**PIECING TOGETHER THE HISTORY OF THE EARLIEST SILICATE AND ORGANIC RESERVOIRS IN THE SOLAR SYSTEM.** N. A. Starkey[1] and I. A. Franchi[1], [1]Planetary and Space Sciences, The Open University, Milton Keynes, MK7 6AA. UK. Email: natalie.starkey@open.ac.uk

**Introduction:** Cometary interplanetary dust particles (IDPs), collected in Earth's stratosphere, currently represent the best way to sample outer Solar System primordial dust. The fine-grained (sub-µm) minerals of IDPs show some strong similarities to the textures expected for primary condensates from the solar nebula. In addition, IDPs have been shown to contain extreme C, N and H isotopic signatures [1–5] suggesting they retain interstellar material.

In this study we have analysed a set of fine-grained fragments of cluster IDPs by Raman, SEM and NanoSIMS, combining isotopic analyses of the silicate and characterized organic components within the same sample on fine-grained primordial material. The new results presented here are combined with the results from our previous IDP study [5], and some data from [6] to provide a large, comprehensive compositional study of IDPs. The number of IDPs analysed to date by Raman and high precision O isotopes remains very small, particularly when the number of potential parent bodies is considered, or the huge volume of the protoplanetary disk that may have contributed to these parent bodies. Although the provenance of any one IDP cannot be known, or even unambiguously assigned to an asteroidal or cometary origin, this large dataset can be used to assess models for the formation and evolution of the early Solar System silicate and organic reservoirs. In addition, IDPs can be used to understand how material from these different reservoirs was incorporated into primitive bodies, and any subsequent processing they may have experienced.

**Methods:** Raman measurements were carried out using a Horiba Jobin Yvon LabRam HR800 with a 473 nm (blue) excitation laser (<70 µW at the sample surface) at The Open University to assess first order carbon D and G bands of the organic material. Analyses were obtained as maps of point spectra (spot 2µm) with a step size of 1µm in the x and y direction. A x50 long working distance objective lens was used. Carbon bands were fitted in the range 800 to 2100 $cm^{-1}$, assuming a linear baseline and Gaussian-Lorentzian profile model. Raman band parameters were obtained for each IDP by averaging the peak parameters from all spectra obtained from each particle (minimum spectra per sample was ~15).

Isotopic analyses were carried out on a NanoSIMS 50L at The Open University. A Cs+ probe with a current of 1.5 pA for C and N isotope measurements, 3 pA for D/H and 25 pA for O isotopes was rastered over the samples. Negative secondary ions were collected on electron multipliers during three analytical set-ups in imaging mode and one in spot mode (1: $^{12}C$, $^{13}C$, $^{16}O$, $^{12}C^{14}N$, $^{12}C^{15}N$ and $^{28}Si$; 2: $^{1}H$, $^{2}H$, $^{12}C$ and $^{18}O$; 3: $^{16}O$, $^{17}O$, $^{18}O$, $^{28}Si$ and $^{24}Mg^{16}O$; 4: $^{16}O$ (on FC), $^{17}O$, $^{18}O$, $^{24}Mg^{16}O$). C, N, H and O mapping image data were processed using the L'image software (L. Nittler, Carnegie Institute of Washington). C, N and H isotope results were normalized to Cold Bokkeveld IOM and are reported as $\delta^{13}C_{PDB}$, $\delta^{15}N_{AIR}$ and $\delta D_{SMOW}$. O isotope ratios from spot analyses were normalised to Standard Mean Ocean Water (SMOW) using San Carlos olivine that bracketed the analyses in order to generate $\delta^{17}O$ and $\delta^{18}O$ values. Typical spot-to-spot reproducibility (2σ) for repeated analyses on flat, homogenous standards of San Carlos olivine were ±1.8 ‰ for $\delta^{17}O$ and ±0.8 ‰ for $\delta^{18}O$.

**Results:** The spot analyses of the fine-grained material in the IDPS provides approximately bulk O isotopic compositions, and reveals that some IDPs are more $^{16}O$-rich ($\delta^{18}O$ = -30 ‰) than any bulk meteorite compositions, extending to O isotope compositions in between chondritic- and solar-like values (Fig.1). The continuum of IDP O isotope compositions observed previously [5], from $^{16}O$-rich (solar-like) to relatively $^{16}O$-poor (chondritic-like), is further apparent with the new data, such that the IDPs define a clear, continuous trend along the CCAM and slope=1 [7] lines. This trend applies to all but 2 of the IDP fragments analysed. One of the particles to fall off the main trend is composed of a single hibonite grain attached to small pieces of fine-grained chondritic material and it has an O isotope value that is indistinguishable from that of the FUN inclusions observed in Ca-Al-rich inclusions. The presence of this grain within the IDP collection suggests that the (possibly cometary) source of this particular IDP incorporated high-T components from the inner Solar System (as noted previously for samples collected from comet Wild2 [8,9]). The other IDP fragment that is distinct from all the other samples contains a region (~5 µm in size) that has very high $\delta^{18}O$ of ~+60 ‰ (Fig.1), but still within error of the slope=1 line. The texture of this IDP fragment, including the $^{16}O$-poor region, resembles many of the other fine-grained IDPs in this study. Interestingly, the rest of this IDP fragment has relatively normal $\delta^{18}O$ (~0 ‰). The range of O isotope compositions available in this single fragment is interesting in itself but it also appears that this IDP fragment has sampled material that has not

previously been recognized in the wider meteorite or IDP collections, but may share some common origin with the cosmic symplectic in Acfer094 with $\delta^{18}O$, $\delta^{17}O$ = 180 ‰ [10]. The isotopic composition of the C, N and H associated with this oxygen hotspot is similar to the rest of the IDP, and to many other IDPs in the collection. Furthermore, with a C/H ratio of 1.1, similar to meteoritic IOM, the silicates present appear to be largely anhydrous. Further investigation of the remaining material is planned.

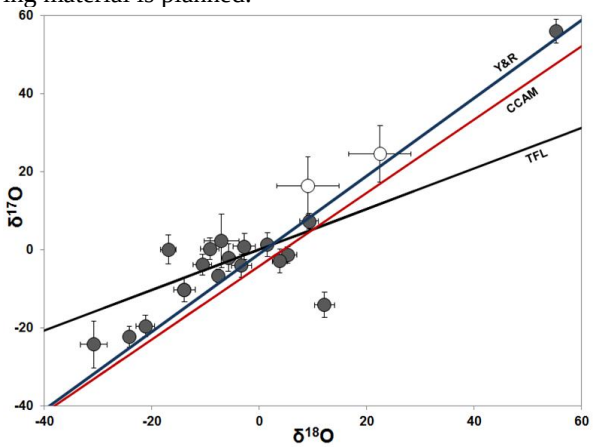


Figure 1. 3 O-isotope diagram for IDPs (data from [5] and unpublished). Grey circles indicate spot analyses and white circles indicate imaging analysis. Error bars are 2σ.

The remainder of the dataset allows for a comparison between O isotopes (that result from the silicate portion of the particles) with the C, N and H isotope analyses, and Raman measurements of the organics. The important aspect here is that the analyses are taken from the very same cluster fragment, or region of the fragment, and are also combined with an estimate of the presolar grain abundances for each fragment from O isotope mapping. In general, the $^{16}O$-rich IDPs display more primitive organic signatures than the more $^{16}O$-poor IDPs, with lower $\delta^{13}C$, down to -43 ‰ and higher $\delta^{15}N$, up to +385 ‰. They also tend to display higher C/H values (≥1) suggesting that they are dominated by anhydrous minerals, and, therefore, are more likely to result from a cometary source (CP-IDPs). In addition, the $^{16}O$-rich IDPs tend to display more 'primitive' Raman parameters, with high D band positions and large G band widths, reflecting the disordered nature of the carbon present in the samples. These Raman parameters suggest that the IDPs (whether $^{16}O$-rich or $^{16}O$-poor) are more primitive than any known meteorite samples. However, no systematic pattern is observed in association with bulk δD, indicating a more complicated history for the hydrogen reservoir(s). Finally, the $^{16}O$-rich (low $\delta^{18}O$) IDPs display lower presolar grain abundances than the more chondritic-like ($^{16}O$-poor) IDPs.

**Interpretation:** The presence of large fragments of chondritic components in IDPs and Stardust samples is well documented in the literature, and therefore it is expected that chondritic-like O-isotope signatures in the fine-grained material indicates a strong input of such material. The more $^{16}O$-rich solar-like samples must be dominated by an early-formed component, possibly associated in some way with CAI formation, the only other common material with solar-like oxygen. These more 'primitive' looking IDPs, in terms of O isotopes, also contain the most primitive looking organic signatures. This feature suggests that the parent bodies of the $^{16}O$-rich IDPs incorporated both unprocessed silicate and organic reservoirs. This may, in turn, suggest they formed earlier in Solar System history, or at higher heliocentric distance, away from the inner Solar System region of high-T processing. As such, they are more likely to represent cometary sources (in agreement with their higher C/H values).

The $^{16}O$-poor IDPs, on the other hand, are more likely to have formed later on in Solar System history if the chondrule-like fragments present in IDPs are of a similar age to meteoritic chondrules and/or formed at lower heliocentric distance in order to facilitate transport of high-T inner Solar System material to their accretion zones. As such, these IDPs may be more asteroidal in nature but still show some features not generally observed in meteorites, e.g. highly disordered carbon and GEMS. In this model we assume that the Solar System initially contained $^{16}O$-rich (solar-like) dust that was distributed homogenously. The relatively low presolar grain abundances in the $^{16}O$-rich IDPs suggest they may have been, at least partially, destroyed during early homogenization of solar nebula dust. The higher presolar grain abundances in the $^{16}O$-poor, chondritic-rich IDPs indicates presolar grains continued to accrete onto the protoplanetary disk, long after the initial main cloud collapse.

**References:** [1] Aleon, J. et al. (2001). Geochim. Cosmochim. Acta. 65, 4399- 4412. [2] Busemann, H. et al. (2009). Earth Planet. Sci. Lett. 288, 44-57. [3] Floss, C. et al. (2006). Geochim. Cosmochim. Acta 70, 2371–2399. [4] Messenger, S. (2000). Nature 404, 968-971. [5] Starkey, N. A and Franchi, I. A. (2013). Geochim. Cosmochim. Acta., In Press doi: 10.1016/j.gca.2012.11.040. [6] Davidson, J. et al. (2012). Met. Planet. Sci. 47 (11), 1748-1771. [7] Young, E. D. & Russell, S. S. (1998). Science 282, 452-455. [8] McKeegan, K. D. et al. (2006). Science 314, 1724-1728. [9] Nakamura, T. et al. (2008). Science 321, 1664-1667. [10] Sakamoto, N. et al. (2007). Science 317, 231-233.