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Raman Microspectroscopy Performed on Extraterrestrial Particles

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ABSTRACT Raman analyses have been performed on Interplanetary Dust Particles (IDPs) collected in the lower stratosphere by NASA high-flying aircrafts, dust from comet 81P/Wild2 collected by Stardust mission, and three particles collected in the upper stratosphere by the balloon-borne DUSTER instrument. All samples contain amorphous carbon (aC) with different degrees of structural order. Fe oxides were detected in the IDPs, aliphatic chains were found in comet grains, and three particles collected in the upper stratosphere are calcium carbonate (calcite or aragonite). Raman spectroscopy is a valuable tool for the nondestructive analyses of micrometer-scale constituents of complex natural materials.

KEYWORDS carbon, comet Wild 2 grains, DUSTER, interplanetary dust particles, Raman spectroscopy, stratospheric dust

INTRODUCTION

Interplanetary dusts are the building blocks from which planetesimals accreted in the early solar system,[1,2] leading to the formation of planets and minor bodies, that is, comets and asteroids, which could contain interstellar inclusions.[1,2,3] Laboratory characterization of asteroidal and cometary dust collected in the terrestrial stratosphere and by the Stardust space mission using different analytical techniques is critical to understanding solar system formation and evolution.[4] Raman microspectroscopy, a nondestructive tool for the study of extraterrestrial dust particles in the micron-size range, detects iron oxides and silicates. It also provides information on the structure of amorphous carbon,[5–9] thanks to its high cross-section in Raman scattering processes when using visible laser excitation. In this study, we compared Raman measurements performed on dust collected in the lower (IDPs) and upper (DUSTER particles) stratosphere and from comet Wild 2 to better understand their interrelationships and extraterrestrial origins.

MATERIALS AND METHODS

Three sets of samples were analyzed by Raman microspectroscopy at the Laboratorio di Astrofisica Sperimentale, Catania, Italy.[10] The experimental apparatus consisted of a confocal microscope (DILOR) focusing the light beam of an Ar ion laser source ($\lambda = 514.5$ nm) on the sample, always keeping

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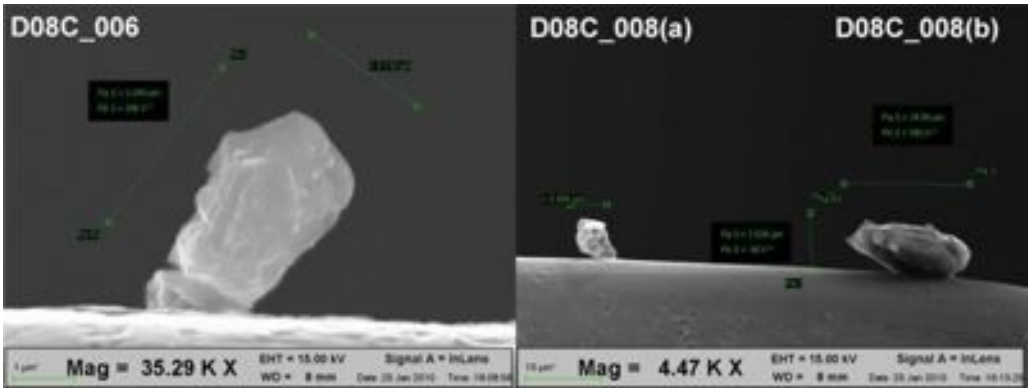

FIGURE 1 **Stratospheric dust particles collected by balloon-borne DUSTER instrument and analyzed with micro-Raman spectroscopy [SEM images are from reference.[14]]. The particles names are D08C_006, D08C_008(a), and D08C_008(b). In reference[14], the names of the two particles −08(a) and −08(b) are inverted. (color figure available online.)**

the laser power at 60–70 μW focused on the sample surface. The same objective (100×) collected the light beam scattered by the sample, which was collimated into a parallel beam following back the same path of the laser beam. Finally the Raman light was focused on the entrance slit of a triplemate spectrometer (SPEX) equipped with a 1200 gr/mm holographic grating and a CCD detector. The laser light spot on the sample was ~2 μm; the spatial resolution, set by a confocal pinhole, was 4 μm; and the instrument spectral resolution was 8 cm^{-1} with a peak position accuracy of 2 cm^{-1}.

The cometary grains and IDPs were deposited on special sample holders designed for combined analyses with different analytical techniques.[10,11] Three micron-sized upper stratospheric particles, collected by the balloon-borne instrument DUSTER at an altitude of 37 km,[12–15] have a maximum elongation of 16, 5, and 3 μm (Fig. 1). They have been transferred, using the Focused Ion Beam (FIB) technique, onto different pin edges of FIB copper grid.[14,15]

RESULTS AND DISCUSSION

Raman spectra of 3 grains from the upper stratosphere collected by DUSTER exhibit the typical amorphous carbon (aC) D (1361 cm^{-1}) and G (1580 cm^{-1}) bands (Fig. 2, left). Slight variations of the band parameters suggest different aC order degree within single particles. Two grains (08a, 06) show a weak peak (1–2σ) at 1080 cm^{-1} (Fig. 2A, B, C, D) that is due to calcite or aragonite.[16] The EDX data for these particles showed a stoichiometric calcium carbonate ($CaCO_3$) composition for these grains, supporting the Raman identification. Particles 08a and 08b exhibit a weak and large peak between 600 and 800 cm^{-1} (Fig. 2B, 2D, 2F) that could be due to aC (L_1 and L_2 peaks, typical of amorphous carbon with low sp^3 content, but this assignment still needs to be confirmed).[8] However, it was noted that Raman spectra acquired close to the FIB-deposited copper contact exhibit strong aC Raman signals that decreases when moving away from it. This observation suggests that the amount of aC can be influenced by the FIB-deposited. Additional analyses are planned to verify the potential of this potential detrimental contamination to analyze aC material in samples that were manipulated by the FIB/Pt process.

The high aC content in DUSTER grains let the 1086 cm^{-1} band be very weak.[16] The aC prevents minerals detection: (1) Its Raman cross-section relative to visible excitation is much higher than that of most minerals; (2) aC on the grains surface prevents deep laser penetration.[6,9]

The analyzed IDPs collected in the lower stratosphere[11] have different morphologies: Three are chondritic aggregate particles of different porosity, one is a cluster of Fe sulphide grains, and another is a compact Fe-rich sphere. The presence of maghèmite or magnetite rims on the three aggregate IDPs suggests that they experienced pyrometamorphism due to flash heating during atmospheric entry. While all five IDP Raman spectra show the presence of Fe-oxides, only two exhibit the aC, D, and G bands [L2021D12 (porous) and L2021C13 (low porosity)].[11]

The comet Wild 2 grain Raman spectra show the characteristic D and G bands of amorphous carbon with different degrees of structural order.[10] When

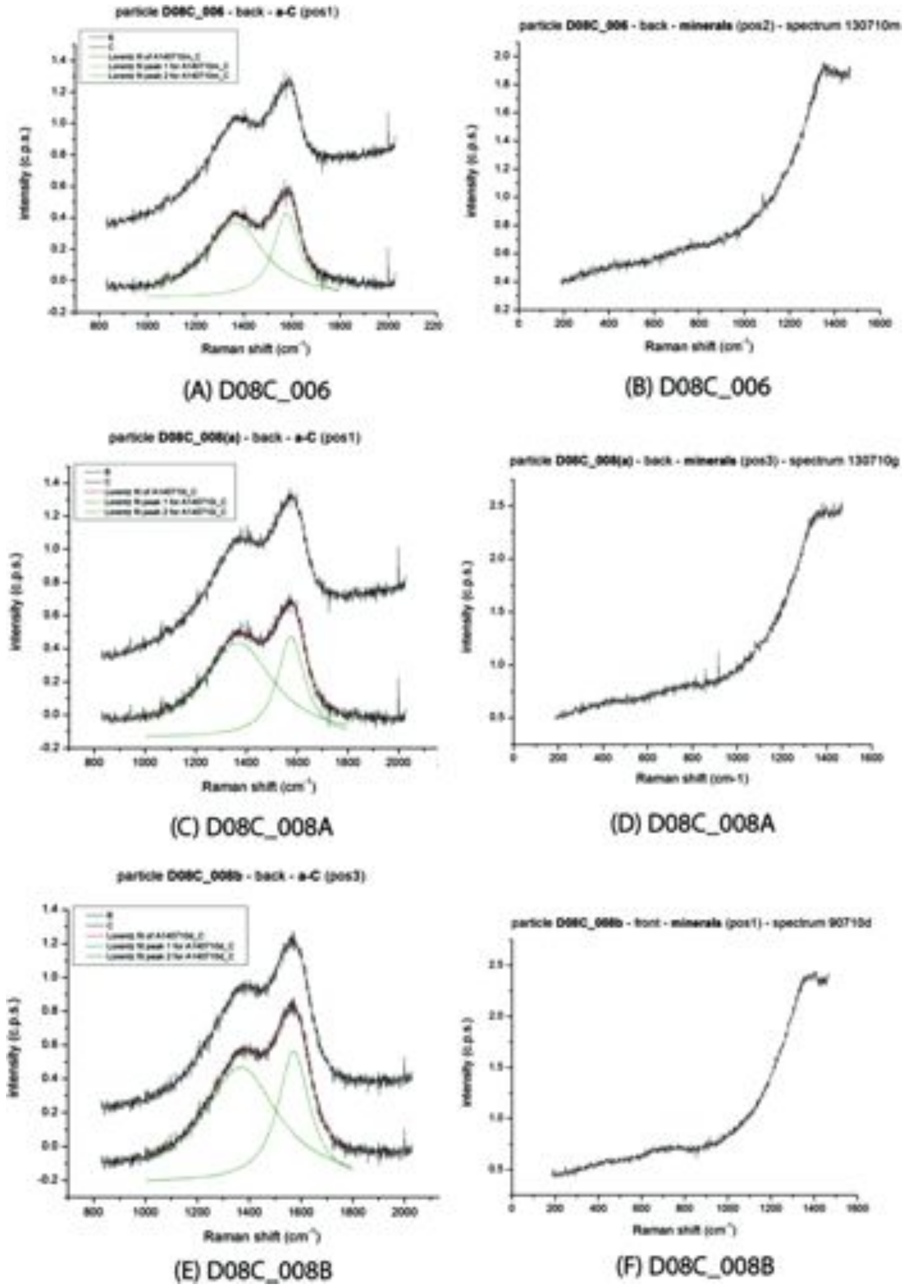

FIGURE 2 **Raman spectra of DUSTER particles. Left column: spectra in carbon region (center at 1450 cm^{-1}); right column: Spectra in minerals region (center at 850 cm^{-1}). Spectra (A), (C), and (E) are characterized by the strong D ($\sim$1360 cm^{-1}) and G ($\sim$1580 cm^{-1}) bands of the amorphous carbon (aC). All particles show, within the spatial resolution of the instrument, an aC coating. Spectra (B) and (D) display a small peak at 1080 cm^{-1} that can be assigned to calcite or aragonite ($CaCO_3$),[15] while spectrum (F) does not show any detectable peak around that frequency. Spectra (B), (D), and (F) moreover display two very faint broad bands centered at $\sim$400 and $\sim$800 cm^{-1}: these could correspond to L_1 and L_2 peaks typical of amorphous carbon with low sp^3 content.[8]. (color figure available online.)**

aC dominates, as in the comet samples, other compounds present are masked. The aliphatic hydrocarbons C-H stretching bands, $\sim 2900\,\Delta\text{cm}^{-1}$, are present in three cometary grains: C2054,0,35, 30,0, shows the band with two peaks (at $\sim$2848 and $\sim$2882 cm^{-1}), due to methylene (CH_2) and methyl (CH_3); for the other two grains (C2054,0, 35,32 and C2044,2,41,11,0), the band is broad and with no resolved peaks.[10]

The D and G peaks of the three sets of samples have been fitted with two Lorentzians after the subtraction of a straight baseline.[7,17] Raman spectra of metamorphized and thermally processed meteorites have D, G peaks that are quite narrow and well-separated, with low ω_D and high ω_G; on the contrary, Raman spectra of aC in primitive meteorites have broad and blended D and G bands, with high ω_D and low ω_G. Stardust grains match well with many IDPs.[11]

The intensity ratio I_D/I_G is another important spectral parameter to be considered in order to have a better understanding of the degree of structural order of carbonaceous materials.[7,8,18] Nevertheless both carbons with a very high degree of order (for example thermally ordered carbonaceous materials) and most disordered amorphous carbons have similar values of the intensity ratio.[18] The Tuinstra-Koenig relation—

$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a} \tag{1}$$

—is valid for values of the graphitic domain size $L_a > 20$ Á (C(514 nm) = 44 Á), while in the range $L_a < 20$ Á, the following relation holds:[6]

$$\frac{I(D)}{I(G)} = C'(\lambda) \cdot L_a^2 \tag{2}$$

where $C'(514\,\mathrm{nm}) = 0.0055\,\text{Á}^2$. So the intensity ratio is not a useful unambiguous indicator for detecting the state of metamorphism of carbonaceous materials; D and G band parameters are more useful indicators, and they are often considered. Still it is possible to infer some information about the size L_a of the graphitic domains of these particles. We can assume that DUSTER carbon is in stage 2 of the amorphization trajectory (graphite → nCG → aC → taC) showed by Ferrari and Robertson[7,8], that is, in a stage between *nanocrystalline graphite* and *amorphous carbon*. The I_D/I_G versus D, G band position does not show any clear trend. From the average intensity ratios measured for the three DUSTER particles ($<I_D/I_G> = 0.85 \div 0.88$), we obtain the mean size of graphitic domains, $L_a = 12.4 \div 12.6$ Á; moreover we can deduce an sp^3 content of $11 \div 12\%$.

At this time the carbonaceous component and the aC bands Raman parameters for the DUSTER particles are not compared to the D and G bands parameters of the comet grains and IDPs. We first need to understand if an aC contamination by the FIB-deposited Pt process actually occurred and—in that case—the exact nature of the aC. Does it produce new aC materials or does it also affect the degrees of aC order, or both?

CONCLUSIONS

Raman analyses were performed on three sets of fine-grained natural materials: upper stratospheric DUSTER particles, IDPs, and cometary grains. Two of the three analyzed DUSTER particles showed the $CaCO_3$ peak for calcite or aragonite. We plan to perform additional micro-Raman and micro-IR analyses focused on disentangling the calcite/aragonite identification. IDPs show features due to minerals, for example, iron oxides; the comet grains are dominated by aC, which could mask the presence of possible minerals in the samples. The comparison between known extraterrestrial materials, IDPs, comet Wild 2 dust, and DUSTER particles D and G bands parameters will provide information on the aC degrees of order/disorder and thus hints to their possible origins.

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