

CARBONACEOUS PHASES CHARACTERIZED IN TWO INDIVIDUAL STARDUST PARTICLES: FTIR AND RAMAN SPECTRA OF FEBO AND ADA. B. Wopenka, *Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130 (bwopenka@levee.wustl.edu)*, G. Matrajt, *Department of Astronomy, University of Washington, Seattle WA, 98195 (matrajt@astro.washington.edu)*, S. Bajt, *Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore CA, 94550*, D. Joswiak, *Department of Astronomy, University of Washington, Seattle WA, 98195*, D. Brownlee, *Department of Astronomy, University of Washington, Seattle WA, 98195*.

Introduction: We present the results of a molecular spectroscopic investigation of the carbonaceous phases of two Stardust (SD) particles called Febo (8 μm) and Ada (12 μm), extracted from tracks # 57 and 26, respectively. Both of these particles were previously investigated with TEM, C-XANES and nanoSIMS [1]. Febo is composed of a large pyrrhotite grain, an enstatite and olivine grains, and a large volume of fine-grained material (with chondritic composition) in which C-rich phases (≤ 200 nm) were found. Ada is composed of multiple nodules of fayalite that are each surrounded by rims of crystalline SiO_2 (tridymite). Small C-rich phases were found at the periphery of this particle (TEM). The carbon-rich areas of both particles also contain O and N (XANES) and are enriched in D and ^{15}N (nanoSIMS) [1]. In the present study we focused on the investigation of the C-rich areas in both particles by analyzing microtomed sections using FTIR and Raman spectroscopies, in order to gain further insight about the molecular make-up of these carbonaceous organic materials.

Analytical Methods: The tracks with the particles, received inside aerogel keystones, were processed using the "acrylic embedding" technique developed at the University of Washington [2]. Contiguous ultramicrotomed sections of various thicknesses (70 to 95 nm) were placed over Ni supports and TEM grids and analyzed with TEM followed by FTIR and then Raman. Infrared spectra were obtained at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (Berkeley, CA), using a Thermo-Nicolet Magna 760 FTIR bench (KBr beamsplitter) and a SpectraTech Nic-Plan IR microscope in reflectance mode, and an MCT-A detector. Raman analysis was performed with a Raman microprobe based on an axial spectrograph with volume holographic transmission gratings (KOSI HoloLab 5000), 532-nm excitation laser, a Leica microscope, and an Andor CCD array detector that could simultaneously detect the whole spectral range from 100 to $4000 \Delta \text{cm}^{-1}$ with a spectral resolution of 2.5 cm^{-1} . The sample sat on the platform of a computer controlled x-y-z-stage, which allowed for precise selection and repeated analysis of several individual, photo-documented micrometer-sized analysis spots within each SD thin-section. Peaks were deconvolved with a mixed Gaussian-Lorentzian algorithm.

FTIR Results: The two particles have very different IR reflectance spectra (Fig. 1). Ada has two strong peaks in the region of $2800\text{-}3000 \text{ cm}^{-1}$. Those peaks are at 2918 and 2848 cm^{-1} , and correspond to the asymmetric and symmetric stretch of $-\text{CH}_2$ groups in long aliphatic chains, respectively. In addition, Ada has a weak peak at 2954 cm^{-1} which corresponds to the asym. stretch of $-\text{CH}_3$ groups. Febo, on the other hand, does not show any distinct peaks in the region

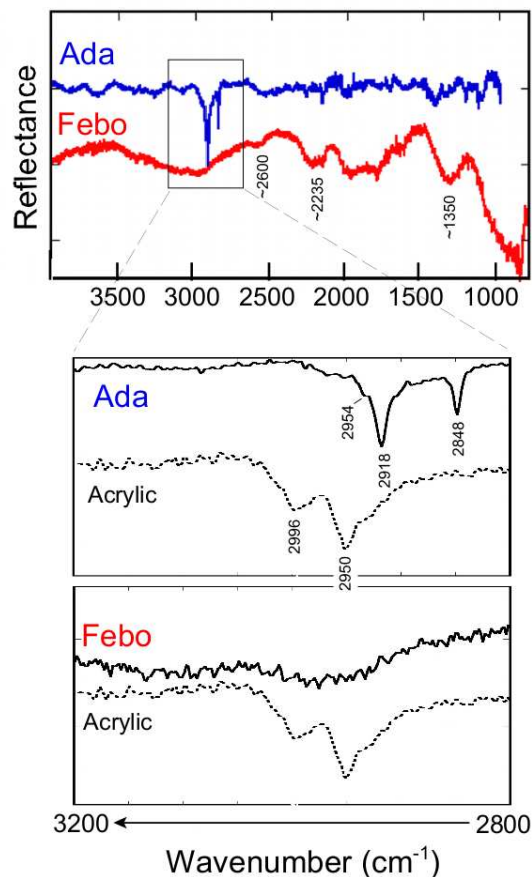


Figure 1: FTIR spectra.

of $2800\text{-}3000 \text{ cm}^{-1}$ corresponding to the non-aromatic (e.g., aliphatic) C-H stretching zone, but rather has a very broad ($\sim 1000 \text{ cm}^{-1}$ wide), weak, unstructured band between $2500\text{-}3500 \text{ cm}^{-1}$. In addition, Febo has several broad peaks between 2400 and 1200 cm^{-1} , none of which could be unambiguously assigned yet. The peaks observed in Ada and Febo were not caused by contamination. Both the acrylic resin (see Fig. 1) and aerogel [3] have very distinctive peaks that are at different positions than the peaks found in our particles.

Raman Results: The Raman spectra for Febo and Ada show bands that are characteristic for both inorganic and carbonaceous organic components. With respect to the inorganic peaks (not shown here), Raman could confirm the presence of pyrrhotite (peaks at 317 and $375 \Delta \text{cm}^{-1}$) in certain areas of

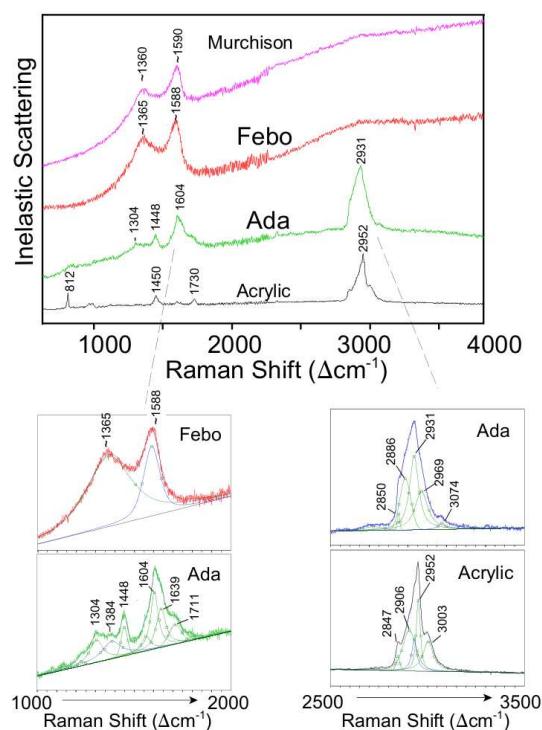


Figure 2: Raman spectra

the Febo grain [4]. Raman, however, could not detect peaks for fayalite or tridymite in Ada, but rather showed (in some of the analyzed $1\mu\text{m}$ areas) strong, wide, glass-like peaks (at ~ 318 and $\sim 595 \Delta\text{cm}^{-1}$) of a yet unidentified phase. The latter may be an Fe-silicate that is an artifact due to heating of nanocrystalline fayalite and tridymite under the laser beam. Of special interest here is that both particles also showed Raman peaks that are characteristic for organic compounds, and those organics are distinctly different for Febo and Ada (Fig. 2). The organic Raman signature could be obtained in the fine-grained chondritic area of Febo (but not in its sulfide grain), and it shows the typical "double-hump" feature that also was found for previously analyzed SD particles [5]. The wide peaks centered at ~ 1365 and $\sim 1590 \Delta\text{cm}^{-1}$ are referred to as D and G bands and are characteristic of aromatic sp^2 -bonded carbonaceous molecules such as large arrays of condensed benzene rings (PAHs) or so-called "disordered carbonaceous material", which is essentially "dirty" (i.e., lots of heteroatoms like N, O) graphite-like material. The D and G bands are also found in Murchison, which we show for reference and comparison. The SD particle Ada, on the other hand, shows a very different type of organic Raman signature, at least in one of the analyzed areas. This characteristic organic spectrum of Ada (Fig. 2) is dominated by strong C-H stretching peaks in the $\sim 2900 \Delta\text{cm}^{-1}$ region and also has ten peaks between 1100 and $1800 \Delta\text{cm}^{-1}$ that are very different from the D and G band profiles for disordered aromatic carbonaceous material. The strongest bands are found at 1304 , 1384 , 1448 (CH_2 bending), 1604 (ring C-C stretch), 1639 , and 1711 ($\text{C}=\text{O}$) Δcm^{-1} . We rule out contamination with acrylic, because the band profile in the C-H stretching region in Ada is very different from the one of polymethylmethacrylate (Fig. 2). The C-H stretches

for acrylic are at 3003 , 2952 , 2906 , $2847 \Delta\text{cm}^{-1}$, whereas the ones for Ada are characteristic for alkane-type saturated hydrocarbons and are at 3074 , 2969 (asym. CH_3), 2931 (asym. CH_2), 2886 (sym. CH_3), and 2850 (sym. CH_2) Δcm^{-1} . In addition, acrylic has bands at 364 , 488 , 600 , 812 (strong), 966 , 988 , 1119 , 1450 (strong), 1604 , 1730 (strong), which were absent in the spectra for Ada and Febo.

Conclusions: Both FTIR and Raman show that Ada and Febo contain very different organic molecules. We found evidence for hydrogen-saturated alkane chains (in Ada) and benzene-based aromatic carbonaceous molecules (in Febo). Both techniques confirmed that the peaks observed are not caused by contamination introduced by the capturing and mounting media (aerogel or acrylic). Ada contains alkane-type saturated hydrocarbons, i.e., aliphatic material (which is different from aerogel or acrylic), and which is absent in Febo. In addition the aliphatic Raman signature observed in Ada is different from the one previously observed in SD particles [5,6]. Raman clearly shows that Febo contains aromatic material (such as "disordered graphite"), and its IR spectrum confirms Febo's non-aliphatic character. Our Raman and FTIR results of Febo and Ada confirm previous observation obtained with C-XANES and nanoSIMS [1], showing that the organic material in these two SD particles is heterogeneously distributed. Our results are also in agreement with previous Raman findings on three other SD particles [5] in that they show that different SD particles seem to contain different kinds of organic materials.

References: [1] Matrajt et al (2008) *M&PS*, in press. [2] Matrajt and Brownlee (2006) *M&PS*, **41**, 1715-1720. [3] Bajt et al (2008) *M&PS*, submitted [4] Wopenka et al (2007) *M&PS*, **42**, A5048 [5] Rotundi et al (2008) *M&PS*, in press [6] Sandford et al (2006) *Science*, **314**, 1720-1724.