RAMAN AND LASER-INDUCED FLUORESCENCE SIGNATURES OF ISOTOPICALLY PRIMITIVE AND NORMAL IDPs. B. Wopenka[1] and C. Floss[2], [1]Dept. of Earth and Planetary Sciences and [2]Laboratory for Space Sciences and Physics Dept., Washington University, St. Louis, MO 63130, USA. (bwopenka@levee.wustl.edu).

Introduction: Interplanetary dust particles (IDPs) are among the most primitive solar system materials available for laboratory study. Isotopic work on IDPs has shown the existence of a sub-group of isotopically primitive IDPs, characterized by the presence of bulk N isotopic anomalies and high abundances of presolar phases [1]. One intriguing observation is that these primitive IDPs have uniformly low bulk CN^-/C^- ratios compared to normal IDPs. Because the N isotopic anomalies found in IDPs have been associated with carbonaceous organic matter, we used Raman spectroscopy to characterize the carbonaceous phases in the particles; this technique can be very sensitive to subtleties in the bonding of amorphous sp^2-bonded carbon. Raman spectra may also provide information on the overall mineralogy of these IDPs. Our goal is to determine whether particles with primitive isotopic signatures have characteristic features in the Raman/visible fluorescence spectra that distinguish them from isotopically normal IDPs.

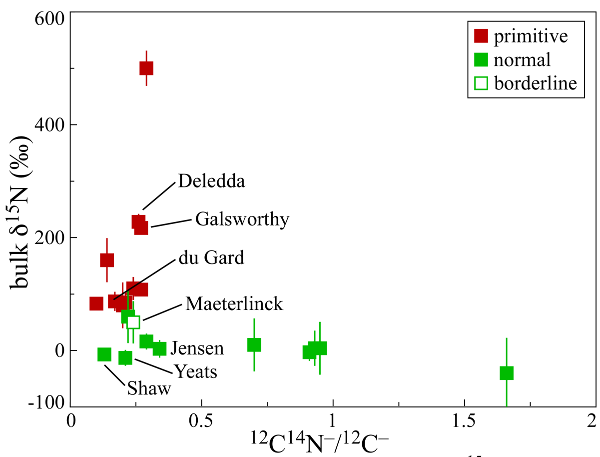

Figure 1. CN^-/C^- ratios versus bulk $\delta^{15}N$ (‰) for isotopically primitive and normal IDPs. Data are adapted from [1]. One IDP is labeled 'borderline; see text for details.

Isotopic Observations: Figure 1 shows the bulk N isotopic compositions and CN^-/C^- ratios of 21 IDPs from the study of [1] that were investigated here (nicknames are from [1]). Ten of the IDPs, classified as isotopically primitive, have ^{15}N enrichments and low CN^-/C^- ratios (< 0.3). The remaining 11 IDPs have normal N isotopic compositions, with CN^-/C^- ratios that range from 0.1 to 1.7. Note that the CN^-/C^- ratios differ from those reported by [1], due to a recalibration of the data, but the conclusions remain unaltered. The primitive IDPs also contain presolar silicates, with an overall abundance of ~375 ppm [1], whereas no presolar grains were found in the normal IDPs. Carbon isotopic compositions are normal in all of the IDPs.

Experimental: Raman and fluorescence spectra were measured on fragments of these IDPs remaining after the earlier isotopic study; in order to exclude potential artifacts in the sp^2 bonding/molecular structure caused by the SIMS analyses, the spectroscopic study was carried out on regions of the individual particles that were outside of the areas analyzed by the NanoSIMS. A KOSI HoloLab 5000 Raman microprobe with 532 nm excitation was used. The entire spectral range from 100 to 4000 Δ cm^{-1} can be detected simultaneously with a spectral resolution of 2.5 cm^{-1} (see [2] for more instrumental details).

Laser-induced Fluorescence: The IDPs show varying degrees of laser-induced fluorescence (Fig. 2). The degree of fluorescence for each spectrum (FF, the "Fluorescence Factor") was defined as the difference in the photon signals at 2200 and 400 Δcm^{-1}, normalized to the intensity at 400 Δcm^{-1}. Eight of the 11 normal IDPs have high fluorescence, with FF $\geq$ ~1, while 8 of the 10 primitive IDPs have very low or no fluorescence (FF < ~1), as shown in Fig. 3. The degree of fluorescence is strongest in the IDPs with high CN^-/C^- ratios, suggesting a correlation with the overall abundance of nitrogen. The three normal IDPs with low fluorescence (Jensen, Shaw, Maeterlinck) all have low CN^-/C^- ratios, like the primitive IDPs.

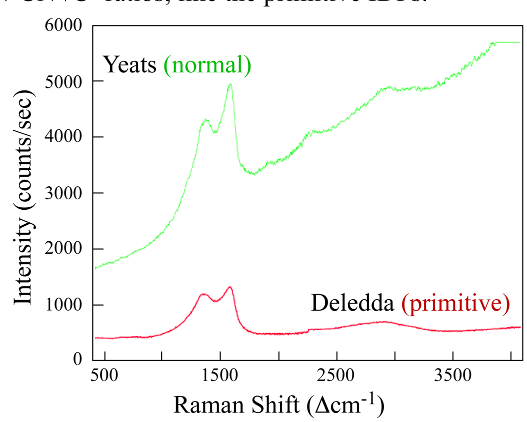

Figure 2. Raw spectra illustrating the difference in fluorescence typical for the two particle types.

Raman Results: All 21 IDPs have the D and G bands characteristic of amorphous sp^2-bonded carbon. An overlay of the spectra, after baseline correction and normalization to the intensity of the G band, shows that normal IDPs have less intense D bands than the primitive IDPs (examples in Fig. 4). The baseline-corrected spectra were separated into their respective D and G bands (two peak mixed Lorenztian-Gaussian deconvolution). Despite some overlap and large errors, the D bands in the isotopically primitive IDPs tend to be wider than those in normal IDPs (Fig. 5).

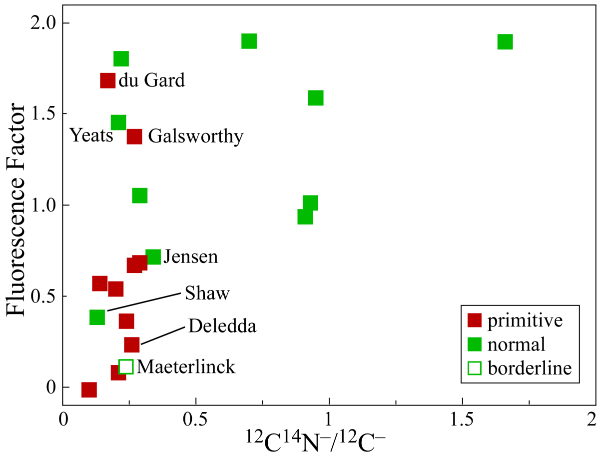

Figure 3. CN^{-}/C^{-} ratios versus the fluorescence factor for isotopically primitive and normal IDPs.

In addition to the D and G bands characteristic of amorphous sp^2-bonded carbon, the spectra of some of the IDPs also show Raman bands for other phases, i.e., glass, olivine and sulfides. Here too we observe a difference between the primitive IDPs, the majority of which exhibit additional glass and/or mineral bands, and the normal IDPs, which tend to show only the bands associated with carbonaceous matter. The two normal IDPs that do also show additional glass and mineral bands (Jensen and Shaw) both have low fluorescence.

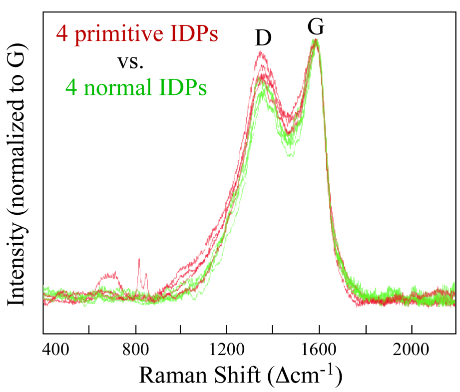

Figure 4. Baseline-corrected Raman spectra for isotopically primitive and normal IDPs.

Discussion: Primitive IDPs have wider Raman D bands than normal IDPs, indicating that their carbonaceous matter has experienced less thermal processing than the organic matter in the normal IDPs. The most striking difference, however, between isotopically primitive and normal IDPs is the amount of laser-induced fluorescence, which is correlated with the overall abundance of N. This difference must be due to the presence and/or abundance of different types of organic molecules (possibly with different amounts of conjugated double bonds) in the carbonaceous matter. Exceptions to this general trend are 1) two clearly primitive IDPs (du Gard and Galsworthy) which show high degrees of fluorescence, and 2) three normal IDPs (Jensen, Shaw and Maeterlinck) which have low fluorescence (Fig. 3). These exceptions suggest the presence of multiple carbonaceous phases in both the ^{15}N-rich and normal IDPs.

Two of the normal IDPs with low fluorescence (Jensen and Shaw) have low D band widths similar to those of other normal IDPs (Fig. 5). However, the third IDP, Maeterlinck, not only has a very low fluorescence factor (FF < ~0.11), but also has the highest D band width of any IDP in this study (Fig. 5). Despite the lack of a bulk ^{15}N enrichment, both its Raman and fluorescence characteristics are consistent with a primitive designation. Isotopic imaging studies have shown that the N isotopic compositions of insoluble organic matter in primitive meteorites are highly variable, with $\delta^{15}N$ ranging from normal to ~3000 ‰ or more [e.g., 3, 4]. These variations occur on a scale similar to that of the typical sizes of IDPs. Maeterlinck, therefore, could be a member of the primitive sub-group of IDPs, but one that fortuitously sampled an isotopically normal portion of its parent body.

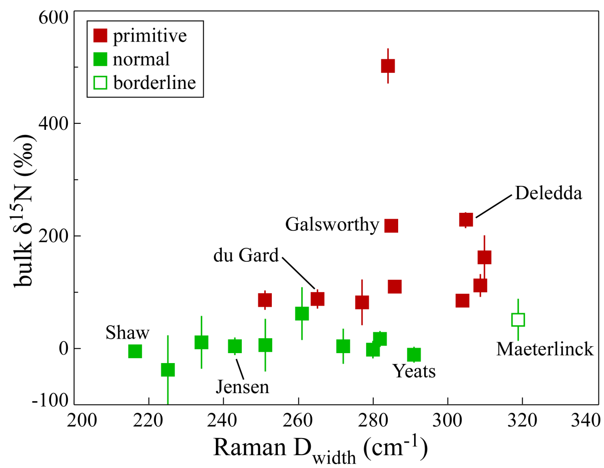

Figure 5. Average FWHM Raman D band width versus bulk $\delta^{15}N$ (‰) for isotopically primitive and normal IDPs. D_{width} errors (n = 5–8) are ~20 cm^{-1}.

Conclusions: Our Raman/visible fluorescence data indicate that fine-scale heterogeneity is present in the carbonaceous matter of IDPs, and suggest that there may be multiple carriers for the N isotopic anomalies in the primitive IDPs.

References: [1] Floss et al. (2006) *GCA* 70, 2371. [2] Wopenka (2012) *MAPS* in press. [3] Busemann et al. (2006) *Science* 312, 727. [4] Floss and Stadermann (2009) *ApJ* 697, 1242.

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