

DISTRIBUTION OF ORGANIC COMPONENTS WITHIN INTERPLANETARY DUST PARTICLES. Q. H. S. Chan¹ and I. A. Franchi¹, ¹Planetary and Space Sciences, School of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK. (e-mail: queenie.chan@open.ac.uk).

Introduction: Interplanetary dust particles (IDPs) are composed of highly-disordered carbon associated with compounds such as ketone and aliphatic hydrocarbons [1], and polycyclic aromatic hydrocarbons (PAHs) [2]. The organic matter in IDPs contains some of the largest enrichments of deuterium (elevated D/H) measured in solar system materials, which suggests that the IDPs are composed of primordial solar system materials that have been fractionated in a cold molecular cloud [3, 4]. The large chemical and isotopic variations observed for IDPs also echo with the spatial heterogeneity of organic matter at micrometer-scale [e.g., 1, 4, 5]. In order to characterize the organic contents of the IDPs and understand the distribution of organic components and their correlation to mineral phases within the particles, we have conducted a range of coordinated studies with Raman spectroscopy and scanning electron microscopy (SEM), and plan nanoscale secondary ion mass spectrometry (NanoSIMS).

Samples and Methods: Five IDPs (L2036-CA1, L2055-T1, L2055-U1, L2071-K1 and L2076-Q1) selected for this study were picked by a micromanipulator under an optical microscope objective and were pressed flat with a spectroscopic grade sapphire window into annealed high-purity gold foils mounted on aluminium stubs.

Electron images of the IDPs were obtained with a FEI Quanta 650 field emission gun scanning electron microscope (FEG-SEM) at the Natural History Museum in London. The C distribution and elemental compositions of the IDPs were determined by energy dispersive X-ray micro-analysis (EDX) using a Bruker XFlash FladQUAD 5060F detector. A low accelerating voltage was used for secondary electron (SE) imaging (2 keV) and EDX analysis (6 keV) to enhance the SE image resolution, analytical spatial resolution (<200 nm), and minimize beam damage/C contamination.

The IDP samples were analyzed using a Jobin-Yvon Horiba LabRam HR (800 mm) Raman microprobe at the The Open University prior to and after FEG-SEM analysis. The excitation wavelength was 514.5 nm (green), and the Raman probe spatial resolution was 0.8 μm at the 50 \times magnification. Analyses were obtained as maps of point spectra. The laser power at the sample surface was $\sim 60 \mu\text{W}$ leading to an intensity of approximately $110 \mu\text{W}/\mu\text{m}^2$. Wavelength calibration against a silicon wafer sample was checked daily prior to sample analyses. At least 30 spectra of each IDP were used for

data processing. The Raman band parameters were determined by simultaneous peak fitting to the two-peak Lorentzian and Breit–Wigner-Fano model and linear baseline correction. Details of the Raman technique are given in [6, 7].

Results and Discussion: High-resolution SE, back-scattered electrons (BSE) images and EDX spectra were obtained for each IDP (e.g. Figure 1).

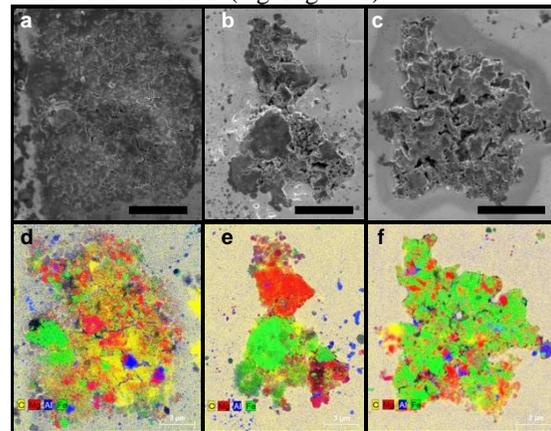


Figure 1. High-resolution SE images and EDX spectra of L2055-T1 (a, d), L2036-CA1 (b, e), and L2076-Q1 (c, f). Scale bars are 5 μm .

Cometary source. The five samples are generally fine-grained, porous, composed of predominately anhydrous minerals such as Mg-silicates (enstatite, forsterite) and low-Ni sulphides (pyrrhotite ($\text{Fe}_{0.92}\text{S}$ – $\text{Fe}_{0.95}\text{S}$), which is common in IDPs [8]), and display a bulk elemental composition similar to that of chondritic materials [9]. The texture and composition suggest that they are all anhydrous chondritic porous (CP) IDPs, which represent the most primitive astromaterial that have evaded parent body alteration processes [4]. The IDP samples can be further sub-classified into three groups based on their texture: (**group 1**) fine-grained (<0.5 μm), porous IDPs (L2055-T1, L2055-U1, L2071-K1; Figure 1a,d), (**group 2**) coarse-grained enstatite and Fe-Ni metal (>3 μm) with a fine-grained, porous matrix, (L2036-CA1; Figure 1b,e), and (**group 3**) medium-grained (~ 1 – $1.5 \mu\text{m}$) sulphide–silicate intergrow with a fine-grained, porous matrix (L2076-Q1; Figure 1c,f). Other minerals found in the samples include troilite (stoichiometric FeS) in L2036-CA1, Al-diopside in L2076-Q1, and high-Ni Fe-sulphides (pentlandite) in L2055-T1. Although high-Ni Fe-sulphides are common in hydrated IDPs, their association with aqueous alteration has been questioned by Flynn et al. [10].

C distribution. The high resolution FEG-SEM analysis shows in detail the relationship between the C-containing phases and the IDP mineralogy. While the C-rich phases often occur in the matrix as fine-grained material around the silicate grains (Figure 1d), some occur as discrete C-rich grains ($\sim 0.5 \mu\text{m}$, Figure 1e). Since many carbonaceous phases are Raman active, Raman spectroscopy allows the differentiation of organic material within the IDPs. Raman-active organic matter (OM) – as shown by the presence of the D and G bands – occurs in all mineral phases. The Raman parameters of the OM are sensitive to the structure of the aromatic skeleton and the nature the organic precursor. Figure 2 shows a comparison between the G band parameters of the OM in the IDPs and meteoritic insoluble OM (IOM). The error bars (1σ standard deviation) indicate significant OM heterogeneity within each IDP sample. No correlation was observed for the Raman parameters within each sample ($R^2 = 0-0.6$), suggesting that despite the significant intra-sample OM heterogeneity, the OM does not exhibit any generic relationship.

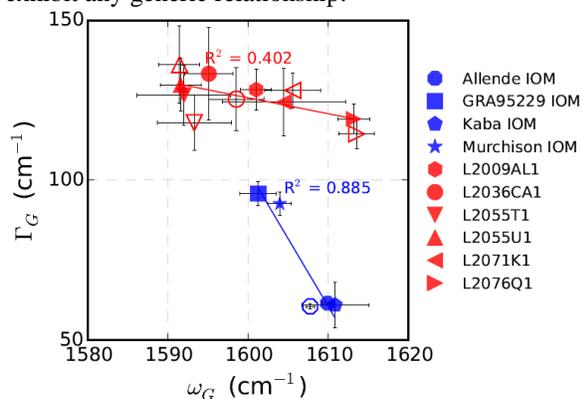


Figure 2. Raman G-band parameters (full width half-maximum [Γ] and peak positions [ω]). Blue markers – meteorite IOM, red markers – IDP OM. Fill/open markers – before/after pressing onto Au.

In agreement with previous studies [e.g., 1, 11], the D band parameters indicate that IDP OM has affinities to highly-disordered organics in primitive CM and CR chondrites. However, the Γ_G clearly deviates from chondritic OM (Figure 2). Γ_G has a correlation to the H/C ratios [12]. A wider Γ_G suggests a potentially larger H/C and aliphatic/aromatic ratios in the IDPs compared to the meteoritic OM that is commonly processed by parent body alterations [4, 11]. Aliphatic hydrocarbons are usually associated with higher D/H [4], and we will study this in more detail with NanoSIMS analysis. The G band parameters are negatively correlated and the correlation was suggested to associate with OM maturity [12], where more primitive material occupies the upper left region of the plot (Figure 2). The maturity trend of the IDP OM clearly deviates from that of the

meteoritic OM – only limited Γ_G variation is observed for IDP OM. Since different types of organic precursors should mature in a distinctive manner [13], the observed deviation in the G band parameters trend suggests that the organics in IDP and meteorite are structurally different, and/or they gained maturity in a different manner. IDPs are not thermally-altered and therefore the deviation should indicate structural variation of the precursors accreted.

L2055-T1 and L2055-U1 are from the same cluster and the Raman parameters of their OM exhibit a close affinity (Figure 2). Although L2036-CA1 shows a clear textural variation from the group 1 IDPs, its Raman parameters also fall within the continuum displayed by the group 1 samples. With a higher G band position ($1613.2 \pm 2.0 \text{ cm}^{-1}$) and a smaller sample heterogeneity, the OM in L2076-Q1 is clearly distinct from the other IDP samples. The OM contained within different IDP components are structurally different, however, no correlation was observed for the same mineral phase across different IDPs (Figure 3), suggesting incomplete mixing of solar system components.

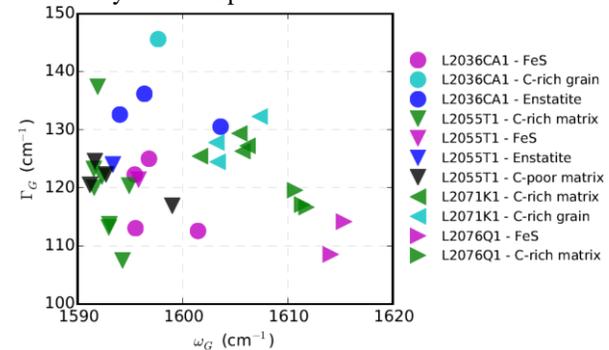


Figure 3. OM Raman spectral parameters variation associated with different mineral phases.

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References: [1] Busemann H. *et al.* (2009) *EPSL*, 288, 44-57. [2] Clemett S.J. *et al.* (1993) *Science*, 262, 721-725. [3] Messenger S. *et al.* (2003) *Space Science Reviews*, 106, 155-172. [4] Keller L.P. *et al.* (2004) *GCA*, 68, 2577-2589. [5] Quirico E. *et al.* (2005) *PSS*, 53, 1443-1448. [6] Chan Q.H.S. *et al.* (2016) *GCA* <http://dx.doi.org/10.1016/j.gca.2016.10.048>. [7] Kebukawa Y. *et al.* (2017) *GCA*, 196, 74-101. [8] Zolensky M.E. and Thomas K.L. (1995) *GCA*, 59, 4707-4712. [9] Zolensky M. *et al.* (1993) *GCA*, 57, 3123-3148. [10] Flynn G. *et al.* (2016) *LPI Contributions*, 1921. [11] Caro G.M.M. *et al.* (2006) *A&A*, 459, 147-159. [12] Busemann H. *et al.* (2007) *MAPS*, 42, 1387-1416. [13] Wopenka B. and Pasteris J.D. (1993) *The American Mineralogist*, 78, 533-557.