

Quantative Measurements of Trace Elements and Three-Dimensional Atomic Scale Characterisation of Presolar O-rich Oxides and Silicates: An Atom Probe Tomography Approach. N. D. Nevill^{1,2,3}, P. A. Bland¹, D. W. Saxey⁴, W. D. A. Rickard⁴, P. Guagliardo⁵, L. Daly^{1,6,7}, S. M. Reddy^{1,2}, N. E. Timms¹ & L. V. Forman^{1,8}, ¹Space Science and Technology Centre, School of Earth and Planetary Sciences, Curtin University, GPO Box U1987, Perth, Western Australia, 6845, ²Lunar and Planetary Institute, Universities Space Research Association, 3600 Bay Area Blvd., Houston, Texas, 77058 USA, ³Astromaterials Research and Exploration Science, NASA Johnson Space Center, 2101 NASA Parkway, Mail Code XI3, Houston, TX, 77058, USA, ⁴Geoscience Atom Probe, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, 6845, ⁵Centre for Microscopy, Characterisation and Analysis, The University of Western Australia; Perth, Western Australia, 6009, Australia, ⁶School of Geographical and Earth Sciences, University of Glasgow, Gregory Building, Lilybank Gardens, Glasgow G12 8QQ, UK, ⁷Australian Centre for Microscopy and Microanalysis, University of Sydney, Sydney, 2006, New South Wales, Australia, ⁸Dept of Earth and Planetary Sciences, Western Australian Museum, Locked Bag 49 Welshpool DC, Western Australia 6986, Australia.

Introduction: Presolar grains are records of a single moment in stellar evolution which have survived nebula and parent body processing within our Solar System. These grains condensed within a range of stellar environments including asymptotic giant branch stars, red giant branch stars, nova, supernova (SN) and hydrogen burning electron capture supernova (ECSN) [1,2]. Isotopic and chemical compositions can be used to unravel details about environmental conditions at the time of their condensation and physical and chemical processes occurring at the time. For example, nucleosynthesis, stellar evolution, physical properties of stellar atmospheres, mixing from inner core to outer envelope, galactic chemical evolution, interstellar medium and parent body processing.

NanoSIMS enables detailed characterisation of isotopic compositions and rapid *in situ* identification of O-rich presolar oxides and silicates using their characteristic ¹⁷O/¹⁶O and ¹⁸O/¹⁶O isotopic ratios. Spectroscopic techniques e.g., auger spectroscopy and transmission electron microscopy, have provided additional details on major and minor chemical signatures. However, due to spatial resolution limitations, interaction volumes and interferences from surrounding grains for *in situ* techniques, attaining quantative characterisation of trace elements, has proved challenging [1,3].

As the most sensitive geochemical tracers of environmental changes, trace elements are essential to unravelling the geochemical record of their parent stellar environments and evolutionary pathways [4]. We carried out correlated *in situ* isotopic and chemical analyses of 13 presolar grains to better understand stellar evolution. In this work, we achieved this using a custom approach, coordinating NanoSIMS, Scanning Electron Microscopy Energy Dispersive X-Ray Spectroscopy (SEM-EDX) and Atom Probe Tomography (APT). Our objective was to develop an approach which could enable precise targeting of presolar grains for atom probe tomography and successfully execute atomic scale analyses of presolar oxides and silicates, to achieve quantative analysis of their trace elements for the first

time. We also aimed to test the capability for Atom Probe tomography to measure isotopic compositions and stoichiometries of presolar oxide and silicate grains.

Approach and Methodology: We systematically searched polished thin sections Acfer 094 and ALH 77307 using NanoSIMS 50L for O-rich presolar oxide and silicate grains. These carbonaceous chondrites are well known for their presolar grain abundances and are considered among the most primitive and pristine meteorites ever discovered.

High spatial resolution (<200 nm pixel dimension) isotopic images were initially obtained using the NanoSIMS 50L for ¹⁶O, ¹⁷O, ¹⁸O, ²⁸Si, ²⁹Si, ³⁰Si, ³²S, identifying thirteen oxide and silicate grains with oxygen isotopic signatures exceeding solar. Then ¹⁶O, ¹⁷O, ¹⁸O, ²⁴Mg ¹⁶O, ²⁷Al ¹⁶O, ⁵⁶Fe ¹⁶O, ⁴⁸Ti ¹⁶O ion images were collected for chemical context when locating grains within mineralogically complex mineral matrices. The latter improved the odds of locating target grains and resulted in a 100% success rate once implemented down to a grain size of 160 nm. Measurements used a focused 16 keV Cs⁺ primary ion beam.

Chemical data obtained using the Tescan Clara SEM at JdLC, Curtin University, in coordination with NanoSIMS ion imaging, was used to identify target grains for extraction and preparation for APT. Hyperspectral mapping was collected using 10kV at 3pA with a high sensitivity Ultim Max 170 SDD energy dispersive x-ray (EDX) detector which measures at a higher sensitivity and accuracy when data is taken at the same beam energy as the previous instruments [5]. This was important to try and improve accuracy of this micrometric technique when measuring nanoscale grains [3].

Five of the identified presolar grains were then prepared into needle-like shapes with fine tips for APT acquisition using the button method [6]. Targets for APT acquisition were primarily selected based on the surface area of the grain, whether this surface area was maintained amongst isotopic ion maps, and the accuracy at which each grain could be identified. Sample preparation was completed at the JdLC, Curtin University using

the Tescan Lyra3 GM Dual Beam Focus Ion Beam (FIB) Field Emission SEM (FE-SEM). Needles were milled 40 – 70 nm in diameter at the apex, with $\sim 3^\circ$ to 5° shank angles. Presolar grains were extracted directly from the mineral matrix using the FIB technique [6].

Finally, samples were analysed using APT. Measurements were executed within the Geoscience Atom Probe facility, at the JdLC, Curtin University, using the CAMECA Local Electrode Atom Probe, LEAP 4000X HR. Manual acquisition was required to monitor interactions with measurement parameters and maintain evaporation of specimen ions at the apex.

Results & Discussion: Presolar grains measured using APT were corundum-like (N-AC5), enstatite-like (N-AL1), ‘other’ ferromagnesian silicate (N-AL2) and an ‘intermediate’ ferromagnesian silicate (N-AL4) based on coordinated NanoSIMS, SE-EDX and APT analysis. Classifications were based on chemical compositions, with ferromagnesian silicates classified based on their $\text{Mg}+\text{Fe}(\text{+Ca})/\text{Si}$ ratios per recommended practices [1]. For example, $\text{Mg}+\text{Fe}(\text{+Ca})/\text{Si}$ ratios falling within 1σ of the theoretical ratios of 1 for pyroxene were classified as pyroxene-like, $\text{Mg}+\text{Fe}(\text{+Ca})/\text{Si}$ ratios falling within 1σ of the theoretical ratios of 2 for olivine were classified as olivine-like. When $\text{Mg}+\text{Fe}(\text{+Ca})/\text{Si}$ ratios fall within 1σ of a $1.1 < 1.9$ ratio, an ‘intermediate’ classification is given, and when phases are depleted (ratios above olivine, *i.e.*, $2.3 <$) or enriched (ratios below pyroxene, *i.e.*, < 0.8) in Si, an ‘other’ classification is given [1]. Results were confirmed through $\text{Mg}+\text{Fe}/\text{Si}$, cation/O and Si/O ratios. Three 3D atomic reconstructions of N-AC5 are shown in Fig 1, with their minor and trace element atomic distributions shown, *i.e.*, trace Mg abundances (left), minor Ti abundances (center) and minor Ca abundances (right). All reconstructions include its primary ions Al and O. The total ion count of the APT reconstruction is 9, 293, 930, collected from a $1\text{ }\mu\text{m}$ sized corundum-like (Al_2O_3) grain.

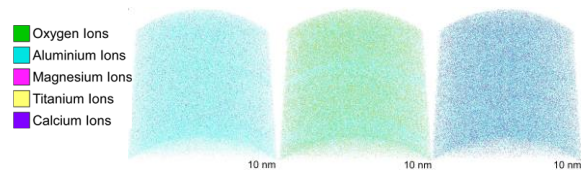


Fig 1: 3D APT LEAP reconstruction of a presolar oxide and its trace element distributions (N-AC5).

Overall, the mass spectra collected from measured presolar grains only showed a few peaks other than those associated with the major ions in minor (*i.e.*, Al, Mn, Ca, Ti) and trace abundances (*i.e.*, Al, Mg). N-AL1 also showed Fe in major abundances (5.43 ± 0.08 at.%) and N-AL4 showed Fe (5.81 ± 0.26 at.%) and Al (2.11 ± 0.18 at.%) in major abundances. All detected ions were homogeneously distributed amongst measured

presolar grains. The sub-nanometer ionic distributions were determined through 3D reconstructions and 1D concentration profiles.

The mass resolution of spectra collected during APT acquisition was sufficiently high and isobaric interferences minimal enabling isotopic compositions to be calculated within measured presolar silicate phases. Results led to the measurement of the highest $\delta^{25}\text{Mg}$ isotopic compositions measured in a silicate ($\delta^{25}\text{Mg} = 2724.94\text{‰} \pm 33.04\text{‰}$) and the constraint of the initial $^{26}\text{Al}/^{27}\text{Al}$ ratio within N-AC5. Within the latter, thermal peak tails were too high to attain any additional isotopic compositions. However, the resolution was sufficient to determine major, minor and trace elemental abundances within N-AC5 and the same issue was not seen within measured presolar silicates. Coordinated NanoSIMS and APT isotopic calculations of O, Si, Mg and Al isotopes, indicated measured presolar oxides and silicates originated from AGB/RGB stars (N-AL1), nova (N-AL4), type II SN (N-AC5 and N-AL2) and the recently identified ECSN (N-AL6) [2,7,8]. N-AL4 is only the third Nova grain to be studied in geochemical detail.

Conclusion: Here we presented the first results on APT acquisition of presolar O-rich silicates and oxides, including quantitative measurements of trace elements for the first time and calculations of a more expansive range of isotopic compositions than can be achieved within the analytical volume of individual presolar grains using NanoSIMS alone. With respect to O-rich presolar grains, APT may be the only technique capable of attaining quantitative abundances of trace elements. Consequently, APT could expand the depth of geochemical detail gained from each presolar grain, and 3D nanoscale characteristics. This is particularly important regarding presolar silicates considering they are on average < 500 nm in size and are considered the most geochemically complex presolar grain type. Continued studies will expand on the database of trace elements in presolar oxides and silicates, and provide detailed information on the compositions of these phases, essential for expanding our knowledge of different stellar environments and their evolutionary journeys.

References: [1] E. Zinner (2014) in *Meteorites and cosmochemical processes*, 1, (eds. A. Davis) 181–213. [2] J. Leitner and P. Hoppe, (2019) *Nat. Astron.*, 3(8), 725–729. [3] F. J. Stadermann et al. (2002) *Met. Planet. Sci.*, 44(7), 1033–1049. [4] R. O. Allen and B. Mason (2010) *GCA*, 37(6), 1435–1456. [5] Tescan Orsay Holding (2020) *TESCAN MIRA - SEM analysis of materials at sub-micron scale*. [6] W. D. A. Rickard et al. (2020) *Microsc. Microanal.*, 26(4), 750–757. [7] J. José, M et al. (2004) *Astrophys. J.*, 612(1), 414–428. [8] L. R. Nittler et al. (2008) *Astrophys. J.*, 682(2), 1450–1478.