Atom Probe Tomography and Three-Dimensional Atomic Scale Characterisation of Interplanetary Dust Particles: Inorganic and Organic, Hydrous and Anhydrous Assemblages. N. D. Nevill[1], P. A. Bland[1], D. W. Saxey[4], W. D. A. Rickard[4], M. Z. Quadir[5], S. M. Reddy[1,4], N. E. Timms[1], L.V. Forman[1,6] & L. Daly[1,7,8], [1]Space Science and Technology Centre, School of Earth and Planetary Sciences, Curtin University, GPO Box U1987, Perth, Western Australia, 6845, [2]Lunar and Planetary Institute, Universities Space Research Association, 3600 Bay Area Blvd., Houston, Texas, 77058 USA, [3]Astromaterials Research and Exploration Science, NASA Johnson Space Center, 2101 NASA Parkway, Mail Code XI3, Houston, TX, 77058, USA, [4]Geoscience Atom Probe, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, 6845, [5]John de Laeter Centre, School of Civil and Mechanical Engineering, Curtin University, Bentley, Perth 6102, Australia, [6]WAM- Department of Earth and Planetary Sciences, Western Australian Museum, Locked Bag 49 Welshpool DC, Western Australia 6986, Australia, [7]School of Geographical and Earth Sciences, University of Glasgow, Gregory Building, Lilybank Gardens, Glasgow G12 8QQ, UK, [8]Australian Centre for Microscopy and Microanalysis, University of Sydney, Sydney, 2006, New South Wales, Australia.

Introduction: Interplanetary dust particles (IDPs) preserve primordial fragments from our Solar System and external stellar systems, sampled from a vast range of dust forming bodies that often display smaller degrees of parent body processing than is seen in meteorites. IDPs preserve some of the smallest astromaterials from our Solar System, many of which are believed to be among the most important materials for studying physical and chemical processing, and formation mechanisms occurring within the interstellar medium (ISM), Solar Nebula and external planetary systems [1]. However, their formation processes and provenance are poorly constrained, owing in part to spatial resolution limitations of traditional analytical techniques.

Atom probe tomography (APT) uses a pulsed laser to field-evaporate material at the atomic scale from needle-shaped samples, and time-of-flight spectrometry for 3D reconstruction of element and isotope distribution in samples after data acquisition. This technique has the highest spatial resolution available of any technique used within the geoscience field [2]. However, measuring multi-phase specimens and porous media in APT can be challenging, two primary characteristics of IDPs.

Here we present a custom method for APT needle design and the first results of a 3D atomic scale study of interplanetary dust particles, salt crystals and extraterrestrial insoluble and soluble organic matter designed to overcome the challenges of studying IDP-like materials.

Approach and Methodology: A 12µm cluster particle was selected from collector plate L2055 which was exposed to the 26P Grigg-Skjellerup, Jupiter-family comet trail dust stream in the stratosphere of the Earth. IDPs from comets are proposed to be more porous than IDPs from asteroids, providing a better candidate for testing suitable methods for APT acquisition of IDPs.

The coordination of epoxy embedding to mitigate porosity, a custom needle design (Fig 1) and manual APT acquisition, proved successful for IDPs in producing high quality mass spectra and spatial data. Epoxy mass spectra showed 12 – 14 peaks due to the extensive breakdown of molecules under the APT electric field. Peaks were consistent across all trial and IDP embedded needles, important when isolating natural phases.

Using the Tescan Lyra3 Focused Ion Beam (FIB) Field Emission Scanning Electron Microscope (FE-SEM), three transmission electron microscopy (TEM) foils were prepared for determining the primary composition of the measured cluster. This was important as each phase interacts with the electric field in APT differently and IDPs are mineralogically complex assemblages composed of organic, inorganic, hydrous and anhydrous phases. Results from TEM analysis and three trial needles were used to constrain measurement parameters for APT acquisition. Trial needles of epoxy were prepared and analysed to establish the relationship between epoxy and the electric field as it had not been measured in APT at the time of data collection.

Needle preparation used a customised method, with shank angles of 7 – 12°, larger than typical for an APT needle and a thicker base to improve structural integrity as it was assumed epoxy would be structurally weak under the electric field based on previous studies of polymeric organics in APT within material sciences. Fig 1 comparatively shows a traditionally prepared needle with one created for this study [2]. Tips were ~ 50 – 70 nm in diameter at the apex.

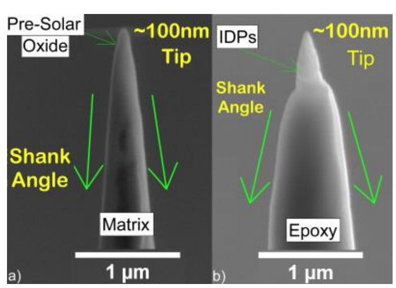

Fig 1: *a) Traditional design: APT Pre-solar Al_2O_3 needle b) Custom design: epoxy APT needle. A larger shank angle and a thicker cylindrical base (~600 – 800 nm in diameter) is shown.*

A TALOS field-emission (FE) 200X G2 (S)TEM at the JdLC, Curtin University as used for TEM measurements. Quantative X-ray maps and STEM images of 417 grains were collected over a surface area of 45.2 µm^2, with 33 grains producing electron diffraction (SAED) patterns sufficient for phase confirmation.

The CAMECA LEAP 4000X HR atom probe microscope at the Geoscience Atom Probe facility, JdLC, Curtin University, was used for APT measurements. Four needles were prepared adjacent to the extracted TEM foils to retain as much spatial context as possible between the different analyses. Manual acquisition kept the laser focused at the apex and allowed for changes in acquisition parameters in response to changing physical properties down the shank of the needle.

Epoxy was readily separated from natural bulk organic matter using isosurfaces created using ion peak C^{++}. This charge state was present within the mass spectra of all naturally occurring organic matter, but absent from synthetically formed epoxy. A 3D reconstruction of natural organic matter from an IDP and epoxy is shown in Fig 1 with a comparative thermal map highlighting the difference in charge states between the natural and synthetic polymeric organics.

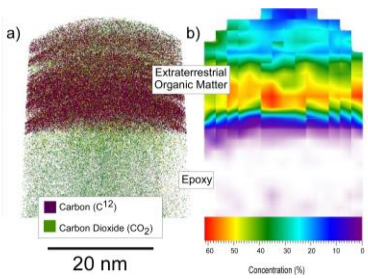

Fig 2: *a) A three dimensional APT LEAP reconstruction of natural bulk organic matter embedded in epoxy. b) thermal map of the distribution of ^{++}C ions.*

Inorganic phases were initially identified by 3D atomic distributions from which the primary ion was constrained and used to create isosurfaces for further study. Isosurfaces enable study of phases and their mass spectra without interference from surrounding phases.

Results and Discussion: TEM investigations displayed a fine grained, pyroxene rich, Hybrid IDP with petrographical similarities to IDPs thought to originate from the 26P/Grigg Skjellerup comet. Identified phases include Mg-rich silicates, silica glass, hydrous silicates (e.g., aluminosilicates), Ti-oxides, Metallic Fe, Fe-oxides, Al-oxides, Mg-oxides, Ca-oxides, S-rich inclusions (i.e., Ca- and Mg-rich sulfates), chromium, halite-like grains, enstatite whiskers and organic matter.

Structurally amorphous, texturally spongy organic matter with a mesh-like network of carbon and hollow voids a few nanometers in size was found via TEM analysis. This bulk organic matter was measured during APT acquisition. Where porosity was sufficiently mitigated, spatial resolution relationships were retained. Many soluble organic species remained unfragmented and complex assemblages broken into the building blocks from which they formed, enabling the primary functional groups to be identified. Intact soluble organic matter revealed spatial variability at sub-nanometer scales. 1D concentration profiles showed certain species increased at depth while others varied in abundance, *e.g.*, CH_2O^+. Types of N functional groups also varied between each region of organic matter within the same specimen, suggesting formation in isolated and restrictive regions likely external to the parent body.

Hydrous phases were rare amongst the TEM foils, sparsely distributed throughout measured sections except for one region where hydrous phases were clustered (*e.g.*, gypsum, halite, aluminosilicates) embedded amongst nanophase anhydrous oxides and ferromagnesian silicates. Results imply heterogeneous micrometer scale aqueous alteration occurred on the parent body [3]. The region clustered with hydrous phases preserved pseudo-spherical silica nanospheres which were shown within an APT needle extracted in close proximity. This APT needle preserved silicates, organic matter, and salt crystals. Measured nanospheres indexed as monoclinic tridymite, consistent with formation from aqueous processing in a low temperature environment. However, silica nanospheres lacked paracrystallinity and were dehydrated based on APT mass spectra. N was detected at trace levels within some grains. Taken together, these results indicate exposure to a thermal heating event, likely within the solar nebula considering the bulk of the IDP does not appear to be strongly heated and there was minor development of magnetite. Study of non-stochiometric amorphous silicate phases supports this occurrence as shown through loss of MgO and CaO, and formation of a vesicle rim with chemical zoning within the largest inclusion [1].

Mass spectra of nanophase halite crystals in APT preserved minor abundances of K and trace enrichments in Mg, Si and Al within some of the crystals. Crystals were free of embedded inclusions. However, crystals decomposed during acquisition, likely due to exposure to the high intensity electric field, resulting in the loss of their crystal structure. Salt crystals were proposed to derive from interactions with a trans- Neptunian object at some point in the evolutionary history of host comet.

Conclusion: The APT technique is a promising new approach for studying IDPs, particularly considering many phases preserved within IDPs reach the spatial limitations of currently applied techniques thus providing an opportunity to gain more detailed geochemical information on the primordial components of our Solar System. Studying hydrous, anhydrous, organic and inorganic phases shows APT could be an effective complimentary technique for future studies of small astromaterials including those from sample return missions.

References: [1] J. P. Bradley (2014) in *Meteorites and cosmochemical processes*, 1, (eds. A. M. Davis) 181–213. [2] S. M. Reddy et al. (2020) *Geostand Geoanal Res, 44(1),* 5–50. [3] Nakamura-Messenger et al. (2011) *Met. Planet. Sci., 46(6),* 843-856.