



Production, processing and characterization techniques for cosmic dust analogues

A. ROTUNDI^{1*}, J. R. BRUCATO², L. COLANGELI², G. FERRINI^{2,3}, V. MENNELLA², E. PALOMBA²
AND P. PALUMBO¹

¹Ist. di Mat., Fis. e Appl., Università "Parthenope", Via A. De Gasperi 5, I-80133 Napoli, Italy

²INAF, Osservatorio Astronomico di Capodimonte, Via Moiariello 16, I-80131 Napoli, Italy

³Dip. Scienze Fisiche, Università di Napoli "Federico II", Mostra d'Oltremare pad. 19, I-80125 Napoli, Italy

*Correspondence author's e-mail address: rotundi@uninav.it

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Abstract—The laboratory analyses of cosmic dust analogues—that in the context of this paper include interstellar, circumstellar as well as cometary dust—have a critical role in the study of circumstellar and cometary dust. The morphological, structural and chemical characterization of these analogues are critical for comparisons of their infrared and ultraviolet spectra with those obtained by astronomical observations, as well as for modeling purposes. Besides, the results from these laboratory studies are important to the success of space missions to comets when testing and calibrating the payload instruments. The interpretations of returned scientific data would benefit from the comparison with data recorded by the instruments in a laboratory setting for different classes of previously characterized analogues. We produced various types of condensed samples: (1) Mg,Fe-silicates, (olivine, pyroxene), (2) carbon-rich dust, and (3) mixed carbon-silicate dust. The samples were prepared using different techniques, *viz.* (1) laser bombardment of solid targets in an Ar and O₂ atmosphere, (2) arc discharge in an Ar and H₂ atmosphere, and (3) grinding powders of natural minerals. We simulated various post-condensation processes, such as thermal annealing, ultraviolet irradiation, ion bombardment and exposure to atomic hydrogen. These processes produced compound samples of a wide range of physico-chemical properties. To identify their textures, morphologies, grain compositions and crystallographic properties we used electron microscopy and far-ultraviolet to far-infrared (millimeter range) spectroscopy.

INTRODUCTION

Cometary dust includes condensed volatiles consisting of carbon-hydrogen-oxygen-nitrogen (CHON) in mixed silicate-CHON particles (Kissel and Krueger, 1987; Jessberger *et al.*, 1988; Fomenkova *et al.*, 1992, 1994). The grains occur in more or less fluffy aggregates with variable proportions of the silicate and organic components, which could be amorphous or crystalline, structurally-mixed, complex dust ranging from pure silicate to pure CHON particles. Comets formed by accreting materials present in a protoplanetary nebula that included silicate dusts, carbonaceous materials and volatile compounds and molecules. These materials are also present in various astronomical environments, such as circumstellar disks and in the interstellar medium. Crystalline or amorphous grains formed depending on the temperature of their environment. Spectral analyses of circumstellar dust show that crystalline grains are observed only around evolved stars with high mass-loss rates, whereas low mass-loss rate stars do not

exhibits any crystalline bands (Cami *et al.*, 1997; Sylvester *et al.*, 1999). Annealing of amorphous silicate dust in stellar outflows will result in a series of kinetically controlled reactions. They will eventually lead to the formation of crystalline silicates, providing that the grains remained "hot" for a sufficiently long time (Brucato *et al.*, 1999a; Fabian *et al.*, 2000; Hallenbeck *et al.*, 1998, 2000; Rietmeijer *et al.*, 2002a,b). One would expect the observation of some crystalline silicate features in the interstellar medium but no reliable evidence for this has been found yet (Lutz *et al.*, 1996; Demyk *et al.*, 1999). Following the current opinion that silicates coming from the pre-solar cloud and in-falling onto the protosolar nebula were initially amorphous, successive thermal processing at high temperatures would have been necessary to induce their crystallization. Comets were generally considered as objects wherein the pristine amorphous presolar material was preserved. But recently the infrared space observatory (ISO) data showed evidence for the presence of crystalline silicates in at least some Oort cloud comets (Crovisier *et al.*,

1997). It suggests that cometary grains experienced thermal processing at some time during their pre-cometary residence. Two possible scenarios could explain the presence of crystalline grains in comets, *viz.* turbulent radial mixing in the solar nebula (Bockelée-Morvan *et al.*, 2002; Nuth *et al.*, 2000) and annealing of dust by nebular shocks (Harker and Desch, 2002). During comet formation, volatiles present in the proto-solar nebula may have been removed and/or reprocessed (Nuth *et al.*, 2000). However, once arrived in the outer region of the accretion disk, pre-cometary grains may have coagulated into porous particles that become the sites where fresh volatiles could condense. Grain coagulation built up large cometesimals during the energetic T-Tauri phase of the young Sun. The high flux of photons and particles could have modified the nature of ices and silicate cores forming new molecular species (Strazzulla and Baratta, 1992).

Important aspects of cometary dust origin and evolution can be deduced by astronomical observations, by theoretical modeling and by direct investigation of dust with cometary origin. In fact, some fraction of chondritic interplanetary dust particles (IDPs) have a cometary origin and probably contain primordial matter from our planetary system (Rietmeijer, 1998 (and references therein), 2002). Thus, studies of IDPs that are collected in the stratosphere by means of airborne inertial-impact, flat-plate collectors (Brownlee, 1978) are of critical importance for comet science. The near-Earth orbit environment offers another possibility for the collection of meteoroids of different origins. In the last few years a number of dust capture experiments were carried out in low-Earth orbit for example onboard the Russian MIR space station (*e.g.*, Westphal *et al.*, 1997) and the long duration exposure facility (Zolensky *et al.*, 1994). The inventory of the extraterrestrial material available presently will be soon enriched by *in situ* collected dust from small solar system bodies, by sample return missions such as Stardust (Brownlee *et al.*, 2000) and Muses-C (Fujiwara *et al.*, 1999). A comprehensive overview of the available analytical techniques, used in experiments on "nanosamples", is given in Zolensky *et al.* (2000).

Laboratory activity devoted to simulate cosmic dust formation and evolution in different space environments represent a concrete tool to improve our knowledge of comets. Presently, a number of laboratories are conducting cosmic silicate and carbon dust analogues condensation experiments (*e.g.*, Nuth *et al.*, 2002; Fabian *et al.*, 2000; Blanco *et al.*, 1996) using similar but also different techniques than those reported in this paper. There are basically two different methods to generate the vapours in these experiments, *viz.* (1) the instantaneous evaporation of stoichiometric crystalline materials (this work; Fabian *et al.*, 2000) and (2) pre-mixing metal-oxide vapours (Nuth *et al.*, 1999). It seems that the method used to generate the initial vapour might have an impact on the results, which is an interesting topic to be addressed in future research. For example, the smokes prepared by the second method report the condensation of individual, amorphous

nanograins with predictable metastable eutectic compositions (Nuth *et al.*, 2002; Rietmeijer *et al.*, 2002b). Condensed smokes prepared by the first method have generally compositions that closely mimic the metal-oxide ratios of the target materials, such as described in this paper. The production and characterization in the laboratory of cometary dust analogues (CDA) is also crucial to develop space missions directed towards comets. To this aim we produce and process CDA to simulate the building blocks of comet nuclei in different phases of their evolution in a step by step procedure emphasizing the composition and structure of cometary dust including various pure silicates and carbon-based materials. These dust analogues can be amorphous, crystalline and partially crystallized. We then study the compositions and structures of mixed analogues made of these silicates and carbon-rich materials. To account for cometary material crystallization, due to thermal annealing during the perihelion passage, and/or structural changes due to cosmic phenomena like ultraviolet and ion bombardment, we apply the following processing techniques: thermal annealing, ultraviolet irradiation, ion bombardment and exposure to atomic hydrogen. An accurate characterization of each kind of the produced materials is performed using scanning electron microscope (SEM), energy dispersive x-ray (EDX) analysis, spectroscopy ranging from the far ultraviolet into the millimeter range. The main aim is to gain critical knowledge on increasingly complex, but well-characterized, materials that will be realistic analogues of cometary dust as defined by models developed on the basis of results from (1) previous space missions (*e.g.*, GIOTTO Halley mission; ISO), (2) ground-based observations, and (3) laboratory analyses of IDPs.

EXPERIMENTAL

In Table 1 we report the samples produced and studied so far. They are grouped in three main classes of materials (*i.e.*, silicates, carbon-based and mixed carbon-silicates) that each required a specific production technique and post-production processing and analyses. The silicates we used are natural mineral that present low percentages of impurities detected during the chemical analysis that do not interfere with the spectral properties. We labeled the samples with names of the corresponding pure mineral. Analogue morphology was characterized using a Stereoscan 360–Cambridge field emission scanning electron microscope (FE-SEM), operating at a maximum accelerating voltage of 25 KeV and with a nominal spatial resolution of 2 nm. To analyze the chemical composition of the samples we used an EDX detection system attached to the FE-SEM that is capable to detect elements down to Be. For the silicates quantitative EDX data reduction is made following Papike (1987). Since the laser-ablation technique (see "Silicate Dust Analogues: Condensed Samples") might alter the composition during evaporation and condensation, the chemical composition of the condensed

TABLE 1. List of the samples produced with the relative production and processing technique and a brief description of the resulting sample.

Class	Sample	Production	Processing	Crystallographic properties
Silicates	Augite Enstatite Fayalite Forsterite Goethite Hematite Ilmenite Jadeite Kaolinite Montmorillonite Opal	Grind, sieve and sediment minerals	–	Crystalline size selected
	Enstatite Fayalite Forsterite	Laser vaporization	–	Condensate of amorphous grains
	Enstatite Forsterite	Laser vaporization	Thermal annealing	Partially crystallized condensed grains
Carbon based	Carbon soot	Laser vaporization in Ar atmosphere	–	Condensate of amorphous grains
		Arc discharge in Ar atmosphere	–	Condensate of amorphous and crystalline grains
		Arc discharge in H ₂ atmosphere	–	Condensate of amorphous and crystalline grains
		Laser vaporization in Ar atmosphere	Thermal annealing	Amorphous condensates and crystallized grains
		Arc discharge in Ar atmosphere	Thermal annealing	Amorphous condensates and crystallized grains
		Arc discharge in H ₂ atmosphere	Thermal annealing Ultraviolet irradiation Ion bombardment Exposure to H ₂	Amorphous condensates and crystallized grains
Mixed	Forsterite plus carbon Fayalite plus carbon	Laser vaporization	–	Condensate of amorphous grains
	Forsterite plus carbon	Laser vaporization	Thermal annealing	Amorphous condensates and crystallized grains

silicates needs to be determined. Chemical analysis is also necessary to characterize the mineral stoichiometry or the non-stoichiometry of amorphous grains produced in the condensation experiments.

To study the optical behavior, structure and composition of the samples, infrared spectroscopy has been applied. Transmission spectra in the range 2.5–25 μm have been obtained at spectral resolution of 2 cm^{-1} by means of an infrared Fourier transform interferometer (Bruker, Mod. IFS 66V) for all produced and processed samples.

Sample Preparation—For FE-SEM characterization of sample morphology and size distributions, the samples are dispersed on, or directly deposited onto, a smooth silicon wafer chip designed for high-resolution SEM analysis. For EDX analyses the samples are placed on a smooth carbon pin-stub or smooth silicon wafer for the silicate and carbon-based samples, respectively. Few hundreds of micrograms of dust analogue sample are embedded in KBr matrix by using the standard pellets technique suitable for infrared spectroscopy, whereas they are dispersed or directly collected on ultraviolet

grade fused silica substrates for ultraviolet spectral analysis. For thermal processing, the most suitable substrate to use was the smooth silicon wafer chip.

Silicate Dust Analogues

Natural Single Crystals—Fragments of natural silicate minerals are grounded in agate mills for pre-selected times. The grain size is selected using a sieving apparatus for size ranges of 0–20, 20–50, 50–100, 100–150 and 150–200 μm . For grain sizes $<1 \mu\text{m}$ a sedimentation procedure is applied. A solution is prepared dispersing ~ 500 mg of silicate grains in pure (99.8%) ethanol. A glass beaker ($\phi = 10$ cm) is filled with 4 cm in height of solution, which undergoes ultrasound shaking technique for 15 min in order to be homogenized and to balance the electrostatic forces that promote agglomeration of the suspended grains. After 9 h of sedimentation the upper part of the solution is aspirated and dispersed onto the smooth silicon wafer designed for high-resolution FE-SEM. Size distribution and average grain dimension of the samples are determined by FE-SEM image analysis based on a particle counting method (Rotundi *et al.*, 2000) which, maintaining a constant spatial resolution, avoids underestimating the smallest particles (Dorschner *et al.*, 1978).

Condensed Samples—Condensed silicates are produced by using a Nd-YAG solid-state pulsed laser. The fundamental laser wavelength output is 1064 nm with a mean energy of 650 mJ and power energy emitted per laser pulse of 10^8 W cm^{-2} . A set of two crystals is used to get II and IV harmonics at 532 and 266 nm, respectively. The energy output is 80 mJ at 266 nm, 120 mJ at 532 nm, and 190 mJ at 1064 nm. An optical set-up allows us to select one or more wavelengths to direct onto the sample. Using a focusing lens the power laser beam density can be varied in the range of 10^6 to 10^9 W cm^{-2} . The optical properties of silicates used as target materials typically vary with wavelength in a way that the absorption coefficient of the bulk target is lower by orders of magnitude at 1064 nm with respect to 266 nm. Therefore, by using a laser beam in the ultraviolet, rather than in the infrared, it is possible to vaporize silicates efficiently even if, in our case, the power energy is remarkably reduced at 266 nm. The targets are prepared by pressing silicate powder, obtained by grinding bulk minerals in an agate mill, between two stainless steel disks at 10 tons, producing pellets 13 mm in diameter and ~ 5 mm in thickness. The flat pellet surface optimizes the interaction between the incident laser beam and the silicate powder target. When the temperature of the target material rises to the boiling point, evaporation removes the material as a vapor. The target is mounted inside a vaporization chamber, designed to work in different gas environments. The pressure inside the chamber is usually maintained at 10 mbar. The gas used in the experiments presented here is O_2 . The oxidizing atmosphere prevents iron atoms from forming pure iron grains during the vaporization and condensation process and maintains the

chemical composition of the condensed grains very similar to that of the target. Nevertheless, we cannot exclude that part of the iron atoms oxidize. The samples thus produced are collected on substrates that are placed at a distance of ~ 10 cm from the target. The collection of the condensed dust or vapor phase condensates is performed normally to the target: the preferred collection direction. To allow this collecting geometry the target is vertically mounted inside the vacuum chamber, at an angle of 45° from the laser beam direction. The condensates are collected on different types of substrates depending on the analyses to be performed and further sample processing. The size range of the rather spherical vapor condensed grains, organized in chain-like aggregates can be selected by the sedimentation procedure (see "Silicate Dust Analogues: Natural Single Crystals"). The particle size distribution is determined by FE-SEM image analysis using the Global Image software.

Processed Samples—Condensed samples are produced and characterized (see "Silicate Dust Analogues: Condensed Samples") and these samples, deposited on silicon wafer chips, are then placed into a ceramic oven for thermal processing. The annealing process is performed under vacuum (10^{-6} mbar) at 1000°C for 1 h. The heating rate and the stability in temperature is controlled by an electronic device connected to a temperature sensor located on the samples holder. The annealing temperatures are reached at a rate of $23^\circ\text{C min}^{-1}$. These samples are analysed by FE-SEM and infrared spectroscopy to investigate thermally induced morphological and structural modifications due to re-crystallization.

Carbon-Based Analogues

Condensed Samples—Carbon-based vapor condensed samples are produced by laser vaporization technique (see "Silicate Dust Analogues: Condensed Samples") or by arc discharge (applied voltage = 100 V, current = 10 amp) between two amorphous carbon electrodes, in a controlled atmosphere composed of argon and/or hydrogen, at a pressure of 10 mbar. The material is deposited on silicon wafer chips for FE-SEM analyses of morphology and grain-size distributions in terms of material characteristics as was defined by Rotundi *et al.* (1998) for carbon-based samples.

Processed Samples—A wide range of processed, carbon-based materials was produced by thermal annealing, ultraviolet irradiation, ion bombardment and exposure to atomic hydrogen. Thermal annealing was applied to carbon-based material at fixed temperatures for time intervals of 3 h at a pressure of $<10^{-5}$ mbar in a stainless steel oven. For each new annealing run a new sample is used and an average heating rate of $\sim 10^\circ\text{C min}^{-1}$ is applied (Mennella *et al.*, 1995). To study effects induced by ultraviolet photons in hydrogenated carbon grains, samples were irradiated, at low temperature (~ 12 K) and at a pressure of 10^{-7} mbar by using a microwave-excited hydrogen flow discharge lamp with a MgF_2 window. At the

sample position the source provides a flux of ultraviolet photons, with an energy >6 eV, of $\sim 5 \times 10^{14}$ photons $\text{cm}^{-2} \text{s}^{-1}$ (Mennella *et al.*, 2001). Ion bombardment processing is performed at room temperature, in a vacuum chamber at pressure $<10^{-7}$ mbar. The Varian ion gun of 3 keV He^+ has been focused on a 1 cm^2 surface of the target sample. Low sample heating was assured by a low current (1.5 μA). Energy doses of 6.6 eV/C-atom, 66 eV/C-atom and 660 eV/C-atom have been used selecting fluences in the range 10^{15} to 10^{17} ions cm^{-2} (Mennella *et al.*, 1997). To investigate the interaction of hydrogen atoms with carbon particles, we have produced a beam of atomic hydrogen by microwave-excited dissociation of molecular hydrogen (99.9999% purity). The source consists of a Pyrex tube with an outer diameter of 10 mm and a thickness of 1 mm that is inserted in an Evenson cavity operated at 2.45 GHz with a 45 W microwave power output. We have estimated that a flux of 3.8×10^{15} H atoms $\text{cm}^{-2} \text{s}^{-1}$ per standard cubic centimeter per minute (sccm) of H_2 gas impacts on the sample located 9 cm from the source orifice. During source operation, the pressure in the chamber is $\sim 1.3 \times 10^{-3}$ mbar, allowing a mean free path for H atoms of ~ 7 cm (Mennella *et al.*, 2002).

Mixed Carbon-Silicate Dust Analogues

These samples are produced by laser vaporization using multiple natural bulk targets of either forsterite or fayalite and carbon fixed on the rotating holder placed facing towards the laser beam. It was not an ideal arrangement because the laser vaporization technique depend significantly on the target's thermal properties, its absorptivity at the selected laser wavelength and its surface smoothness. An improvement in the production of these analogue samples used pellets of pre-mixed either forsterite or fayalite plus carbon powders. After grinding the bulk materials (*e.g.*, natural forsterite and ultra-pure carbon rods) in a agate mill, a mixture composed of 150 mg of carbon and 450 mg of micron-sized forsterite grains, weighted with a microbalance (sensitivity of 1 μm), was pressed between two stainless steel disks at 11 tons into pellets of 13 mm in diameter, and <3 mm thick. It was necessary to use a higher pressure and lower thickness than those used for the preparation of the targets for the condensed silicates (see "Silicate Dust Analogues: Condensed Samples"), because the mixed pellets were very friable. For the same reason, we had to use two brand-new stainless steel disks, since even the smallest surface roughness jeopardized the useful pellet production. The laser beam is focused on these pellets selecting a 260 nm wavelength in order to maximize the absorption coefficient of the silicate and thus ensure an equilibrated evaporation of the two components. The morphology of the mixed samples were determined by FE-SEM image analysis and the particle size distributions was determined with the support of the Global Image software. The mixed samples were condensed in an oxygen-rich atmosphere without any control on the oxidation states of iron in the mixed sample

prepared with fayalite (Table 1). As a result we anticipate finding a complex condensed glass chemistry of reduced and oxidized iron and iron-bearing silicates, oxides, metallic iron and possible carbides. We have not yet analysed the condensed silicate compositions which still awaits analytical transmission electron microscope analysis. At this point our major concern was focused on the relative proportions and distribution patterns of the condensed carbon and silicate portions in the mixed samples using FE-SEM EDX analysis. At present the optimum procedure for determining the carbon and silicate distribution in these particular samples has not yet been established. Yet some preliminary results indicate that the C/Si ratio can be used as a quantitative, first-approximation, probe for the degree of mixing of the starting material, that is assuming there is no extraneous carbon and silicon in the system and carbon does not partition into the silicates. Thermal processing of the condensed samples followed the same procedure that was used for silicate analogues (see "Silicate Dust Analogues: Processed Samples").

RESULTS AND DISCUSSION

Silicate

The grounded crystalline grains were separated in different size intervals using a sedimentation procedure for the smallest (0–5 μm) size bins. Their grain-size distributions, average dimensions, chemical compositions, and optical behavior were determined. In the light of recent ISO observations (Cami *et al.*, 1997; Crovisier *et al.*, 1997; Meeus *et al.*, 2001; Sylvester *et al.*, 1999) the data for the crystalline silicate analogues are highly relevant. The optical behavior for crystalline analogues as a function of grain size and composition determined in the laboratory can support the interpretation of astronomical observations and were used, for example, to reproduce cometary spectra such as the Hale–Bopp (C/1995 O1) infrared spectrum determined by Crovisier *et al.* (1997). Brucato *et al.* (1999b) could fit the observed infrared spectrum by a combination of Mg-rich crystalline olivine, amorphous silicates and carbon-based analogues. From an extensive analysis of the spectral features of crystalline silicates, Jäger *et al.* (1998) was able to demonstrate that crystalline Mg-rich silicates are responsible for the observed sharp peaks at long wavelengths in the oxygen-rich circumstellar environments represented by the ISO spectra.

Another application of the silicate analogue data involves development, design and performance testing of space mission payloads. The silicate size fractions were used for calibration measurements of some instruments of the ESA/ROSETTA mission that is dedicated to cometary dust spectroscopic measurements using the visible and infrared thermal imaging spectrometer (VIRTIS; Coradini *et al.*, 1998), morphological/structural and dimensional characterization by the micro-imaging dust analysis system (MIDAS; Romstedt *et al.*, 2002)

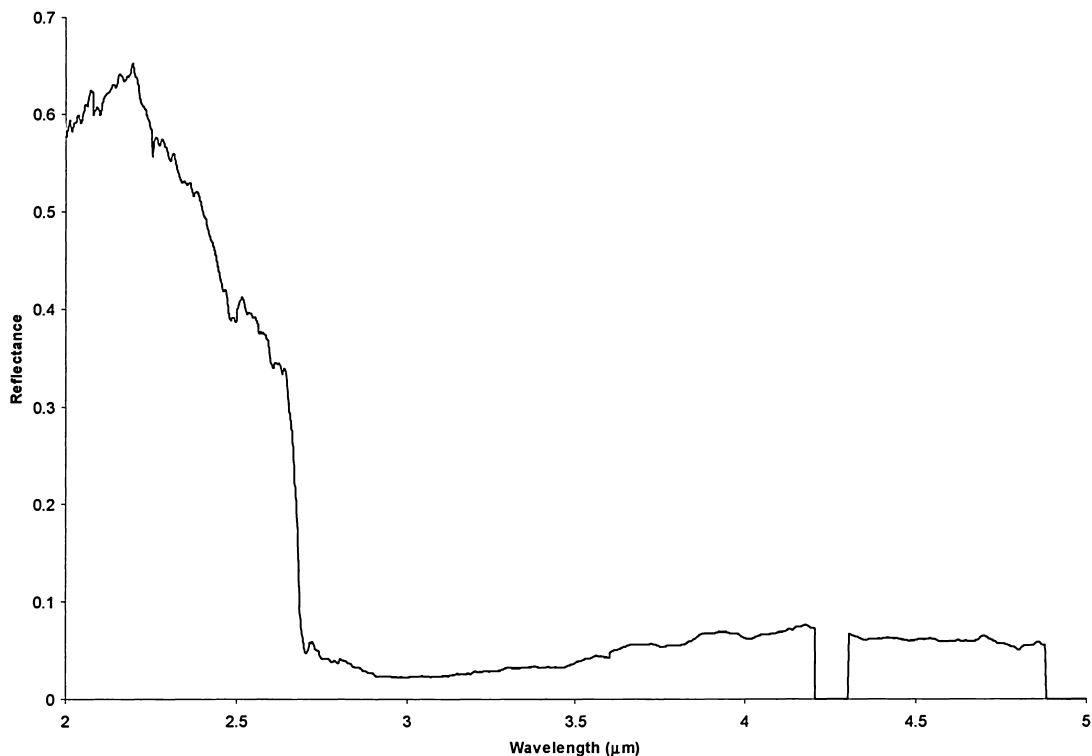


FIG. 1. Reflectance spectra acquired with the flight model of VIRTIS-H of enstatite mineral powder with well-characterized chemical and mineralogical properties and grain-size distributions.

and the grain impact analyser and dust accumulator (GIADA; Bussoletti *et al.*, 1999) for flux measurements and dust dynamics. As an example, we show the feedback from the VIRTIS team (Coradini *et al.*, 1998). Preliminary reflectance spectra acquired with the flight model of VIRTIS-H on a set of materials, including samples from our laboratory, are shown in Fig. 1 (Reess *et al.*, 2002). The spectra will be used for additional calibration procedures and for comparison with our laboratory spectra of the same samples.

The interstellar dust includes both crystalline silicates and amorphous silicates. The latter are invoked to explain typical infrared bands observed towards the diffuse interstellar medium (Whittet *et al.*, 1997) or young stellar objects (Jäger *et al.*, 1994) and comets (Hanner *et al.*, 1994). The exact nature of these silicates that are responsible for the infrared features is still uncertain. Thus, laboratory measurements on different types of amorphous silicates are of great importance for univocal interpretations of the astronomical data. Laboratory studies have to account for the spectroscopic properties of grains and for cosmic abundance of elements condensable in space environments. According to cosmic abundance evaluation by Snow and Witt (1996) silicates in space are expected to contain iron and magnesium; pyroxenes and olivine are considered good candidates to reproduce astronomical observations. Although the designation "amorphous olivine" has no sense as a mineralogical term, because it would be an olivine glass (Rotundi *et al.*, 2000), we will refer to the laser-

produced silicates as amorphous forsterite (FORA), amorphous enstatite (ENSA) and amorphous fayalite (FAYA). The condensed samples show two populations of grains: (1) agglomerates of small spheroidal grains and (2) isolated spheres (Fig. 2) with size distributions and average dimensions listed in Table 2. While the agglomerates of small grains are a proper product of the condensation process, the isolated spheres might be interpreted as resulting from post-condensation autoannealing (Rietmeijer *et al.*, 2002a,b). The best fit of the size distributions for the condensed silicates is given by a log-normal function for the agglomerates of small grains and a power law ($N(d) \propto d^{-P}$) for the isolated spheres. With the typical $1 \mu\text{m}$ sized EDX probe during FE-SEM analysis, only an average composition of the individual aggregate grains could be obtained. This is also true for the isolated spheres that we believe to be texturally homogeneous glasses. In this case we obtained the following compositions: $(\text{Mg}_{0.08}\text{Fe}_{0.92})_2\text{SiO}_4$, $(\text{Mg}_{0.92}\text{Fe}_{0.08})_2\text{SiO}_4$ and $\text{En}_{84}\text{Fs}_{12}\text{Wo}_4$, for the condensed FAYA, FORA and ENSA spheres. We do realize however that the assumption of a homogenous condensate glass may be incorrect and that these spheres are ultrafine-grained mixtures of non-stoichiometric silicates and oxides but still in relative chemical proportions that they resemble the compositions of crystalline starting materials. The minor iron present in the FORA sample is due to impurities present in the forsterite natural mineral used as a target for laser condensation. When only present as a minor percentage it will cause a well-documented shift in peak

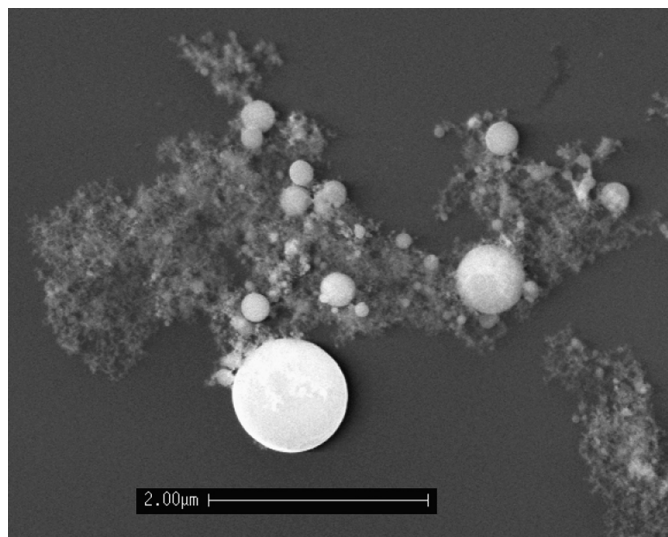


FIG. 2. FE-SEM photomicrograph of amorphous fayalite, deposited onto a smooth silicon wafer chip, showing the two populations of grains typical of condensed silicates: (1) small spheroidal grains with average dimension of 13.4 ± 0.3 nm forming agglomerates and (2) isolated spheres with average diameter of 35.0 ± 0.9 nm, probably due to post-condensation autoannealing.

TABLE 2. Average dimension of amorphous silicate calculated for the two populations constituting the samples.

Sample	Small agglomerated spheres (nm)	Isolated sphere (nm)
FAYA	13.4 ± 0.3	35 ± 1
FORA	29.4 ± 0.8	73 ± 12
ENSA	23.5 ± 0.5	130 ± 15

position in the infrared spectra compared to the pure-Mg olivine (Fabian *et al.*, 2001). The optical behavior of the FAYA and FORA materials have been studied in the wavelength range from $2.5 \mu\text{m}$ to 2 mm (Ferrini *et al.*, 1999; Mennella *et al.*, 1998a; Brucato *et al.*, 2002), while the ENSA spectroscopy was studied in the range $2.5\text{--}20 \mu\text{m}$ (Brucato *et al.*, 1999a). The infrared optical behavior of these condensed silicates confirms an amorphous structure for the ENSA and FAYA samples. For the FORA sample signatures of a crystalline component were detected in the infrared spectra. FE-SEM imaging shows a small amount of irregular crystalline grains that closely resemble the grains in the target material. They were probably unmelted fragments of the target. The survival of target fragments probably depends on the absorptivity coefficients of the different silicates at the laser wavelength emission: $\sim 250 \text{ cm}^2/\text{g}$ for forsterite and $\sim 1000 \text{ cm}^2/\text{g}$ for fayalite. This experimental artifact may actually have a positive aspect because it inadvertently simulates the co-existence of crystalline and amorphous silicates in space. In the context of structural transformations of the silicate component of cosmic dust from one astrophysical environment to another, it becomes

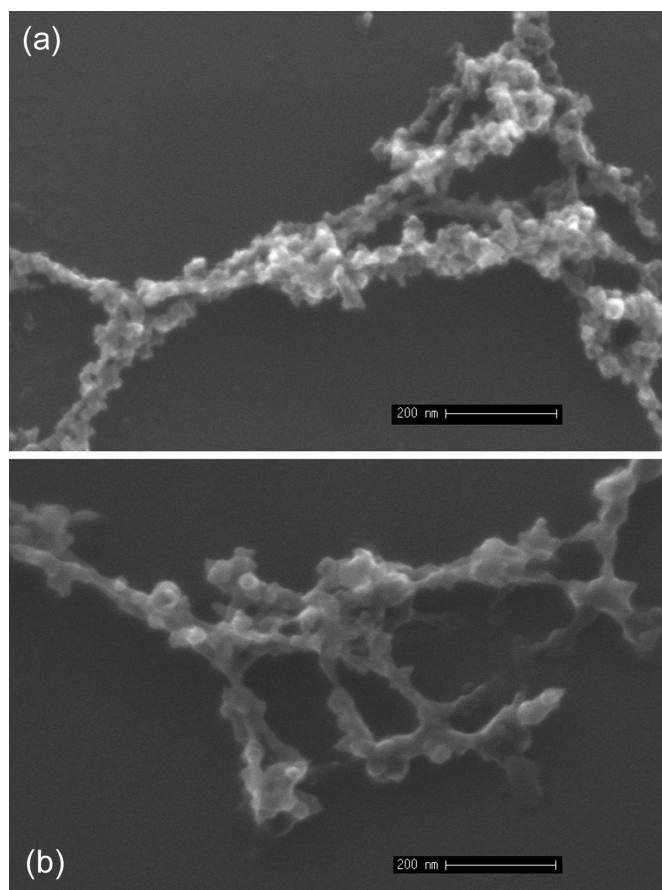


FIG. 3. FE-SEM photomicrographs of condensed forsterite, deposited onto a smooth silicon wafer chip, (a) before and (b) after thermal annealing (1 h at $1000 \text{ }^\circ\text{C}$). Morphological changes are visible along the agglomerated grains edges. Spherical agglomerates grains, typical of vapor condensed amorphous material, changed into more elongated structures with sharpened contours.

important to simulate the structural modifications induced by thermal annealing on silicates (Brucato *et al.*, 1999a; Fabian *et al.*, 2000; Rietmeijer *et al.*, 2002a,b). This type of processing can help to constrain the presence of crystalline silicates in comets as due to re-crystallization of pre-cometary amorphous silicates due to thermal processing. There is evidence for an evolution in the morphology of the annealed samples. Figure 3 shows two FE-SEM photomicrographs of forsterite samples before and after annealing with changes visible along the agglomerated grains edges. That is, the spherical agglomerates grains that are typical of a vapor condensed amorphous material have changed into more elongated structures with sharpened contours, hinting of a re-crystallization process.

Carbon-Based

Condensed carbon-based samples study has been undertaken to constrain the composition, morphology and structure of the interstellar dust. Nanosized amorphous carbon grains

are considered to be the main source for the ultraviolet interstellar extinction feature (Duley and Seahra, 1998; Mennella *et al.*, 1998b; Schnaiter *et al.*, 1998). Carbon-based condensates produced by arc discharge have been studied in depth by FE-SEM and transmission electron microscopy (TEM) (Rotundi *et al.*, 1998) to explore the morphological and textural properties as a function of systematic changes seen in the spectra of these analogues. These samples constitute ~70% of the amorphous material organized in "chain-like aggregates" (CLA) of individual spheres with diameters ranging from 7 to 15 nm (Fig. 4a). The remaining one-third of the sample is made of different forms of crystalline carbons. They include poorly graphitized carbon, "bucky-onions" (10 to 40 nm in diameter) (Fig. 4b), graphitic carbon ribbons and (rare) single crystal platelets. While the condensed carbon-based samples synthesized by the arc discharge technique form a complex mixture of solid carbon phases, the analogues produced at the same pressure and atmospheric composition using laser ablation consist only of carbon with the CLA texture. This confirms what was already stated by Rotundi *et al.* (1998): CLA is the only texture strictly related to the condensation process and it is not affected by auto-annealing. In addition, the optical behavior of these laser-condensed samples (Mennella *et al.*, 1999) confirmed the earlier conclusion by Rotundi *et al.* (1998) that pre-graphitic and graphitic structures cannot account for the ultraviolet peak shift observed in our experiments, that is, CLA carbon is mainly responsible for the spectral variations.

Processing of carbon-based cosmic dust analogues is of great importance in the study of cosmic dust since it can give hints on the carriers of spectral features in different space environments wherein the same materials occur but at different stages of textural and chemical evolution. For example, the spectral evolution that can be traced for dust in the interstellar and circumstellar environments might be a function of varying amounts of hydrogen in pure carbon materials affecting the structure of carbon grains. In order to constrain the possible interpretations of the $3.4\ \mu\text{m}$ band of the diffuse interstellar medium, a systematic study on the interactions of condensed nanometer-sized carbon grains with atomic hydrogen was performed (Mennella *et al.*, 2002). It could be shown that the interstellar component (*i.e.*, the C–H bond in the CH_2 and CH_3 groups) is responsible for the $3.4\ \mu\text{m}$ stretching band and that the associated bending features at 6.85 and $7.25\ \mu\text{m}$ are formed in the diffuse medium. That is, the carrier readily loses memory of its birth-site as a result of processing in the interstellar medium, which determines a new equilibrium value for the degree of hydrogenation. For instance, carbon grains that were produced in asymptotic giant branch (AGB) stars (Schnaiter *et al.*, 1999) or that originated in dense regions of the interstellar medium, which are either completely dehydrogenated or weakly hydrogenated, can contribute to the interstellar band once they are hydrogenated by exposure to H atoms in the diffuse medium.

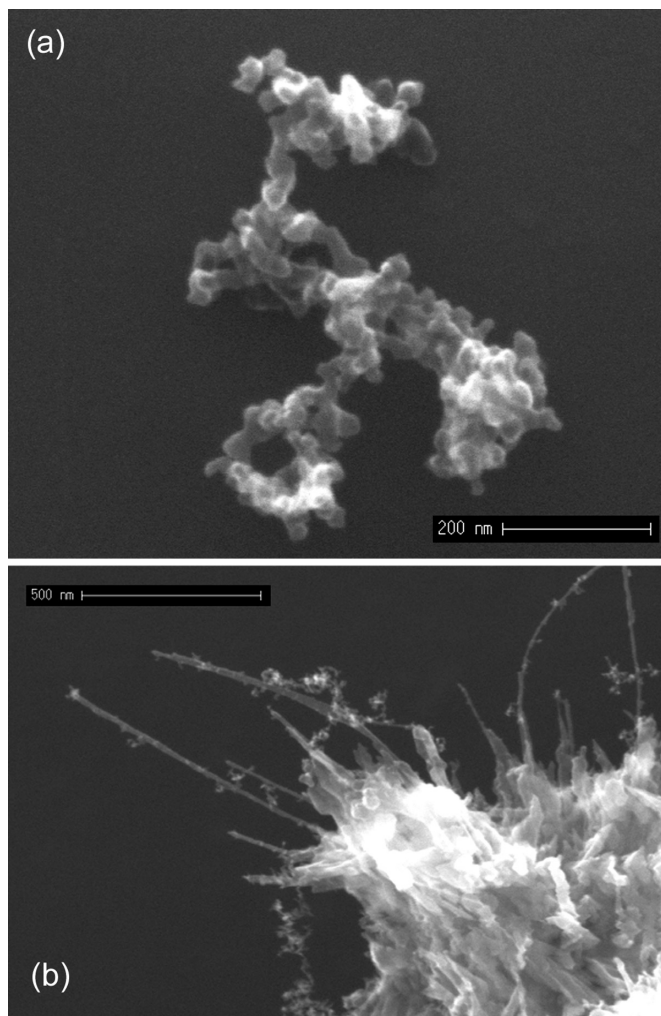


FIG. 4. FE-SEM photomicrographs showing amorphous carbon condensed from a vapor produced by the arc discharge technique onto a smooth silicon wafer chip. (a) Organized in "chain-like aggregates" (CLA) of individual spheres with diameters ranging from 7 to 15 nm, ~70% in area of the soot sample; (b) forming "bucky-tubes" up to about 100×10 nm.

Ultraviolet processing in the laboratory is aimed at studying the effects induced by energetic ultraviolet photons on hydrogenated carbon particles. Experiments have been performed under simulated diffuse and dense interstellar medium conditions. The effects of ultraviolet irradiation were monitored by infrared and ultraviolet spectroscopy. An estimation of the destruction cross section by ultraviolet photons for the hydrogenated carbon particles was derived from the reduction of the $3.4\ \mu\text{m}$ intensity band as a function of the ultraviolet fluence. The results of the infrared spectroscopy study can shed light on the enigmatic difference observed for the $3.4\ \mu\text{m}$ band between dense and diffuse interstellar medium clouds. This difference is compatible with the transformation of hydrogenated carbon particles produced by ultraviolet photons and hydrogen atoms and with the changes of the grain

properties in the two environments (Mennella *et al.*, 2001). Small carbon grains, processed by ultraviolet radiation and cosmic rays, have been proposed as carriers of the 217.5 nm bump present in the interstellar extinction curves (Hecht, 1986; Sorrell, 1990). A good understanding of the reasons for the observed ultraviolet interstellar extinction profile variations has recently been obtained in terms of the contribution of different nanometer-sized hydrogenated carbon grains with different degrees of ultraviolet processing along different lines of sight (Mennella *et al.*, 1998b). As a first approximation of the cosmic-ray irradiation active in space, we have studied the effects induced by 3 keV He⁺ ions on the ultraviolet spectrum of small cosmic analogue carbon grains. Relevant ultraviolet spectral variations are observed after ion irradiation and are interpreted in terms of grain "nanostructure" changes induced by the interactions with ions. The results of these experiments suggest that hydrogenated amorphous carbon grains can not be transformed into graphite grains by cosmic-ray irradiation. Systematic ion bombardment of hydrogenated amorphous carbon leads to the formation of pure carbon, that is, increasing the ion doses the spectral behavior of hydrogenated amorphous carbon gradually starts to resemble that for pure carbon. Optical properties of the carbon dust depend on the carbon structure and the presence of heteroatoms (Robertson, 1991). Due to a tendency of carbon atoms to form aromatic clusters, the loss of hydrogen causes a re-organization of the texture into areas of short-range order. The result is a "nanostructure" that occurs in small areas of about 5–7 nm in size wherein carbon atoms in a graphite-like arrangement have clustered together. This textural re-ordering that developed during ion bombarding is ironically also inhibited by the same process. In fact, carbon atom re-arrangement reaches a standstill because the continuous ion radiation destroys any type of existing or developing structured texture. The spectroscopically amorphous carbon can not be transformed into any type of structured elemental carbon by ion bombardment because two competing processes—graphitisation and amorphisation—occur. The ion bombardment simulation experiments (Mennella *et al.*, 1997) conclusively show that the existence of graphite in space must be extremely rare and would require unusual, as yet unidentified, astrophysical processes.

Mixed Carbon-Silicates

Mathis (1996) proposed a composite interstellar dust model that consists of small graphite particles, small silicate particles, and composite fluffy aggregates of carbon (either amorphous, hydrogenated amorphous, or graphitic), silicates, and oxides. Through laboratory experiments, astrophysical and mineralogical arguments, the presence of graphite in space environments has been questioned (*e.g.*, Mennella *et al.*, 1997; Draine and Malhotra, 1993; Rietmeijer, 1988). Other theoretical models and laboratory measurements compared to astronomical observations suggested that nanosized amorphous

carbon grains occur instead of graphite particles (Duley and Seahra, 1998; Mennella *et al.*, 1998b; Schnaiter *et al.*, 1998). Laboratory measurements also give support to the composite grain hypothesis. Using the measured thermal dependence of the absorption coefficients for two different kinds of amorphous carbon grains, either produced by condensation in an argon atmosphere or *via* burning benzene in air, and both crystalline and amorphous Fe-rich and Mg-rich olivines, Mennella *et al.* (1998a) concluded that the carriers of the diffuse far-infrared to millimeter interstellar dust emission spectrum are composite grains with a fixed ratio of silicate to carbon mass of 4.47 ± 0.36 . This value is consistent with the mass ratios of 4 to 6 reported by Mathis (1996).

Although silicate and carbon dusts have different and independent origins (Meeus *et al.*, 2001) in the diffuse interstellar medium, mixed carbon-silicate particles are predicted to exist by laboratory measurements of the thermal dependence of carbon and silicates absorption coefficients fitting astronomical observations (Mennella *et al.*, 1998a) and by recent interstellar dust models (Mathis 1996). Mixed particles are also implied by core–mantle models (see, among many publications, Li and Greenberg, 1997). Physical mixtures of silicates and carbon appear to be inconsistent with IDP observations that show compact grains, 100 to 1000 nm in diameter, of ultrafine silicates and sulphides embedded in a matrix of volatile carbonaceous and amorphous carbon material (Rietmeijer, 2002), and with spectro-polarimetric observations to constrain the nature of the 3.4 μm absorber in the interstellar medium (Adamson *et al.*, 1999). These observations have shown that, unlike the 9.7 μm silicate band, the 3.4 μm C–H stretching feature along the same line of sight is not polarized. It is produced rather by small, unaligned grains than by carriers residing in a mantle on silicate cores. The presence of mixed particles has been inferred in comet P/Halley (*e.g.*, Kissel and Krueger, 1987; Jessberger *et al.*, 1988; Fomenkova *et al.*, 1992, 1994) and found in IDPs (Rietmeijer, 2002). When mixed silicate-carbon particles occur in various astrophysical settings the question arises how they were formed. Mathis (1996) assumed that composite grains formed during coagulation, since fitting separate small grains into a completely filled matrix seems difficult. Mixed particles formed in dense clouds (Mathis, 1996) could become part of comets through interstellar grains clumping. On the other hand, the presence of mixed grains in aggregate IDPs, and thus also in comets, suggests that post-accretion parent body processing of silicate and carbon dust can not be ignored (Rietmeijer, 2002). Laboratory experiments on the evolution from frozen gas to refractory molecular solid driven by ion irradiation (Strazzulla and Baratta, 1992) support the idea that mixed particles form on comet nuclei by cosmic-ray bombardment of materials in different stages of evolution. These stages included (1) pre-cometary grains processing in the diffuse interstellar medium, (2) pre-cometary grains processing in increasingly larger cometesimals during the accretion stage of the solar nebula,

and (3) cometary material processing during prolonged residence in the Oort cloud and the Kuiper belt.

Another way to explain the presence of mixed particles is by simultaneous condensation of silicate and carbon-rich dust. Is there an astronomical environment wherein this co-condensation process might be achieved? It can be hypothesized to occur in some ISO sources with a peculiar stellar evolution from an O-rich to a final C-rich environment (Waters *et al.*, 1998). Furthermore, simultaneous condensation of carbon and silicates might occur during supernova shocks that caused the evaporation of silicates and carbon-rich grains (Jones *et al.*, 1994) and the subsequent co-condensation as physical mixtures.

Our experiments of laser ablation on silicate-carbon mixed targets produced aggregates of submicron or micron-sized individual carbon and silicate components. These components although being a physical mixture still maintain their own identity, such as in the proposed composite interstellar dust models based on both observation and laboratory measurements (Mathis, 1996; Mennella *et al.*, 1998a). They resemble the carbonaceous and ferromagnesian silicate principal components (PCs) in the matrix of aggregate IDPs (Rietmeijer, 1998, 2002). Our analogues will be excellent starting materials to study the notion that the formation of mixed silicate-carbon particles could be a post-accretion modification process. A typical mixed grain is shown in Fig. 5a which typically forms out of fluffy aggregates of carbon-rich based material; it is represented by the fluffy aggregates of small particles (average diameter = 25.2 ± 0.8 nm) with a minor fraction of large embedded silicate spheres.

Regarding the structure of the fayalite-carbon sample, we can infer that it is amorphous from its infrared optical behavior that shows the typical broad bands testifying the total loss of long range order (Rotundi *et al.*, 2000). While the C/Si ratios match those of the physical mixture that was used as the starting material in the target for laser ablation, the condensation of the silicates and carbons did not produce a well-mixed "carbophilite" phase. Instead, co-condensation yielded separated silicate and carbon condensates aggregated into a physical mixture. This physical rather than chemical mixing is confirmed by the optical behavior of these samples in the 2.5–100 μm range. The mass absorption coefficient in this range shows two broad bands peaking around 10 and 20 μm that are characteristic of the Si–O stretching and O–Si–O bending vibrational modes of amorphous olivine while the fluffy carbon aggregate mainly produces a continuum and a shoulder at 6.4 μm (Rotundi *et al.*, 2000). Preliminary thermal annealing on the mixed carbon-forsterite samples showed an overall texture (Fig. 5b) more defined and with sharpened edges with respect to the condensed sample (Fig. 5a).

FUTURE WORK AND PROSPECTS FOR COMETARY DUST ANALOGUE STUDIES

The preparation and laboratory analyses of cosmic dust analogues serves a dual purpose, *viz.* (1) gaining scientific

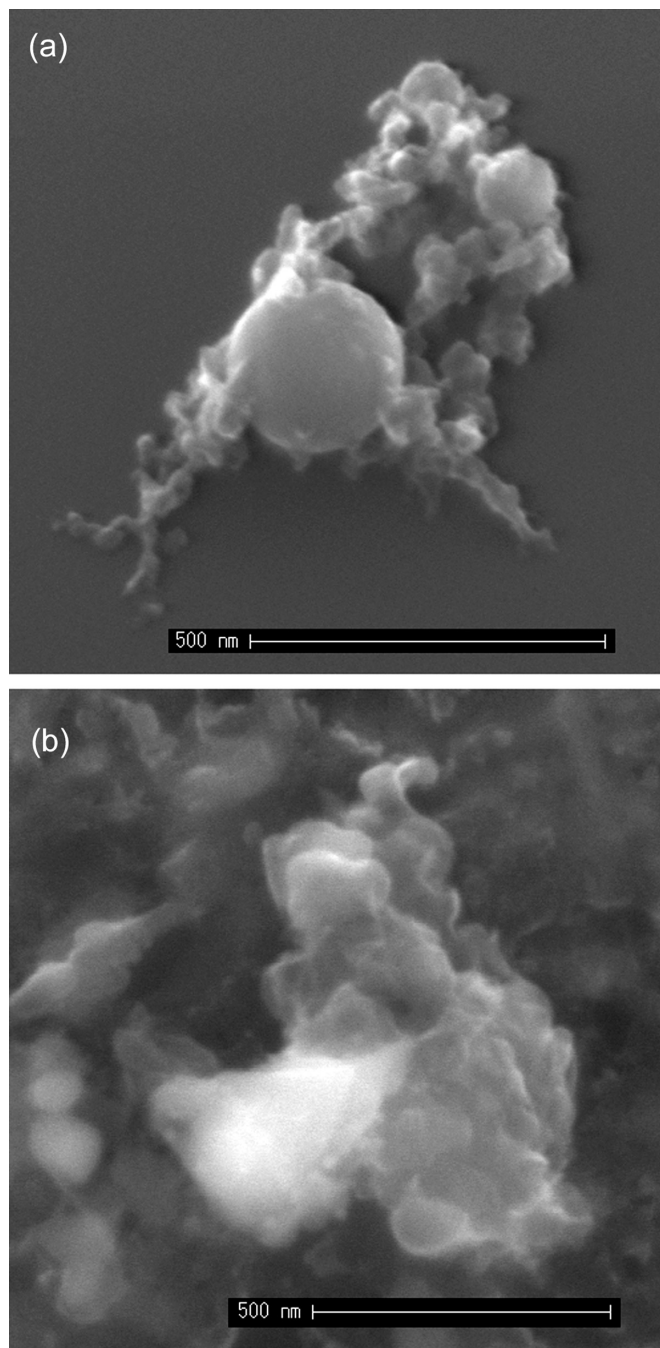


FIG. 5. FE-SEM photomicrographs of (a) a condensed mixed sample of carbon plus forsterite onto a smooth silicon wafer chip. Three different populations are visible: (1) agglomerates of tiny grains (bottom left corner) similar to the CLA texture of amorphous carbon, (2) slightly larger spheroidal grains agglomerated (upper right) and (3) isolated spheres (center). (b) Sample after thermal annealing. The overall texture of the annealed sample is more defined showing sharpened grain edges with respect to the amorphous sample. The roughness of the substrate of the annealed sample is visibly increased due to the heating.

knowledge on dust-forming and modification processes in environments that cannot yet be reached for sample collection, and (2) to develop, prepare and calibrate instruments that will make the necessary remote sensing observations. The potential implications for the first goal are demonstrated by success of the ISO mission. At this time, the second goal has considerable practical interest for the development of space missions to study short-period comets. These missions include CONTOUR (comets 2P/Encke and 29P/Schwassmann-Wachmann 3), Deep Impact (comet 9P/Tempel), STARDUST (comet Wild), and ROSETTA that will encounter comet 46P/Wirtanen in 2012, and planning for a future comet nucleus sample return mission. To these ends, several laboratories around the world are involved in these simulation studies (Carrez *et al.*, 2002a,b; Koike *et al.*, 2002; Nuth *et al.*, 2002).

For example, samples of analogues prepared and characterized by the techniques described in this paper were delivered to various ROSETTA teams working on dust detection and analysis instruments but tailored to their specific needs. By using well-characterized analogues the performance of flight models was successfully evaluated and laboratory measurements supporting instrument development were conducted efficiently. Light-scattering analyses have been performed (Volten *et al.*, 2001) on a sample of grounded and selected (diameters $< 5 \mu\text{m}$) crystalline enstatite grains provided by our laboratory, in support of the optical, spectroscopic, and infrared remote imaging system (OSIRIS; Thomas *et al.*, 1998); (2) atomic force microscope (AFM) investigations were performed on different types of analogues produced in our laboratory to support the development of the MIDAS instrument. The goal was to study the performance of a commercial instrument (PARK SA) against the performance of the MIDAS experiment. In Fig. 6 we show an AFM image of a carbon-based sample produced by arc discharge in argon atmosphere. All the data generated in laboratories at the Cosmic Physics Laboratory (Naples, Italy) on the techniques used in the production and processing of cosmic dust analogues are archived along with the analytical results. The database has been developed using Microsoft Access for easy access and general use.

CONCLUSIONS

We have described here various techniques to produce and fully characterize cosmic dust analogues for the dual purpose of understanding current remote sensing astronomical observations and in preparation of instruments to perform these observations (and other applications) and for mission directed towards short-period comets. We are also aware that some of our techniques are used in other laboratories pursuing similar goals and that there are differences. We emphasize a systematic analogue study whereby we prepare the formation and evolution of the initial, small-scale, building blocks of comet nuclei. Such analogue samples include (1) pre-cometary

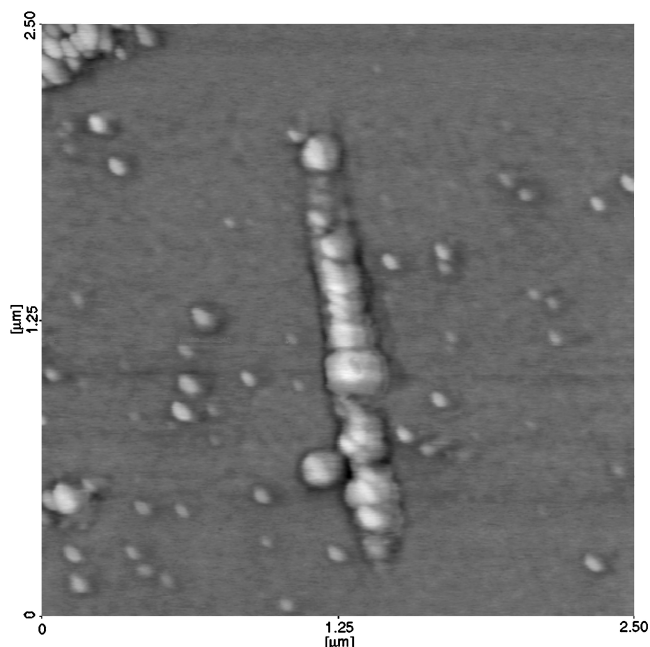


FIG. 6. Atomic force microscope image taken by the MIDAS team (reproduced by courtesy of J. Romstedt) of the amorphous CLA carbon texture shown in Fig. 4. It shows a chain of ~ 20 individual particles across the image. In the upper left corner is an aggregate of particles. The smallest grains on the substrate have a height of 7 nm.

material—grains present in the presolar nebula that are mixtures of amorphous silicates and carbon-based materials; (2) refractory cometary material—a porous matrix of carbon and amorphous and crystalline silicates. The study of amorphous and crystalline silicate analogues is critical for the interpretation of ISO observations that produced the first unambiguous mineral identifications in astronomy, reporting pure Mg-silicates (*e.g.*, forsterite and enstatite), but also silica and diopside, a Ca-rich clinopyroxene, $\text{MgCaSi}_2\text{O}_6$, present in aggregate IDPs (Rietmeijer, 1998, 2002). Carbon-based analogues processing can help to constrain the structure and composition of carbon depending on the astrophysical environment. We have shown how FE-SEM, EDX analyses and infrared spectroscopy of silicate, carbon-based and mixed dust analogues will be relevant to both the academic and practical aspects of space science. As part of future work we intend to produce mixed samples that will incorporate a volatile component and to explore the evolution of cometary material using mixtures of carbon, silicates and ices processed by ultraviolet and ion irradiation and thermal annealing to simulate modifications at the surface due to cosmic-ray bombardment and post-accretion thermal annealing at perihelion.

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