RAMAN ANALYSIS OF HIGH-DENSITY PRESOLAR GRAPHITE GRAINS FROM THE ORGUEIL CARBONACEOUS CHONDRITE. B. Wopenka', M. Jadhav', E. Zinner', 1Department of Earth and Planetary Sciences, Washington University in St. Louis, One Brookings Dr., St. Louis, MO 63130, USA. bwopenka@levee.wustl.edu, 2Laboratory of Space Sciences and the Physics Department, Washington University in St. Louis, St. Louis, MO 63130, USA, 3Present address: Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, HI 96822, USA.

Introduction: We have started a combined Raman, NanoSIMS, and TEM investigation of different density fractions of presolar graphite grains from Orgueil [1]. Here we report on Raman results of 21 grains from mount OR1f3m of the high-density fraction OR1f (2.02–2.04 g cm⁻³), which were analyzed with a Kaiser Optical Systems Raman microprobe and 532 nm excitation before any NanoSIMS analyses were done. This sequence is important, because we noticed that primary beam bombardment during SIMS analysis can have an effect on sp² hybridized C-C bonds, and thus can change the Raman spectral response and interpretation. Raman spectral parameters (positions, widths and intensities of Raman peaks) were determined by the deconvolution of raw spectra (i.e., without any background correction) by using a 100% Lorentzian peak shape. The isotopic ratios of the grains are reported in an accompanying abstract [2].

Results: Despite the fact that all grains had the same morphology (onion type with smooth surfaces) we found three different types of sp² carbon spectra. The full Raman spectra (from 500 – 4000 Δcm⁻¹) of selected grains are shown in Fig. 1. Most of the grains (18/21) have indeed the spectra of graphitic (i.e., crystalline) sp² carbon, and thus deserve to be called "presolar graphite". Graphitic carbon is characterized by narrow first- and second-order Raman peaks. Whereas well-crystalline terrestrial Ceylon graphite does not show any D (disorder) peak at ~1350 Δcm⁻¹, all of the 18 graphitic Orgueil grains showed some crystalline disorder, which means that their graphitic in-plane crystallite sizes are reduced relative to that of Ceylon graphite. The disorder (expressed as intensity ratio of D and G peaks which

Fig 1. Examples for pre-SIMS first- and second-order Raman spectra obtained on presolar high-density Orgueil sp² carbon grains. Note that all spectra are shown as raw spectra, i.e., no background subtraction was performed. a) Three types of sp² carbon spectra were observed. 18/21 graphite grains had spectra with narrow bands characteristic for crystalline graphite, 2/21 grains (G-9 and G-19) had kerogen-type spectra characteristic for amorphous carbonaceous material, and one grain (G-13) had an "in between spectrum", that was almost identical to the unusual spectrum of Allende IOM (I_d>I_G). b) The grains with graphitic sp² showed a range of disorder. Peak intensity ratios are listed for the spectra shown, but they did not correlate with any isotopic or elemental compositions of the grains. c) Graphitic sp² grains with and without fluorescence.
can be converted to in-plane crystallite size in Angstroms according to the historical calibration by [3] was found to be different for different grains, but is consistent for different μm spots on the surface of a given grain. We observed a strong (to be expected) correlation between the intensities of the D peak and second-order peak at 2698 Δcm⁻¹ (Fig. 1b). Most graphitic grains show no or very little fluorescence (Fig. 1b), while others show substantial fluorescence (Fig. 1c).

Two (out of 21 measured) Orgueil grains (G-9 and G-19) have non-graphitic Raman spectra, but rather spectra that are typical for non-crystalline macromolecular carbon (i.e., amorphous carbon) that is also found in the insoluble organic matter (IOM) of primitive meteorites [4], in cometary samples from the Stardust mission [5], or in terrestrial kerogens [6]. Those kerogen-type sp² carbon spectra (Fig. 1a), have substantially wider first-order bands (Fig. 2), with I₂/I₁, and very subdued (or non-existent) second-order bands, and their D/G intensity ratios cannot be interpreted in the same way as the ones for graphitic sp². One Orgueil grain (G-13) was found to have a spectrum that is almost identical to the one of IOM from Allende, which has a very characteristic and unusual sp² carbon Raman spectrum (I₂>I₁, with medium wide peaks – see Fig. 1a). Fig. 2 shows the D and G widths of those three different types of sp² carbonaceous materials compared to those of meteoritic IOM.

The intensity of fluorescence (expressed by the difference of the signal at 2200 and 400 Δcm⁻¹ wavenumbers normalized to the intensity of the D band) seems to be correlated with the N content (expressed by the ¹³C/¹²C ratio measured with the NanoSIMS) (Fig. 3), but is not correlated with any other elemental or isotopic compositions measured in these grains [2].

We observe some correlation between the G position of the graphitic grains and their ¹²C/¹³C ratio (Fig. 4). However, no other correlation was found between isotopic ratios and any of the other Raman parameters.

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Figs. 2-4. Correlation plots of optical parameters (Raman and fluorescence) and SIMS results. Plotted Raman data are averages of individual spectral acquisitions measured on 5 different ~1 μm spots for each grain. Standard deviations are comparable to symbol size in Fig. 2 and are ±0.5 Δcm⁻¹ in Fig. 4.