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ISOTOPIC AND MICRO-RAMAN INVESTIGATION OF INTERPLANETARY DUST PARTICLES COLLECTED DURING 2003 EARTH PASSAGE THROUGH COMET GRIGG-SKJELLERUP DUST STREAM. L. R. Nittler¹, H. Busemann¹, and P. Hoppe², ¹Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5421 Broad Branch Road NW, Washington DC 20015, USA, lrn@dtm.ciw.edu, ²Max-Planck-Institut für Chemie Mainz, Germany.

Introduction: In April 2003, NASA flew stratospheric dust collectors to coincide with the expected passage of the Earth through the dust trail of comet Grigg-Skjellerup. Whether any Grigg-Skjellerup particles were collected (along with "normal" Interplanetary Dust Particles or IDPs) and how such would be recognized is still uncertain, though there is evidence for unusual noble gases in some of the particles from these collectors [1]. Isotopic anomalies are powerful tracers of primitive and presolar components in IDPs, with H and N anomalies most likely indicating preserved molecular cloud organic matter [e.g., 2]. Raman spectroscopy is a useful technique for investigating the nature of primitive extraterrestrial organic matter [3-5]. We report a combined isotopic imaging/ micro-Raman imaging study of IDPs, including four from the April 2003 IDP collection.

Methods: Samples: We analyzed two fragments (L2054 E1 and F1) from a cluster IDP and three individual IDPs (L2054 G2, G3 and G4) from the April 2003 collection. For comparison we have also studied three cluster IDP fragments from the L2036 collector, from a previous stratospheric collection. All appear from SEM observation to be fine-grained, chondritic porous IDPs. Isotopic imaging: Individual fragments were pressed into Au foils and analyzed by the Carnegie ims-6f ion probe for D/H and C/H distributions and by the Mainz NanoSIMS for N and C isotopic distributions. Analytical techniques have been described elsewhere [6-8]. Isotopic data were quantitatively extracted for sub-regions ('Regions of Interest' or ROIs) of the images. Terrestrial standards and wellcharacterized meteoritic organic residues were used to calibrate isotopic and elemental ratios. Raman: The L2054 IDPs were also analyzed by Micro-Raman spectroscopy, using a WiTec α -SNOM laser confocal microscope. Spectral images with ~400 nm resolution were acquired by scanning the samples under a 532 nm laser beam. The widths and intensities of the characteristic 'D' and 'G' bands are extracted for C-rich regions by spectral fitting [4].

Results and Discussion: All IDPs show heterogeneity in their H and N isotopic composition on the spatial scale of the measurements (~1 μ m for the ims-6f, ~100 nm for the NanoSIMS). Fig. 1 shows example images and Raman spectra from one IDP. H and N isotopic ratios for 165 ~1-1.5 μ m diameter ROIs from the IDPs are shown in Fig. 2. All L2054 samples exhibit very high D/H and ¹⁵N/¹⁴N ratios, up to 16,000 ‰ and 1300 ‰, respectively. The L2036 samples show less pronounced D enrichments, but similar N isotope ranges. The data in Fig 2. were extracted by degrading the spatial resolution of the NanoSIMS images to directly compare with the ims-6f images. Thus, higherresolution data were also separately extracted for submicron ROIs from the NanoSIMS images to explore the true range of N and C isotopic ratios in the particles. All measured samples except L2054 G3 showed sub-micron ¹⁵N hotspots with $\delta^{15}N=700-1400$ ‰. C isotopic ratios were isotopically normal with the exception of small regions of L2054 E1 and G3, which appear to have significant ¹³C depletions ($\delta^{13}C < -300$ ‰).



Figure 1: Back-scattered-electron, isotopic and Raman images of IDP L2054 E1. Bottom right shows three Raman spectra for two D hotspots (A and B) and a ¹⁵N hotspot (C). Area of Raman image is indicated on isotope images.

As has been observed in other studies [2, 8], there is no general spatial correlation between D and ¹⁵N enrichments, indicating different carriers (and origins) for the anomalies. Moreover, we observe no obvious relationships between C/H and D/H ratios (Fig. 3) nor between CN/C and 15 N/ 14 N ratios. This indicates that the observed organic matter is not a simple mixture of a small number of components, as previously suggested for a few IDPs [9, 10].



Figure 2: H and N isotopic ratios of 165 \sim 1-1.5 µm diameter ROIs of IDPs; circles indicate cluster IDP fragments, squares are individual IDPs.



Figure 3: δD versus C/H for 165 ROIs from IDPs.

As seen in previous studies [3, 5] and in Fig. 1, IDP Raman spectra are dominated by the two first-order bands ('D' and 'G') associated with disordered

C and varying amounts of fluorescence. Fig. 1 shows Raman spectra for three small sub-regions of L2054 E1, associated with 2 D hotspots (A: δD = 16,000 ‰, B: δD = 7500 ‰) and 1 ¹⁵N hotspot (C: $\delta^{15}N$ = 1400 ‰). All three spectra are very similar to the most primitive insoluble organic matter observed in meteorites, e.g. CR2 chondrite EET 92042 [4]. No evidence of thermal processing of the carbonaceous material is visible. Analysis of the Raman data is not yet complete, but Fig. 1 demonstrates that it is now possible to investigate correlations between isotopic composition and Raman spectra on small spatial scales.

All of the L2054 samples analyzed here, cluster and non-cluster IDPs, have at least one sub-region with $\delta D > 4,000$ ‰. In contrast, in the compilation of literature IDP data by [11], only 5 cluster IDPs out of 41 and 2 non-cluster IDPs out of 53 have such high D/H ratios. In fact, 2 of the 3 individual IDPs from L2054 have average $\delta D > 1,000$ %; whereas only 5 out of 53 individual IDPs from [11] even reach this value. This apparent higher abundance of extreme D enrichments in the L2054 IDPs might suggest an origin in comet Grigg-Skjellerup, if large D enrichments are characteristic of cometary dust and typical IDPs come from asteroids. However, given the limited statistics and the fact that most of the data from [11] were acquired using older techniques and instrumentation, we cannot draw any firm conclusions at this point. Analysis of additional IDPs from the April 2003 collection is planned for the near future to expand the statistical database.

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