

Micrometer to Atomic Scale Characterisation of Primitive Astromaterials Using A Novel Method, Metis-Fa: A Coordinated Atom Probe Tomography, Transmission Electron Microscopy and NanoSIMS Approach. Nicole. D. Nevill¹⁻³, Ann N. Nguyen², Zia Rahman⁴, David. W. Saxey⁵, Xiao Sun⁵, Lindsay. P. Keller², William. D. A. Rickard⁵ and Steven. M. Reddy⁵. ¹Lunar and Planetary Institute, Universities Space Research Association, 3600 Bay Area Blvd., Houston, Texas, 77058 USA, ²Astromaterials Research and Exploration Science, NASA Johnson Space Center, 2101 NASA Parkway, Mail Code XI3, Houston, TX 77058, USA, ³Space Science and Technology Centre, School of Earth and Planetary Sciences, Curtin University; Perth, Western Australia, 6845, Australia, ⁴Jacobs, Astromaterials Research and Exploration Science, NASA Johnson Space Center, 2101 NASA Parkway, Mail Code XI3, Houston, TX 77058, USA, ⁵Geoscience Atom Probe, John de Laeter Centre, Curtin University; Perth, Western Australia, 6845, Australia.

Introduction: Presolar grains preserve isotopic, chemical and microstructural records of physical and chemical processing, and formation mechanisms within a vast range of evolved stellar systems, the interstellar medium, solar nebula and their parent bodies. These evolutionary records are preserved at the micrometric to atomic scale, requiring coordinated studies to expand our understanding of evolutionary processes occurring throughout ours and external stellar systems [1].

NanoSIMS enabled rapid *in situ* identification and isotopic characterisation of presolar grains and their stellar origins using ¹⁷O/¹⁶O and ¹⁸O/¹⁶O, and ¹³C/¹²C isotopic ratios [1]. Coordination with transmission electron microscopy (TEM) revealed crystallographic and localised contextual relationships and quantitatively constrained their major and minor compositions [1]. However, trace elements cannot be quantified, the most sensitive geochemical tracers of environmental conditions, essential to unravelling the chemical record of their evolutionary pathway and parent stellar systems [2-3]. Furthermore, owing to the combination of technical limitations (only 5 – 7 isotopes can be measured per NanoSIMS run) and their small grain sizes of 100 nm < 3 µm (with rare exceptions in nanodiamonds (2 nm ≤) and SiC (< 40 µm)), the number of measurable isotopes per grain volume is limited [1,3]. Through more comprehensive isotopic studies of presolar grains, NanoSIMS studies have shown the importance of the latter, identifying Fe and Mg as important indicators of nuclear synthetic processing and their stellar origins, respectively [4-5]. Coordination of NanoSIMS and Atom Probe Tomography (APT) revealed morphological signatures, and isotopic and chemical signatures at major to trace levels without requirements for preselection of elements [6]. However, crystallographic signatures in localized contextual relationships cannot be measured. Consequently, coordination of NanoSIMS, TEM and APT is essential to gain access to almost all contextual, structural and geochemical signatures within each presolar grain.

Transmission electron microscopy requires a 100 nm thin lamella which is unstable in APT and would not produce any viable data. Atom probe tomography

requires a needle-shaped specimen which when measured in TEM removes the local context, impacts the quality of the TEM diffraction images due to the shank angle of the needle, and can alter the chemistry of beam sensitive materials from the higher degree of surface exposure at the tip. To address these issues, we developed METIS-Fa (Multi-technical measurements of Electron Transparent materials using an Indium Sandwich - a FIB approach). A novel method which enables coordination of NanoSIMS, TEM and APT for generalized and targeted studies of individual grains, including beam sensitive materials, without compromising sample preparation requirements for TEM and APT. This method requires only indium and a Focus Ion Beam (FIB), minimizing the movement of fragile materials while still enabling preparation of TEM lamella into APT needles.

Samples: Initial experimental development and testing of the method occurred at Astromaterials Research and Exploration Science (ARES), Johnson Space Centre (JSC), NASA and APT measurements and needle preparation occurred at JdLC, Curtin University. Synthetic silicate samples were used as analogs for presolar silicates when performing a trial run of the method. Samples were extracted from a polished thin section created at JSC, NASA, comprised of 38 wt.% Si, 17 wt.% FeO, 13 wt.% MgO, 12 wt.% Al, 11 wt.% Ca based on electron microprobe analysis (EMPA) [8]. Experimental details, pressure and temperature conditions were presented in [8] and references therein.

Testing of the capability to target individual grains in mineral matrices using this method for acquisition in APT, measured matrix regions in meteoritic thin sections of primitive meteorites. These meteorites and their identified presolar grains for future targeted studies are detailed in [9].

Techniques: The TEM-FIB lamella were prepared using a FIB. An e-beam assisted Pt deposition was used as a protective coating for the synthetic and meteoritic samples. When targeting individual grains, a secondary e-beam assisted Pt deposition button is placed over the desired grain before the protective coating to denote its location.

A JEOL 2500SE field-emission TEM was used for high-resolution imaging, energy-dispersive X-ray (EDX) and electron diffraction data.

The METIS-Fa method was experimentally designed, tested and executed using a FIB at ARES, JSC NASA. Needles for APT were prepared using the Tescan Lyra3 GM Dual Beam Focus Ion Beam (FIB) Field Emission SEM (FE-SEM) at the JdLC, Curtin University.

Atom probe tomography measurements were conducted using a CAMECA Local Electrode Atom Probe, LEAP 4000X HR. Two pure indium needles were analyzed initially to constrain acquisition parameters and stability under the beam. Manual acquisition was required to maintain evaporation of specimen's at the apex and monitor interactions with measurement parameters.

Experimental Design: Indium foil is pressed onto an Al stub with a pneumatic press and mounted into the FIB adjacent to the TEM-FIB lamella of interest. Using a FIB, two indium slices ($5\ \mu\text{m} \times \sim 300\ \text{nm} \times 3\ \mu\text{m}$) are extracted from indium foil and aligned with the TEM-FIB lamella before touching the TEM-FIB lamella. Each slice is then attached through cold welding to the FIB-TEM lamella. This approach eliminates the need for chemical treatments and proved effective for aligning the Indium within the region of interest for APT, holding it in place for up to 4 days during testing. Once both indium slices are attached within their pre-determined region per grain targeting requirements, they are gradually melted onto the FIB-TEM lamella.

When targeting a specific grain, measurements should be taken of the pt button and its distance from edge to edge of the lamella before and after sandwiching. A secondary button should be placed over the same region after the Indium slices have been attached to improve precision when preparing APT needles.

Results: Figure 1 shows two indium slices melted onto a FIB-TEM lamella, adding additional bulk for preparation into APT needles as shown in Figure 2 [7]. The latter was essential so samples could be measured in TEM and APT without compromising sample preparation requirements and consequently data quality and acquisition stability. METIS-Fa proved effective for improving geometry. Figure 3 shows a successful APT run of the synthetic silicate. EMPA, TEM and APT showed no chemical alterations. During targeting testing, a solar silicate grain was successfully identified and measured in TEM, and prepared into an APT needle. However, the indium was melted too long during sample preparation, causing expansion and formation of internal porosity leading to sample loss.

Conclusion: METIS-Fa greatly expands the number of isotopic and chemical signatures measured per grain volume, and enables measurements of contextual, structural, crystallographic, isotopic and geochemical signatures within individual grains. Gaining access to such a vast range of evolutionary signatures required for expanding our understanding of external stellar and planetary systems and the evolution of our solar system. This method was designed for application to a vast range of phases including being sensitive materials and thus provides a way for coordination of NanoSIMS, TEM and APT not just for the study of presolar grains and by extension primitive astromaterials, but studies in a vast range of other fields including the geosciences and material sciences.

Acknowledgments: Thankyou to ARES, JSC, NASA; JdLC Curtin University and Space Science Technology Centre for the use of laboratory facilities and funding [confirm].

References: [1] E. Zinner (2014) in *Meteorites and cosmochemical processes*, 1, (eds. A. Davis) 181–213. [2] R. O. Allen and B. Mason (2010) *GCA*, 37(6), 1435–1456. [3] F. J. Stadermann et al. (2002) *Met. Planet. Sci.*, 44(7), 1033–1049. [4] A. N. Nguyen and S. Messenger, (2014) *Astrophys. J.* 748(2), 149. [5] J. Leitner and P. Hoppe, (2019) *Nat. Astron.*, 3(8), 725–729. [6] N. Nevill et al. (2023) *LPSC 54*, #1707. [7] N. Nevill et al. (2023) *Goldschmidt*. [8] K. Richter et al. (2010) *EPSL*, 291(1-4), 1-9. [9] N. Nevill et al. (2024) *LPSC 55*, #?.

