, even if a two Lorentzian bands fit has higher reduced chi-square than BWF fit, it is nonetheless able to describe quite correctly peak positions and FWHMs of the D and G bands. In the case of spectra collected after irradiation, where Gaussian fit curves match the experimental data better, we decided to average the results from the three different methods (Gaussian, Lorentzian, BWF) to produce more realistic values for the D and G band parameters. The fitting uncertainty is included in the error bars.

Generally speaking, we find that the D and G lines observed in spectra of soots before irradiation are relatively narrow (G-FWHM less than 80 cm$^{-1}$, D-FWHM less than 100 cm$^{-1}$), and in any case much narrower than those of the hydrogenated amorphous carbon (HAC) produced after ion irradiation (Ferini et al., 2004) or photolysis (Dartois et al., 2005) of C-rich ices. The D and G band FWHMs of our soots are also narrower than what observed on HAC (Mennella et al., 2003) and H-free amorphous carbon produced by arc-discharge (Baratta et al., 2004).

The evolution of G band peak position and FWHM as a function of ion fluence (Ar$^+$$^+$ / cm$^2$, 400
keV) is reported in Fig. 6, for both aliphatic-rich and aromatic-rich samples. In both cases, the G-FWHM increases rapidly until fluence reaches about 2x10^{14} \text{ Ar}^{++}/\text{cm}^2, and then tends to saturate, with aromatic-rich soot showing values slightly lower than aliphatic-rich soot. The G-peak moves towards lower Raman shifts in both cases, again showing rapid variations after the first few 10^{14} \text{ Ar}^{++}/\text{cm}^2, and then slowly reaching about 1540 cm^{-1}.

Figure 6

The observed spectral modifications are in agreement with previous irradiation experiments on graphite and amorphous carbon grains produced by arc discharge, reported by Baratta et al. (2004), and are indicative of amorphization processes induced by ion irradiation. In several works (e.g. Ferrari and Robertson, 2000; Casiraghi et al., 2005), an amorphization trajectory has been identified from graphite and nano-crystalline graphite to tetrahedral amorphous carbon, showing the variation of the G band position as a function of the sp^3 content. If one considers the transition from nano-crystalline graphite to amorphous carbon (hydrogenated or not), the G peak has been found to move toward lower Raman shift. A similar effect is observed here for irradiation induced transition from soot to HAC. Unfortunately, as shown by Casiraghi et al. (2005), the G band peak cannot be used to unambiguously derive the sp^3 content; to achieve this goal one should use multi-wavelength excitation for the Raman measurements, especially using UV excitation, which is not our case.

3.3 Comparing different regimes of energy loss

We performed irradiation experiments varying ion mass and energy, i.e. varying penetration depth, energy loss (dE/dx) of ions in the target and the ratio between elastic to inelastic collisions (nuclear and electronic stopping power). In some experiments we used 200 keV protons with fluence up to 8x10^{15} \text{ H}/\text{cm}^2. In the upper panel of Fig. 7 we illustrate an example of spectral comparison between \text{ H}^{+} and \text{ Ar}^{++} irradiated aromatic-rich soot (at the same ion fluence). Proton irradiation induces very little spectral variations with respect to argon irradiation, the only relevant effect being the destruction of the sharp PAHs structures.

Figure 7

In the lower panel of Fig. 7, we compare \text{ H}^{+}, \text{ He}^{+}, and \text{ Ar}^{++} irradiation, in the case of aliphatic-rich soot. Spectra are shifted for clarity, and displayed in order of increasing amorphization (from top to bottom). Comparing curves relative to a fixed ion fluence of 2x10^{15} ions/cm^2, we observe that modifications due to argon (400 keV) ion irradiation are much stronger than those produced by proton or helium irradiation (200 keV), and that \text{ He}^{+} irradiation produces stronger spectral modification than proton irradiation, i.e. higher projectile masses correspond to stronger spectral modifications. We also observe that irradiation with 2x10^{14} \text{ Ar}^{++}/\text{cm}^2 produces a Raman spectrum very similar in terms of band profile to that obtained using 10^{15} \text{ He}^{+}/\text{cm}^2.

To better compare different ions and energies, we need to estimate the ion mean penetration depth (d) and the stopping power (energy loss per unit path length) in the three different cases. This can be done using the SRIM code (at http://www.SRIM.org/; Ziegler et al., 1985). Results are given in Table 2. As reported above, the thickness of soot samples was in the range 1-3 \text{ µm}. Since the samples are quite fluffy, the ions penetrate an effective thickness of soot grains, smaller than the sample thickness. In the SRIM simulation, we use an effective thickness (d) of 0.6 \text{ µm} for the soot target, resulting from the values of the effective density reported above (1.7 g/cm^3 for single soot grains, and 0.45 g/cm^3 for the sample).

Table 2

For \text{ H}^{+} and \text{ He}^{+} the penetration depth is larger than the effective target thickness (d > d_{\text{eff}}), i.e. the ions pass through the soot sample and are implanted in the substrate, ensuring uniform energy loss, because the ratio of elastic to inelastic collisions changes mostly at the very end of the ion
track. On the contrary, in the case of Ar$$^{++}$$ irradiation, the range is lower than the effective thickness ($$d < d_{\text{EFF}}$$), so that ions remain implanted in the soot, and the energy loss is less uniform. In this case, there is a possibility that some deep layer of the soot sample remains unirradiated and that this contribution may be present in the Raman spectra. If so, one should be able to observe traces of narrow D and G bands in the spectra of argon irradiated soot, but this is not the case. Thus, we are quite confident that the Raman signal comes from the upper few hundreds of nanometers at most. This is coherent with the brown/black color of our samples, indicating that the material is very absorbing in the visible wavelength (both before and after irradiation).

A more precise calculation can be done estimating the optical constants of soot. This exceeds the goal of this paper, but a reasonable estimate can be obtained using the optical constants of soot from burned benzene and soot from amorphous carbon electrodes by Rouleau and Martin (1991). For these materials the imaginary index at the laser wavelength used here (514.5 nm) is in the range 0.1-1. Using these values, we estimate the depth in the effective sample (density of 1.7 g/cm$$^3$$) from which the laser radiation would emerge reduced to 50% of the incoming intensity, obtaining 0.1 ± 0.05 µm. The laser radiation would emerge reduced to about 20% of the incoming intensity from a depth of 0.2 ± 0.1 µm. Thus, we can reasonably say that the effective depth probed by the Raman technique is $$d_{\text{PROBE}} = 0.1 \pm 0.05$$ µm. We repeat the SRIM simulation using $$d_{\text{PROBE}}$$ as sample thickness, and results are given in Table 3. Since for all ions it is verified that $$d_{\text{P}} > d_{\text{PROBE}}$$, we deduce that the layers responsible for the detected Raman signal have been irradiated quite uniformly (within ±10%). In Table 3 we also estimate the energy $$\Delta E$$ lost by ions in the volume corresponding to a depth of about $$d_{\text{PROBE}}$$.

### Table 3

Comparing the fraction of energy released by a single ion in ionization processes ($$f_{\text{ION}}$$) and vacancy formation processes ($$f_{\text{VAC}}$$) in the three cases, it is clear that, although ionization processes remain by far the main mechanism of energy loss, vacancy formation processes can be relevant in the case of argon irradiation. This is confirmed by the number of vacancies created in the probed target ($$d_{\text{PROBE}}$$) per impinging ion (see Table 3). This number is about 120 times higher for Ar$$^{++}$$ (400 keV) than He$$^+$$ (200 keV); in the averaged $$d_{\text{EFF}}$$ thickness the ratio is about 30 (see Table 2). In terms of energy released to the probed target, we need to normalize to the energy $$\Delta E$$ lost by ions in the volume corresponding to a depth of about $$d_{\text{PROBE}}$$. From the values given in Table 3, we find that, at a given fluence, Ar$$^{++}$$ releases an energy in elastic collisions about 10 times bigger than He$$^+$$.

A more quantitative comparison can be performed. In Table 4 we compare the six irradiation steps shown in the lower panel of Fig. 7, sorted by increasing amorphization from A (soot before irradiation) to F (amorphous carbon). We compare the G band peak position, ion fluence, total dose (mainly released through inelastic collisions, see Table 3) deposited in the volume corresponding to $$d_{\text{PROBE}}$$, and density of vacancies created in the volume corresponding to $$d_{\text{PROBE}}$$. Note that the doses are comparable with those used by Reynaud et al. (2001). As discussed above, the G band peak position is a good proxy of the amorphization effect. From Table 4 we conclude that the G-peak moves toward lower Raman shift as the density of vacancies increases. The total dose and the G-peak do not correlate, as can be easily deduced comparing step D and step F, coherently with an amorphization process driven by elastic collisions between projectiles and target nuclei. In other words, the spectral variations observed after irradiation should be related more to vacancy formation processes than ionization processes.

### Table 4

The lower panel of Fig. 7 shows that 2x10$$^{15}$$ He /cm$$^2$$ produce stronger spectral modifications than 2x10$$^{15}$$ H /cm$$^2$$. This can be explained by the fact that, in the volume corresponding to an
energy \( \Delta E \), helium ions release an energy \( \Delta E \) about two times larger and produce a density of vacancies about ten times larger than protons (see Table 4).

3.4 Comparison with the Raman spectra of extraterrestrial carbon

Raman spectra of irradiated soot can be compared with those of collected extraterrestrial carbons. In Fig. 8 we illustrate a comparison between spectra of Murray and Tagish Lake carbonaceous meteorites (after Baratta et al., 2008) and the spectra of aromatic-rich soots irradiated at three different fluences. Raman spectra of Murray and Tagish Lake meteorites were collected with the same setup used in this work (Catania laboratory). Spectra are shown after continuum subtraction and after scaling to the D band peak intensity. From this comparison we deduce that the irradiation process can produce an altered soot (central panel) that has a maturity comparable to those observed in meteorites. It appears thus that the soot structure can be used as an artificial analogue of the meteorite backbone carbonaceous structure, at least when analyzing the Raman features.

Figure 8

To extend the comparison with results obtained in the analysis of extraterrestrial organic matter in Stardust samples (Sandford et al., 2006; Rotundi et al., 2008) and other irradiation experiments of carbonaceous materials of astrophysical relevance (Baratta et al., 2004), we plot in the upper panel of Fig. 9 the G band FWHM as a function of G band peak position, comparing ion irradiated soot to interplanetary dust particles (IDPs), carbonaceous meteorites, and grains from comet Wild 2. Values for 40 IDPs and more than 40 chondritic meteorites are included, after Sandford et al. (2006) and references therein; values for 13 Wild 2 grains are after Rotundi et al. (2008).

It must be stressed that, if one compares the results obtained by different laboratories that used different experimental techniques and fitting procedures, systematic differences may be present. This problem has been deeply discussed in a recent work by Rotundi et al. (2008), who performed micro-Raman analysis of particles collected by the Stardust spacecraft. Five groups were involved in these Raman measurements, and some tests were performed to allow an inter-comparison of spectroscopic results obtained in the different laboratories and evaluate the fitting routines used by the different groups. They compared the band parameters found by the five different laboratories in the analysis of the meteoritic insoluble organic matter (IOM) from three primitive carbonaceous chondrites that experienced distinct thermal metamorphism. It was found that, using Lorentzian curves and a linear background, deviations from mean values can be up to about 3 \( \text{cm}^{-1} \) for G-peak position and up to about 6 \( \text{cm}^{-1} \) for G-FWHM. This implies that in the plots of Fig. 9, errors bars (2\( \sigma \)) must always be kept above those values, unless all points are collected and analyzed by the same group, which is not our case. Our experimental determination satisfies this request, having large error bars, to take into account uncertainties due to the fitting procedures, so that differences between laboratories do not affect the general trends and results described here.

Figure 9

In the upper graph of Fig. 9, extremely ordered carbons plot in the lower right, and extremely disordered amorphous carbons plot in the upper left; it was demonstrated that IDPs and meteorites occupy two different but partially overlapping areas, while comet Wild 2 points are scattered and overlap with both IDPs and meteorites. The evolutionary path traced by soot irradiated at various fluences is able to reproduce the spread of differently ordered extraterrestrial carbon reported in the upper panel of Fig. 9. Data points relative to soot before irradiation are in the lower right of the plot; ion irradiation produces a shift of these points towards the upper left of the plot, emulating the distribution of extraterrestrial carbon. Although the evolution of aliphatic-rich soot seems to follow a higher FWHM path with respect to aromatic-rich samples, little can be stated about the difference between aromatic and aliphatic in this plot, due to relatively large error bars.

The lower panel of Fig. 9 includes data from ion irradiated graphite, amorphous carbon (produced by arc discharge), and organic residues produced after irradiation of C-rich ices (also called IPHAC, ion produced hydrogenated amorphous carbon), after Baratta et al. (2004). The collected extraterrestrial material area includes IDPs, meteorites, and comet Wild 2 grains.
4. Discussion

Although the interpretation of Fig. 9 is rather complex, our results strongly support previous amorphization experiments on carbonaceous materials. Irradiated soots extend measurements previously obtained by Baratta et al. (2004), and follow the same G-peak vs. G-FWHM track as the one found in extraterrestrial carbons. In particular, irradiation processes could be responsible for the degree of disorder observed in primitive meteorite IOM, some IDPs, and some Wild 2 grains. However, the possibility of thermal metamorphism of extraterrestrial carbon complicates the interpretation of Fig. 9. It is in fact known that thermal metamorphism suffered by extraterrestrial carbon would counterbalance the effects of cosmic irradiation (see arrows in the upper panel of Fig. 9), and what we observe nowadays is a result of the balance between such processes. If one can estimate the doses received by grains independently from the Raman measurements, then the measured Raman spectra (corresponding to the balance between metamorphism and irradiation observed today) would give constrains on the degree of metamorphism experienced so far. Effects of thermal metamorphism on the Raman spectra have been largely discussed by Buschmann et al. (2007) in the case of meteorites.

Since IR spectroscopy indicates that soot materials may be analogous to some component of the interstellar carbon grains (Pino et al., 2008), one can speculate about the possibility that some soot-like pre-solar material was incorporated in asteroids or in comets. Our results indicate that, so far, such component has not been observed in collected extraterrestrial carbons. As pictured in Fig. 9, both aliphatic-rich and aromatic-rich soots before irradiation show a degree of order which is not observed in extraterrestrial carbons. In Fig. 9, the extraterrestrial material that is closer to unirradiated soot is almost certainly the one that experienced thermal metamorphism (e.g. the Allende meteorite); this would suggest that, if pre-solar soots were present in the early solar nebula, these at some point must have suffered irradiation processes and have been transformed into some form of HAC. Let us now consider the extraterrestrial carbonaceous materials separately.

4.1 Comet Wild 2 and interplanetary dust particles

Recent Wild 2 cometary grains analyses obtained by different groups indicate that they are rich in various and complex organic compounds and show compositional and structural heterogeneities (Sandford et al., 2006; Rotundi et al., 2008; Muñoz-Caro et al., 2008). Organics possible modifications during particles high speed entry into the collecting aerogel is still debated in the community. Although evidences of such modifications exist, it has been pointed out that the presence of comet Wild 2 points in the upper left plot of Fig. 9 indicates that at least some of the organics from this comet are primitive and were captured with relatively little alteration (Sandford et al., 2006). Muñoz-Caro et al. (2008) claimed that the structure of the carbon component of Wild 2 grains is a form of HAC, that should not be a direct product of unaltered residue from the photolysis or irradiation of C-rich ices, but may result from its subsequent evolution. This is in agreement with what is shown in the lower panel of Fig. 9. Such HAC can either be primordial or be a result of irradiation processes of materials originally more structured, such as soot particles; alternatively, it may have been produced by significant metamorphism of more disordered carbons, such as ice residues.

The case of IDPs has been discussed in details by Baratta et al. (2004). They compared Raman features of IDPs and arc discharge amorphous carbon, and found that laboratory analogues can reproduce the observed spectral variety and pose an upper limit to the highest dose accumulated by IDPs due to ion irradiation in the interplanetary medium (~0.5 displacements per C atom), compatible with the exposure time of these particles. The total number of displacements (disslodgement of an atom from its original position) is given by the sum of vacancies and replacements. A dose of 0.5 displacements per C atom would imply that, on the average, about one carbon atom out of two has been dislodged from its initial position (amorphization process). From our results on irradiated soots, we can deduce that extraterrestrial carbons are only present in the area of Fig. 9 that would correspond to ion fluences below \((3 \pm 1) \times 10^{14} \text{ Ar}^{+} \text{cm}^{-2}\) at an energy of
400 keV. The error bar in this estimate (about 30%) is large enough to account for uncertainties in G-peak position and G-FWHM previously mentioned (see discussion above about fitting routines and associated error bars). Such fluence would correspond to 0.2 ± 0.1 displacements per C atom (estimated using SRIM) in the target volume probed by the Raman laser \( (d_{\text{PROBE}}) \), not far from what was obtained by Baratta et al. (2004). This dose corresponds to an energy of approximately 1 eV per 16 amu released in elastic collisions.

What is stated above is valid on an averaged scale sizing at least 100 nm. This implies that one has to average, on the volume probed by the Raman laser, the contribution of slow solar wind ions (about 1 keV per amu), that would affect very few tens of nanometers, with the contribution of solar ions with higher energy, from tens of keV to hundreds of MeV (higher penetration depth), coming from solar flares and co-rotating events (Johnson, 1990). It is still possible that at the nanometer-scale level, some of the fluffy material composing IDPs may have accumulated a dose higher than the one estimated above.

If some of the extraterrestrial carbon plotted in Fig. 9 never experienced thermal metamorphism, then one can conclude that it accumulated less than about 1 eV per 16 amu released in elastic collisions, on an averaged scale sizing at least 100 nm. This would pose an upper limit for the exposure time to cosmic or solar ions, a limit valid only for carbons that never experienced any process able to counterbalance irradiation effects. In the present outer Solar System conditions, unprotected objects orbiting beyond the termination shock can accumulate high doses and their crusts can be deeply affected by irradiation-induced chemistry (see e.g. discussion in Brunetto and Roush, 2008), so that on these bodies a highly disordered amorphous carbon component can be expected to be present. At 40-80 AU instead, such dose cannot be accumulated in a time shorter than the age of the Solar System itself, from estimates of fluxes and doses relative to elastic nuclear collision components (see Figure 6 in Strazzulla et al., 2003). This is coherent with the 1 eV per 16 amu limit discussed above. In the inner Solar System, the very upper layers (<100 nm) of asteroids and comets can accumulate such dose easily due to irradiation by slow solar wind. Although this contribution may be very important for space weathering studies (e.g. Brunetto and Strazzulla, 2005), it is highly improbable that such thin weathered skin could be recovered in the form of meteorites.

### 4.2 Carbonaceous meteorites

The case of carbonaceous meteorites is quite interesting. The bombardment of solids in the solar nebula by flare shocks and energetic particles may account for various properties of meteorites, such as chondrule melting and spallogenic isotopes (Feigelson and Montmerle, 1999, and references therein). Meteoritic evidence, in particular from the \( ^{10}\text{Be}/^{9}\text{Be} \) ratio (the sole 'extinct radioactivity' which can be of spallogenic origin only), suggests that intense particle irradiation must have taken place in the primitive solar nebula, similarly to processes taking place in circumstellar accretion disks of young stars (Montmerle, 2002, and references therein). Recent results on meteorite IOM showed that amorphous organic matter is more abundant in the most primitive chondrites (Busemann et al., 2007). In Fig. 9, primitive IOMs of carbonaceous meteorites fall in the region with G peak below about 1580 cm\(^{-1}\) and width above about 100 cm\(^{-1}\), a region that is well reproduced by irradiated soot. Our results support the idea that IOM observed in primitive meteorites experienced irradiation-induced amorphization prior to the accretion of the parent bodies (Busemann et al., 2007).

To evaluate the contribution of irradiation on carbons in the early Solar System, it is mandatory to determine the radiative and magnetic properties of the Sun as well as the solar particle emission during its evolution before and in the main sequence. Ribas et al. (2005), considering the integrated high-energy emission from 0.1 to 120 nm (12,000 – 10 eV), found that 2.5 Gyr ago the solar high energy flux was about 2.5 times the present value, and 3.5 Gyr ago was about 6 times the present value. Estimating the particle irradiation of the early solar wind is difficult because winds of solar-like stars have not yet been detected (see detailed discussion in Ribas et al., 2005). Using simple relationships involving rotational velocities and X-ray fluxes, Wood et al. (2002) suggest that the...
The situation is inverted for cosmic rays irradiation. The charged flux of cosmic rays in the Solar System is modulated by the solar wind, because cosmic rays must penetrate the heliosphere, the region of space dominated by the outflow of magnetized solar wind from the Sun (in the present conditions, the heliosphere extends out to distances of 75-95 AU from the Sun). Svensmark (2006) showed that in the first billion year of the Solar System history, the cosmic rays flux was suppressed due to the high solar activity. As soon as the activity declined with solar evolution, variations in cosmic rays flux started to reflect variations due to changes in the star formation rate.

Feigelson et al. (2002) observed analogs of the ≤1 Myr old pre-main-sequence Sun, who exhibited X-ray flares 10^{1.5} times more powerful and 10^{2.5} times more frequent than the most powerful flares seen on the contemporary Sun. Extrapolating the solar relationship between X-ray luminosity and proton fluence, they estimated that the young Sun exhibited a 10^{5}-fold enhancement in energetic protons compared to contemporary levels, a flux sufficient to produce the observed meteoritic abundances of several important short-lived radioactive isotopes.

From what is reported above, a reasonable scenario is that, during a time of about 10^5-10^7 years before being incorporated into planetesimals, primordial (i.e. pre-solar) carbons were exposed to particle fluxes 10^4-10^5 higher than present conditions, and thus may have globally accumulated an irradiation dose higher than the one accumulated in the last 4.6 billion years. As it has been shown by Baratta et al. (2004), about 10^6 years in present solar wind conditions are already enough to exceed the dose limits discussed above for IDPs. Thus, if primitive carbons present in meteorites have been prevented from accumulating such dose once incorporated in their parent bodies, one should again conclude that primordial irradiation has played a major role in determining the degree of disorder observed in primitive IOM.

Although the evolutionary connection between organics in the diffuse ISM, in dense clouds where planetary systems formed, and in comets, IDPs, and meteorites is far from being understood, the present analysis points towards the important role played in this connection by early solar nebula processing due to the enhancement of the solar particle flux.

5. Conclusions

We have used a chemical reactor to produce sooting flame by-products, that are analogues of interstellar carbonaceous dust. Before irradiation, the Raman spectra showed a relatively high degree of structural order in the crystallites, not observed in extraterrestrial carbons. Spectra were analyzed using a combination of Lorentzian-shaped and a Gaussian-shaped bands (G, D1, D2, D3, D4), in consistency with previous works on Raman spectra of soots.

We have performed ion irradiation on several soot samples, ranging from strongly aromatic to strongly aliphatic materials. We observed a progressive reduction of the Raman intensity with increasing ion fluence, an increase of D and G bands FWHM, a shift of the G band peak position towards lower Raman shifts, and an evolution towards a spectrum typical of amorphous carbon. The observed spectral modifications are in agreement with previous irradiation experiments on graphite and on amorphous carbon grains (Baratta et al., 2004), and are indicative of amorphization processes induced by ion irradiation. Comparing results from different experiments, we suggest that the variations observed after irradiation are related more to vacancy formation processes than ionization processes.

We have compared these results with Raman spectra obtained in the analysis of extraterrestrial organic matter and other irradiation experiments of carbonaceous materials of astrophysical relevance. We find that irradiated soot evolves toward an amorphous carbon that has Raman spectra similar to those of some meteorites, IDPs, and comet Wild 2 grains collected by the Stardust mission. Our results suggest that, if pre-solar soots were present in the early solar nebula, these at some point must have suffered irradiation processes and have been transformed into some form of HAC. We also support the idea that IOM observed in primitive meteorites experienced irradiation-induced amorphization prior to the accretion of the parent bodies.

Since the Raman technique is sensitive to an averaged scale of few hundreds of nanometers only,
we estimate that any collected extraterrestrial carbon, who never experienced thermal metamorphism, has not accumulated more than about 1 eV per 16 amu released in elastic collisions, on an averaged scale sizing at least 100 nm. This does not prevent some of the material composing IDPs and comet Wild 2 grains to have accumulated a higher dose on a nanometer-scale level.

Acknowledgements

The authors warmly thank G.A. Baratta and M.E. Palumbo for helpful discussions, and A. Rotundi and an anonymous reviewer for useful comments and suggestions. This work has been supported by the french national program “Physique et Chimie du Milieu Interstellaire” and the French “Agence Nationale de la Recherche” (contract ANR-05-BLAN-0148-02).

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Svensmark, H., 2006. Cosmic rays and the biosphere over 4 billion years. Astronomische
Nachrichten 327, 871.


<table>
<thead>
<tr>
<th>Band</th>
<th>Peak position (cm⁻¹)</th>
<th>FWHM (cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>D4</td>
<td>1180-1220</td>
<td>150-200</td>
</tr>
<tr>
<td>D1</td>
<td>1361-1364</td>
<td>85-95</td>
</tr>
<tr>
<td>D3</td>
<td>1450-1500</td>
<td>240-340</td>
</tr>
<tr>
<td>G</td>
<td>1595-1605</td>
<td>45-70</td>
</tr>
<tr>
<td>D2</td>
<td>1615-1619</td>
<td>15-35</td>
</tr>
<tr>
<td>2*D4</td>
<td>2500-2550</td>
<td>100-200</td>
</tr>
<tr>
<td>2*D1</td>
<td>2720-2760</td>
<td>300-400</td>
</tr>
<tr>
<td>G+D1</td>
<td>2940-2970</td>
<td>200-300</td>
</tr>
<tr>
<td>2*D3</td>
<td>3050-3100</td>
<td>150-350</td>
</tr>
<tr>
<td>2<em>G, 2</em>D2</td>
<td>3180-3220</td>
<td>150-190</td>
</tr>
<tr>
<td></td>
<td>3350-3450</td>
<td>300-500</td>
</tr>
</tbody>
</table>

Table 1. Peak positions and full widths at half maximum (FWHMs) of bands observed in the Raman spectra of aromatic-rich and aliphatic-rich soots. The ranges are given taking into account both variability of soot samples and error bars from fitting routines.
Table 2. The ions used in this work to irradiate soot targets, with the energy, maximum fluence, mean penetration depth (range, \(d_P\)), number of vacancies per ion, fraction of energy released by a single ion in ionization processes (\(f_{\text{ION}}\)) and vacancy formation processes (\(f_{\text{VAC}}\)), as estimated using the SRIM code. The thickness of the soot samples in our experiments is in the range 1-3 \(\mu\)m. In the simulation we introduce an effective thickness \(d_{\text{EFF}}\) = 0.6 \(\mu\)m for the soot target, obtained using a value of 1.7 g/cm\(^3\) for the density of single soot grains, and an average density of 0.45 g/cm\(^3\) for the sample. For H\(^+\) and He\(^+\) the range is larger than the effective target thickness, i.e. the ions pass through the soot sample and remain implanted in the substrate; for these ions, penetration depth into an infinitely thick target is given in parenthesis.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (keV)</th>
<th>Max fluence (\text{ions cm}^{-2})</th>
<th>(d_P) ((\mu)m)</th>
<th>Vacancies (\text{ion}^{-1})</th>
<th>(f_{\text{ION}})</th>
<th>(f_{\text{VAC}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>200</td>
<td>(8 \times 10^{15})</td>
<td>(1.03)</td>
<td>1.5</td>
<td>99.9%</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>He(^+)</td>
<td>200</td>
<td>(1 \times 10^{16})</td>
<td>(0.66)</td>
<td>60</td>
<td>98.3%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Ar(^{++})</td>
<td>400</td>
<td>(8 \times 10^{15})</td>
<td>0.26</td>
<td>1800</td>
<td>83%</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

Table 3. Same as Table 2, but using an effective target thickness \(d_{\text{PROBE}}\) = 0.1 \(\mu\)m in the SRIM simulation. Note that for all ions it is verified \(d_P > d_{\text{PROBE}}\), i.e. the layers responsible for the detected Raman signal have been irradiated quite uniformly. \(\Delta E\) is an estimation of the energy lost by ions in a target volume corresponding to a depth of about \(d_{\text{PROBE}}\).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (keV)</th>
<th>(\Delta E) (keV)</th>
<th>Max fluence (\text{ions cm}^{-2})</th>
<th>(d_P) ((\mu)m)</th>
<th>Vacancies (\text{ion}^{-1})</th>
<th>(f_{\text{ION}})</th>
<th>(f_{\text{VAC}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>200</td>
<td>20</td>
<td>(8 \times 10^{15})</td>
<td>(1.03)</td>
<td>0.3</td>
<td>99.9%</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>He(^+)</td>
<td>200</td>
<td>45</td>
<td>(1 \times 10^{16})</td>
<td>(0.66)</td>
<td>3</td>
<td>99.6%</td>
<td>0.02%</td>
</tr>
<tr>
<td>Ar(^{++})</td>
<td>400</td>
<td>150</td>
<td>(8 \times 10^{15})</td>
<td>(0.26)</td>
<td>380</td>
<td>90.2%</td>
<td>0.8%</td>
</tr>
</tbody>
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Table 4. The six irradiation steps shown in the lower panel of Fig. 7, sorted for increasing amorphization from A (soot before irradiation) to F (amorphous carbon), are compared in terms of G band peak position, ion fluence, total dose released in the volume corresponding to \( d_{\text{PROBE}} \), and density of vacancies created in the volume corresponding to \( d_{\text{PROBE}} \). The G-peak moves toward lower Raman shift as the density of vacancies increases.

<table>
<thead>
<tr>
<th>Step</th>
<th>Ion</th>
<th>G-peak (cm(^{-1}))</th>
<th>Fluence ( (10^{15} \text{ ions cm}^{-2}) )</th>
<th>Total dose (eV per 16 amu)</th>
<th>Density of vacancies ( (10^{20} \text{ vac cm}^{-3}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>1606</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>H(^+)</td>
<td>1603</td>
<td>2</td>
<td>62</td>
<td>0.6</td>
</tr>
<tr>
<td>C</td>
<td>He(^+)</td>
<td>1600</td>
<td>2</td>
<td>140</td>
<td>6</td>
</tr>
<tr>
<td>D</td>
<td>He(^++)</td>
<td>1580</td>
<td>10</td>
<td>700</td>
<td>30</td>
</tr>
<tr>
<td>E</td>
<td>Ar(^++)</td>
<td>1578</td>
<td>0.2</td>
<td>47</td>
<td>75</td>
</tr>
<tr>
<td>F</td>
<td>Ar(^++)</td>
<td>1545</td>
<td>2</td>
<td>470</td>
<td>750</td>
</tr>
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</table>

FIGURE CAPTIONS

Figure 1. Raman spectra of aromatic-rich (upper panel) and aliphatic-rich (lower panel) soot.

Figure 2. First-order spectral deconvolution of aromatic-rich (upper panel) and aliphatic-rich (lower panel) soot, using five components. G, D1, D2 band profiles are Lorentzian, while D3 band profile is Gaussian, and D4 is Gaussian in the upper panel and Lorentzian in the lower panel. Band vibration assignments are given in the text. Before fitting, spectra have been continuum-corrected using a linear baseline. Values of chi-squared divided by the degrees of freedom are included.

Figure 3. Second-order spectral deconvolution of aromatic-rich (upper panel) and aliphatic-rich (lower panel) soot, using six and four components respectively. The band profiles are Lorentzian. Before fitting, spectra have been continuum corrected using a linear baseline. Values of chi-squared divided by the degrees of freedom are included.

Figure 4. In-situ first-order Raman spectra of aromatic-rich (upper panel) and aliphatic-rich (lower panel) soot, before and after irradiation with 400 keV Ar\(^++\) ions. A few irradiation steps are shown for increasing ion fluence.

Figure 5. Comparison of different simplified fitting functions (D and G bands only) in the case of aliphatic-rich soot before (upper panel) and after (lower panel) irradiation with Ar\(^++\) (400 keV). Values of chi-squared divided by the degrees of freedom are included for the different models.

Figure 6. Evolution of the G-peak position and FWHM as a function of ion fluence (Ar\(^++\)/cm\(^2\), 400 keV), for both aliphatic-rich and aromatic-rich samples. Data are obtained using the simplified
fitting functions (see text).

Figure 7. Upper panel: spectral comparison between H⁺ and Ar²⁺ irradiated aromatic-rich soot (at the same ion fluence). Lower panel: comparison between H⁺, He⁺, and Ar²⁺ irradiation, in the case of aliphatic-rich soot. Spectra are shifted for clarity, and displayed in order of increasing amorphization effect (from top to bottom, from A to F).

Figure 8. Raman spectra of the Murray and Tagish Lake meteorites (after Baratta et al., 2008) are compared to Raman spectra of aromatic-rich soot irradiated at three different fluences. Spectra are shown after continuum subtraction, and after scaling the D-peak intensity to unity.

Figure 9. Upper panel: G band full width at half maximum (FWHM) as a function of G band peak position, for ion irradiated soot compared with interplanetary dust particles (IDPs), carbonaceous meteorites, and grains from comet Wild 2 collected by the NASA Stardust mission (values for 40 IDPs and more than 40 meteorites are taken from Sandford et al., 2006 and references therein, values for 13 Wild 2 grains are taken from Rotundi et al., 2008). Experimental points connected by solid thick lines correspond to in-situ experiments, whereas points connected by dashed lines correspond to ex-situ experiments. An arrow marks the evolutionary path due to ion irradiation, i.e. points in the upper left of the graph are obtained at the higher doses. Lower panel: same as upper panel, including data from ion irradiated: graphite (diagonal upper right lines), amorphous carbon produced by arc discharge (vertical lines), and organic residues (horizontal lines) produced after irradiation of C-rich ices (also called IPHAC, ion produced hydrogenated amorphous carbon), after Baratta et al. (2004). Soot are represented by the diagonal upper left lines (light gray). Collected extraterrestrial materials gray area includes IDPs, meteorites, and comet Wild 2 grains.
Figure 2, Brunetto et al., Raman spectra of irradiated soot

Figure 3, Brunetto et al., Raman spectra of irradiated soot
Figure 4, Brunetto et al., Raman spectra of irradiated soot

Arom-rich soot irradiation Ar$^{+}$ 400 keV
(a) before irrad.
(b) 2 x 10$^{-17}$/cm$^2$
(c) 4 "
(d) 8 "
(e) 20 "

Figure 5, Brunetto et al., Raman spectra of irradiated soot

Aliph-rich soot
Lorentz fit, $\chi^2$/DOF = 0.04
BWF fit, $\chi^2$/DOF = 0.01
Figure 6, Brunetto et al., Raman spectra of irradiated soot

<table>
<thead>
<tr>
<th>G band center (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>1600</td>
</tr>
<tr>
<td>1580</td>
</tr>
<tr>
<td>1560</td>
</tr>
<tr>
<td>1540</td>
</tr>
</tbody>
</table>

Fluence (x10$^{14}$ Ar$^{++}$/cm$^2$)

<table>
<thead>
<tr>
<th>G band center (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
</tr>
<tr>
<td>150</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>50</td>
</tr>
</tbody>
</table>

Fluence (x10$^{14}$ Ar$^{++}$/cm$^2$)

Figure 7, Brunetto et al., Raman spectra of irradiated soot

Arom-rich soot

Intensity (counts/sec)

8x10$^{15}$ H$^+$/cm$^2$

8x10$^{15}$ Ar$^{++}$/cm$^2$

Aliph-rich soot

Intensity (a.u.)

Raman shift (cm$^{-1}$)
Figure 8, Brunetto et al., Raman spectra of irradiated soot

(a) Arom-rich soot + $4 \times 10^{13} \, \text{Ar}^+ / \text{cm}^2$
- Murray met.
- Tagish met.

(b) Arom-rich soot + $8 \times 10^{13} \, \text{Ar}^+ / \text{cm}^2$
- Murray met.
- Tagish met.

(c) Arom-rich soot + $2 \times 10^{14} \, \text{Ar}^+ / \text{cm}^2$
- Murray met.
- Tagish met.

Raman shift (cm$^{-1}$)

Figure 9, Brunetto et al., Raman spectra of irradiated soot

G band center (cm$^{-1}$)

FWMH G (cm$^{-1}$)

Irradiated:
- soot
- graphite
- AC
- residues

Meteorites:
- IDPs
- Wild 2 (Stardust)
- Irrad. arom. rich soot
- Irrad. aliph. rich soot
- Gray area: IDPs
- Dotted line area: meteorites

Metamorphism

collected extraterrestrial materials

Irradiation