Novel Applications of FIB-SEM-based ToF-SIMS in Atom Probe Tomography Workflows

Running title: FIB-based ToF-SIMS in APT workflows

William D.A. Rickard[1], Steven M. Reddy[2], David W. Saxey[1], Denis Fougerouse[2], Nicholas E. Timms[2], Luke Daly[3,5], Emily Peterman[4], Aaron J. Cavosie[2], Fred Jourdan[1,2]

[1.] John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

[2.] School of Earth and Planetary Sciences, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

[3.] School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, UK.

[4.] Earth and Oceanographic Science, Bowdoin College, Brunswick, ME, USA.

[5.] Australian Centre for Microscopy and Microanalysis, University of Sydney, Sydney, 2006, NSW, Australia

Corresponding author contact details: Email: w.rickard@curtin.edu.au Telephone: +61 8 9266 7843

Abstract

Atom Probe Tomography (APT) is used to quantify atomic-scale elemental and isotopic compositional variations within a very small volume of material (typically <0.01 μm^3). The small analytical volume ideally contains specific compositional or microstructural targets that can be placed within context of the previously characterized surface in order to facilitate correct interpretation of APT data. In this regard, careful targeting and preparation are paramount to ensure that the desired target, which is often smaller than 100 nm, is optimally located within the APT specimen. Needle-shaped specimens required for atom probe analysis are commonly prepared using a focused ion beam scanning electron microscope (FIB-SEM). Here we utilise FIB-SEM based Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to illustrate a novel approach to targeting <100 nm compositional and isotopic variations that can be used for targeting regions of interest for subsequent lift-out and APT analysis. We present a new method for high-spatial resolution targeting of small features that involves using FIB-SEM-

based electron deposition of platinum ‘buttons’ prior to standard lift-out and sharpening procedures for atom probe specimen manufacture. In combination, FIB-ToF-SIMS analysis and application of the ‘button’ method ensures that even the smallest APT targets can be successfully captured in extracted needles.

Introduction

Atom Probe Tomography (APT) produces 3D compositional information with sub-nanometre resolution (Kelly & Larson, 2012; Miller & Forbes, 2014). APT is ideally suited for the quantitative compositional analysis of fine-scale features that are traditionally difficult to analyse in crystalline and non-crystalline solids, for example grain boundaries (Babinsky, et al., 2014; Schwarz, et al., 2018), other interfaces (Fougerouse, et al., 2018; Reddy, et al., 2016), crystal defects (Fougerouse, et al., 2018; Thompson, et al., 2007a), nanoclusters/precipitates (Fougerouse, et al., 2016; Peterman, et al., 2016; Ping, et al., 2003), sub-micrometre particles (Daly, et al., 2017), and other regions of fine-scale variations in elemental composition, such as growth zoning in minerals (Fougerouse, et al., 2016). APT specimens extracted from such features take the form of needle shaped specimens (tip diameter <100 nm), and, for non-conducting materials, these are prepared in a focused ion beam scanning electron microscope (FIB-SEM) using an *in situ* lift-out technique (Thompson, et al., 2007b). Briefly, the lift-out technique involves removing a 2.5 μm-wide rectangular prism, with a length dependant on the required number of APT specimens. Segments of the prism are then mounted on pre-fabricated posts and ion beam milled with an annular mask to a needle-like shape.

The small specimen diameter of atom probe specimens raises two challenges. Firstly, the targeting of fine-scale features for APT requires correlative imaging, and analytical techniques are thus routinely used to establish the material or geological context of the atom probe

specimen. Complementary approaches for characterization provide context at greater length scales and commonly involve surface analyses such as electron beam imaging, elemental mapping and microstructural mapping (Daly, et al., 2017; Peterman, et al., 2016; Piazolo, et al., 2016; Stoffers, et al., 2015; Tytko, et al., 2012). Secondly, the most challenging aspect of the FIB-SEM preparation of APT specimens is to position the specific region of interest centrally within the needle (<50 nm from the axis of the specimen) and close to its apex (<<1000 nm). Misalignment of just a few tens of nm can cause the region of interest to be outside the field of view during atom probe analysis, or worse, sputtered away during FIB-SEM sample preparation.

To successfully identify, target, and later correlate compositional features analysed at the surface with subsequent APT analyses from the same location, the spatial resolution of the surface analysis needs be less than the diameter of the specimen tip, i.e. < 100 nm. Imaging of the prepared sample surface by field emission-SEM using secondary electron (SE), backscattered electron (BSE) or cathodoluminescence (CL) (e.g. (Valley, et al., 2014)) often allows targeting of specific regions for APT lift-out as it has sufficient spatial resolution (potentially <5 nm), though is limited when compositional or structural features are desired. Electron backscatter diffraction (EBSD) maps have been shown to be excellent for identifying structural features in crystalline materials, such as low-angle boundaries (Meher, et al., 2015; Reddy, et al., 2016; Stoffers, et al., 2015), though this technique does not provide chemical information. EBSD maps can be collected with a spatial resolution down to 50 nm on the polished surface, and even higher-resolution data by transmission Kikuchi diffraction (TKD) can further be collected on APT specimens (Babinsky, et al., 2014; Breen, et al., 2017; Rice, et al., 2016). Mapping by energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS) are useful for identifying chemical variations. However,

the relatively high activation volumes of geological materials, ceramics, and metals at routine SEM acceleration voltages (15-20 kV) results in comparatively poor spatial resolution (typically >0.2 μm), which presents challenges when correlating the information with APT specimens. Additionally, EDS detection limits for all elements are of the order of >0.1 wt.% and as such, it is not usually possible to identify variations in low abundance composition via EDS mapping. Better detection limits are possible with a WDS detector though these detectors are much less common in FIB-SEM instruments due to restrictions in the chamber configuration. In general, the relatively low sensitivity of the aforementioned techniques and/or the large differences between analytical scales with APT makes it difficult to directly correlate the data.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a surface analysis technique that has been demonstrated to be capable of ≤ 50 nm lateral resolution (Whitby, et al., 2011). Conventionally ToF-SIMS is performed on a dedicated instrument, though the ion beam of a FIB-SEM can also be used as a primary ion source (McMahon, et al., 2002; McPhail, et al., 2011), with the benefit of retaining the capabilities of the dual beam microscope. Rastering the ion beam over a sample surface causes material removal by mechanical sputtering and ionisation. The ionised material, which can either be positively or negatively charged, is then analysed by secondary ion mass spectrometry (SIMS). These secondary ions are extracted and passed through a ToF-SIMS analyser, producing mass spectra for each FIB dwell point, which correspond to a pixel on the resulting SIMS map (Alberts, et al., 2014). Repeated scans over the region of interest, called frames, allow for improved signal-to-noise 2D maps and for depth-resolved 3D analyses (Alberts, et al., 2014; McMahon, et al., 2002). SIMS maps are produced from all or a subset of the spatially registered data. The integrated intensity from a peak in the mass/charge spectrum belonging to a particular isotope, element or compound can be displayed

as an intensity map over the region of interest. Here we refer to *in situ* ToF-SIMS measurements made within a FIB-SEM as FIB-ToF-SIMS.

FIB-ToF-SIMS is used for surface and depth-resolved (3D) elemental and isotopic mapping. Significant benefits in light element (e.g. Li) (Sui, et al., 2015) and trace element mapping, with detection limits as low as 5.5 ppm (Whitby, et al., 2011), can be achieved relative to X-ray based techniques such as EDS. The small analytical volume for each dwell point, approximately the same size as the FIB probe (e.g <25 nm diameter), allows for high lateral resolution (<50 nm) elemental maps (Whitby, et al., 2011). Importantly, when low beam currents are used, only a few tens of nanometres of material are sputtered from the sample surface, thus allowing the mapped region to be used for site-specific sample preparation for APT or transmission electron microscopy (TEM). Damage from the ion beam on the surface directly below the FIB-ToF-SIMS analysis region can be reduced by using lower energy primary ions (e.g. 10 kV rather than 20 kV) and by finishing the APT/TEM specimen preparation with a low energy (e.g., 2 kV) 'clean up' routine, as is standard practice for site specific sample preparation.

In this contribution, we present two novel applications of utilising FIB-ToF-SIMS in the workflow of APT targeting and correlative imaging. The first establishes the role of FIB-SEM based ToF-SIMS as a correlative analytical technique to assist in the targeting of atom probe specimens. The second utilises the potential for electron deposition in the FIB-SEM and is a methodology for ensuring that the specific region of interest is captured in the atom probe specimen. This combination of approaches provides an effective improvement in existing APT workflows in regards to both targeting and correlative imaging.

Materials and Methods

FIB-SEM

ToF-SIMS ion imaging and APT sample preparation was conducted using a Tescan Lyra3 FIB-SEM with a Ga^+ ion source and platinum mono gas injection system (GIS) located in the John de Laeter Centre (JdLC) at Curtin University, Australia. The FIB-SEM was also fitted with an Oxford Instruments X-Max 20 mm^2 detector which was used for EDS analysis. EDS analysis was performed at 20 kV and the data was analysed using Oxford Instruments AZtec version 3.4 software. EBSD was performed using an Oxford Instruments Nordlys Nano high-resolution EBSD detector and Oxford Instruments AZtec version 3.4 software acquisition system at 20 kV and a step size of 80 nm.

FIB-ToF-SIMS

The Tescan Lyra3 FIB-SEM at Curtin University was fitted with a ToF-SIMS C-TOF detector made by Tofwerk AG. ToF-SIMS Explorer version 1.3 was used to process and analyse the data. Further details on FIB-ToF-SIMS can be found in (Alberts, et al., 2014; Whitby, et al., 2011). In this study the acquisition was carried out with an ion beam energy and current of 30 kV and 75 pA, respectively. Elemental maps with 1024×1024 pixels (4×4 binning) were collected over square areas between 5×5 µm and 20×20 µm, resulting in a pixel resolution between 20 nm and 80 nm in both x- and y-directions. Collecting the data for 50 frames resulted in an analysis depth of approximately 100 nm. Because a mass spectrum is generated at every pixel in each frame, data were extracted from all or a subset of the full data cube and displayed as an intensity map for a particular ion.

Atom Probe Tomography

APT was performed using a Cameca LEAP 4000X HR located at the Geoscience Atom Probe facility in the JdLC, Curtin University, Australia. The LEAP was operated in laser-assisted mode, with a pulse rate of 200 to 250 kHz, a laser pulse energy between 100 pJ (plagioclase) and 300 pJ (olivine), base temperatures 40 to 60 °K, and a 0.8% automated detection rate. Post-acquisition processing was conducted using Cameca's Integrated Visualization and Analysis Software (IVAS) version 3.8.0.

Samples

This paper presents data from a range of samples which each serve to highlight advantages of the analytical approached used or showcase correlative analyses across a range of length scales. The coal sample (Fig. 1) used was a resin mounted sub-bitumous coal fragment sourced from Collie in Western Australia, Australia. Particles from the Itokawa asteroid (Fig. 2 & 6) (RA-QD02-0010 and RB-CV-0082) were collected by the Japan Aerospace Exploration agency (JAXA)'s Hayabusa sample return mission to the asteroid Itokawa (Fujiwara, et al., 2006; Nakamura, et al., 2011; Yano, et al., 2006). The olivine sample (Fig. 3) used was a single crystal specimen of San Carlos olivine, which is commonly used as a standard for geochemical analyses (details can be found in (Buening & Buseck, 1973)). The Allan Hills (ALH) 77307 carbonaceous chondrite meteorite sample contained sub-µm refractory metal inclusions (Fig. 4) and was supplied by the Antarctic Search for Meteorites, and the Smithsonian Institute and is currently on loan to Prof. Phil Bland. The shocked zircon (Fig. 5) used was a detrital grain from South Africa, details can be found in (Cavosie, et al., 2015).

High resolution chemical and isotopic mapping using FIB-ToF-SIMS

FIB-ToF-SIMS is a novel technique with interesting advantages for studies involving APT, primarily for two reasons. The first is due to the high spatial resolution chemical and isotopic mapping (Figure 1 and 2), and the second is due to the complementary time of flight data mass spectrometry that can help in the interpretation of APT time of flight data (Figure 3). FIB-ToF-SIMS can be conducted immediately prior to APT sample preparation in the same microscope, and thus is easily integrated into an efficient characterisation work flow.

Configuring the ion transfer optics for positive ions enables the detection of metals, alkalis and rare earth elements. Reversing the polarity of the optics to attract negative ions enables the detection of non-metals (e.g. C, S, O) and halogens (e.g. Cl). Detection efficiency varies significantly by element due to ionisation energy and electron affinity, with the most sensitive (in positive mode) being alkalis and the least sensitive being heavy metals. Data acquisition parameters such as ion beam voltage, ion beam current and the size of the analysis region can be selected to optimise for sputter rate and spatial resolution. The depth of the analysis is dependent on the number of frames scanned and the sputter rate of the material.

Secondary ions are generated from a region in close proximity (~10 nm) to the primary ion interaction point and thus the information volume is approximately the same size as the primary ion probe (Benninghoven, et al., 1987). FIB-SEM instruments with a liquid metal ion source (LMIS) such as Ga^+ can achieve probe sizes <25 nm (Smith, et al., 2006), which enables SIMS maps with high spatial resolution. A comparison between chemical or isotopic analysis of

oxygen over a small area (10×10 µm) by EDS and FIB-ToF-SIMS (Figure 1) demonstrates the improved spatial resolution and surface sensitivity of the latter technique. It is noted that typical analytical conditions were chosen for the EDS analysis and that improved spatial resolution would likely be achievable at lower SEM accelerating voltages, however, it not expected to match the spatial resolution of FIB-ToF-SIMS. It can be observed in Figure 1 that only particles at or near the surface (<10 nm, beam energy dependant) are detected in the SIMS map, demonstrating the surface sensitivity of the technique. In many cases, signal intensity limits the effective spatial resolution, as sensitivity varies as a function of the ionisation efficiency of each element (related to the electron affinity). See (Stephan, 2001) for relative sensitivity factors (RSF) for a Ga primary ion source.

The FIB-ToF-SIMS data are collected such that every pixel has a corresponding mass spectrum and the pixels that make a frame are stacked to produce a data cube. SIMS maps or depth profiles for a particular mass peak can be extracted from all or part of the analysed volume. Mass spectra can be extracted from particular regions over areas as small as few pixels from within the analysed volume which can be used to identify chemical associations in micrometre to sub-micrometre domains. For example, the extraction of mass spectra from distinct regions is shown in figure 2 where FIB-ToF-SIMS was used to reveal complex sub-micrometre compositional domains, including olivine-, pyroxene-, and feldspar-normative components; the mass spectra in the figure compares a Ca-Mg-Fe-Si-rich region with a K-Na-Al-Si-rich region. Resolving such domains would not be possible using techniques such as SEM-EDS where the interaction volume is much larger than the size of the domains. A limitation of FIB-ToF-SIMS, as with other SIMS techniques, is that quantification of element abundance is very challenging due to matrix effects influencing secondary ion intensities. Quantification is indeed possible, though a series of standards with chemically similar composition must be measured

in order to calibrate the results. If standards are not available then quantification of sub-μm domains can be achieved by APT or TEM-EDS.

FIB-ToF-SIMS produces mass/charge spectra that can be directly correlated with mass/charge spectra from atom probe analyses (Figure 3). Different ionisation processes between the two techniques mean that in some cases ambiguous peaks can be identified by comparing the two data sets. The data collection conditions for FIB-ToF-SIMS can be configured to collect either positive or negative ions, thus providing additional versatility when targeting specific elements.

An approach for precise targeting and milling of atom probe needles: The button method

One of the main challenges in correlating FIB-ToF-SIMS or other surface analyses (e.g. EDS maps) with APT data is ensuring that the feature identified on the surface is within the APT specimen and in an optimal position. The site specific sample preparation process can be challenging, as the standard APT lift-out method involves the intial extraction of a relatively large volume of material; each wedge segment is usually a 2.5 μm wide rectangular prism, which is ~200 times larger than volume measured by APT. The extracted wedge is then placed on a pre-fabricated post and most of the bulk material is subsequently milled away to form a suitable APT specimen tip shape (Thompson, et al., 2007b).

A relatively simple method to assist in precise targeting and milling of APT needles in the context of surface-based analyses conducted prior to lift-out is demonstrated in Figure 4. Firstly the target for APT was identified using surface imaging or microanalysis (e.g. FIB-ToF-SIMS, BSE, EBSD, or other methods). A ‘button’ of Pt with diameter of 50 to 100 nm (depending on size of feature) was then deposited directly above the region of interest using electron beam deposition (EBD) (Figure 5). Typical deposition conditions are an electron beam current of 0.5

nA, with a 5 kV acceleration voltage, a dwell time of 1 s, and a stage tilt of 0° (so that the e-beam is normal to the surface). The button creates a topographical feature that is discernible after the subsequent ion beam deposition (IBD) protection layer of Pt is applied over the entire lift-out wedge (Figure 5).

Multiple APT targets can be marked by buttons and incorporated into the same IBD-protected wedge, for example, where FIB-ToF-SIMS identified an anomalous ^{40}Ca signature along a twin boundary in an impact-shocked zircon previously characterized by EBSD mapping (Cavosie, et al., 2015) (Figure 5). In this example, the lamellar twin is on average ~1–1.25 µm wide, and is orientated dipping to the polished sample surface. Multiple buttons were placed along the near-linear regions at 1 to 3 µm spacing, allowing multiple APT specimens to be prepared with highly accurate, independent positioning. A standard lift-out and mounting procedure was then conducted, with each button centred on a mounting post (e.g., a silicon post of a prefabricated microtip coupon; Figure 4) for each wedge segment.

Secondary electron imaging of FIB-prepared buttons, using an off-axis detector during positioning of the various annular milling masks, enhances the topography contrast, thus enabling the button (with region of interest below) to be located at the centre of the APT specimen tip. The remnants of the button were then milled away during the final tip shaping (usually at low ion energy) as residual platinum can be problematic during APT analysis. This method enables accurate targeting of fine structures such as nanoparticles (e.g. (Daly, et al., 2017)) and enhanced correlation of the APT measured volume with surface analyses, since the surface location of the analysed region is known to a high degree of accuracy (<100 nm). The method presented here has similarities with a method proposed by Lotharukpong et al.

(Lotharukpong, et al., 2017), though their method also involves a second marker for lateral alignment and uses a continuous line for linear features.

Integration of FIB-TOF-SIMS in an Atom Probe Analytical Workflow

The following is an example of the integrated workflow using the button method to correlate microanalyses, including FIB-ToF-SIMS, from the grain scale to the atom scale (Figure 6). The sample is a particle from the Itokawa asteroid (RA-QD02-0010) (Fujiwara, et al., 2006; Nakamura, et al., 2011; Yano, et al., 2006). The distribution of K is of interest for subsequent and ongoing $^{40}Ar/^{39}Ar$ geochronology work (to measure of the age of a mineral or rock) as the production of the radiogenic daughter isotope $^{40}Ar^{*}$ is due to the natural decay of ^{40}K in a given mineral. Imaging in a SEM using secondary and backscattered electrons revealed topography and variations in the average atomic number within the particle. EBSD with a 80 nm step size was used to identify the presence of K-bearing minerals, such as feldspars, and also found that there was fine scale twinning in the plagioclase phase (see 'all Euler' EBSD map in Figure 6). EDS revealed the presence of K within the plagioclase grain, though the spatial resolution was limited. A series of FIB-ToF-SIMS maps were then collected along a plagioclase grain boundary, with map sizes between 5 x 5 µm and 10 x 10 µm (i.e., pixel sizes 20 nm and 40 nm, respectively). FIB-ToF-SIMS is particularly sensitive to alkali metals (due to their propensity to ionise when sputtered by a Ga^{+} FIB) and as such the ^{39}K maps had a high signal-to-noise ratio and were able to be collected with limited removal of material (usually <100 nm depth). The ^{39}K maps revealed that there was a depletion of K at the twin boundaries. It also revealed 'feather-like' K concentrations only a few tens of nm wide emanating from the grain boundary in the vicinity of the boundaries with other phases. Importantly, these 'feather-like' K features are not evident in either the BSE or EBSD data for the same region.

Based on the FIB-ToF-SIMS maps, a row of Pt deposited buttons (50 nm diameter, ~100 nm height) were then precisely positioned on the 'feather-like' features (Fig. 6). Images were then taken so that the exact position of each of the buttons, which eventually correspond to APT specimens, was known. A standard lift-out and post-mounting procedure was then performed (as per Fig. 4) with careful positioning during final tip shaping to ensure the annular milling was centred on the relevant button. The tips were then removed from the FIB-SEM and analysed by atom probe. The APT results were easily correlated with the surface images as the measured volume was coincident with the region below 'buttons'. The APT reconstruction reveals a 20 nm wide lamella feature, which was identified to be chemically consistent with antiperthite, a K-feldspar exsolution phase found within plagioclase (Fig. 6).

Summary

The challenge of preparing contextualised atom probe specimens that contain small regions of interest has been addressed by integrating FIB-based ToF-SIMS analysis and targeted electron-deposition, here termed the 'button' method. The approach allows consistent and accurate targeting and positioning of compositional features within the <100 nm diameter region at the tip of an APT needle with ~50 nm precision.

FIB-ToF-SIMS provides complementary, high spatial resolution chemical and isotopic information to support surface characterisation studies, and is also applicable for the characterisation and targeting for site specific APT (or TEM) lift-outs. The inclusion of FIB-ToF-SIMS into the APT sample preparation work flow allows for *in situ* elemental analysis with sufficient spatial resolution to resolve features comparable in size to the region that will be analysed in the atom probe, something that is usually not possible using X-ray-based techniques. The detection of light elements, low detection limits, isotopic sensitivity and

comparable mass spectra provide additional advantages to APT studies. The use of surface deposited 'buttons' allows accurate targeting of very fine structures and improves correlation of features imaged via APT with features seen in a variety of high-resolution surface mapping and imaging techniques. The correlation of results from APT and FIB-ToF-SIMS permits compositional analysis of materials at length scales from sub-nanometre to tens of micrometres. This approach enables the contextual analysis of nanoscale features, which has applications in geology, planetary science and materials science.

Acknowledgements

This work was conducted within the Geoscience Atom Probe Facility at Curtin University, which is part of the Advanced Resource Characterization Facility (ARCF). The ARCF, under the auspices of the National Resource Sciences Precinct (NRSP) – a collaboration between CSIRO, Curtin University, and The University of Western Australia – is supported by the Science and Industry Endowment Fund. A portion of this work was funded by the Australian Research Council (ARC) via their Australian Laureate Fellowship program to Prof. Phil A. Bland. DF acknowledges ARC funding DE190101307. The authors would like to thank JAXA for the provision of the samples via the International AO for Hayabusa Sample Analysis 3 awarded to F. Jourdan, N. Timms, T. Nakamura, and P.Bland.

References

Alberts, D., Von Werra, L., Oestlund, F., Rohner, U., Hohl, M., Michler, J. & Whitby, J.A. (2014). Design and performance of two orthogonal extraction time-of-flight secondary ion mass stectrometersfor focused ion beam instruments. *Instrumentation Science & Technology* **42**(4), 432-445.

Babinsky, K., De Kloe, R., Clemens, H. & Primig, S. (2014). A novel approach for site-specific atom probe specimen preparation by focused ion beam and transmission electron backscatter diffraction. *Ultramicroscopy* **144**, 9-18.

Benninghoven, A., Rudenauer, F. & Werner, H.W. (1987). Secondary ion mass spectrometry: basic concepts, instrumental aspects, applications and trends.

Breen, A.J., Babinsky, K., Day, A.C., Eder, K., Oakman, C.J., Trimby, P.W., Primig, S., Cairney, J.M. & Ringer, S.P. (2017). Correlating Atom Probe Crystallographic Measurements with Transmission Kikuchi Diffraction Data. *Microscopy and Microanalysis* **23**(2), 279-290.

Buening, D. & Buseck, P.R. (1973). Fe-Mg lattice diffusion in olivine. *Journal of Geophysical Research* **78**(29), 6852-6862.

Cavosie, A.J., Erickson, T.M., Timms, N.E., Reddy, S.M., Talavera, C., Montalvo, S.D., Pincus, M.R., Gibbon, R.J. & Moser, D. (2015). A terrestrial perspective on using ex situ shocked zircons to date lunar impacts. *Geology* **43**(11), 999-1002.

Daly, L., Forman, L.V., Bland, P.A., Fougerouse, D., Reddy, S.M., Saxey, D.W. & Rickard, W.D.A. (2017). Nebula sulfidation and evidence for migration of "free-floating" refractory metal nuggets revealed by atom probe microscopy. *Geology* **45**(9), 847-850.

Fougerouse, D., Reddy, S.M., Kirkland, C.L., Saxey, D.W., Rickard, W.D. & Hough, R.M. (2018). Time-resolved, defect-hosted, trace element mobility in deformed Witwatersrand pyrite. *Geoscience Frontiers*.

Fougerouse, D., Reddy, S.M., Saxey, D.W., Rickard, W.D.A., Van Riessen, A. & Micklethwaithe, S. (2016). Nanoscale gold clusters in arsenopyrite controlled by growth-rate not concentration: evidence from atom probe microscopy. *American Mineralogist* **101**, 1916-1919.

Fujiwara, A., Kawaguchi, J., Yeomans, D., Abe, M., Mukai, T., Okada, T., Saito, J., Yano, H., Yoshikawa, M. & Scheeres, D. (2006). The rubble-pile asteroid Itokawa as observed by Hayabusa. *Science* **312**(5778), 1330-1334.

Kelly, T.F. & Larson, D.J. (2012). Atom Probe Tomography 2012. *Annual Review of Materials Research* **42**(1), 1-31.

Lotharukpong, C., Tweddle, D., Martin, T.L., Wu, M., Grovenor, C.R.M., Moody, M.P. & Wilshaw, P.R. (2017). Specimen preparation methods for elemental characterisation of grain boundaries and isolated dislocations in multicrystalline silicon using atom probe tomography. *Materials Characterization* **131**, 472-479.

Mcmahon, G., Nxumalo, J. & Phaneuf, M. (2002). Applications of a novel FIB-SIMS instrument in SIMS image depth profiling. *Microscopy and Microanalysis* **8**(S02), 1212-1213.

Mcphail, D.S., Li, L., Chater, R.J., Yakovlev, N. & Seng, H. (2011). From FIB-SIMS to SIMS-FIB. The prospects for a 10 nm lateral resolution SIMS instrument with full FIB functionality. *Surface and Interface Analysis* **43**(1-2), 479-483.

Meher, S., Nandwana, P., Rojhirunsakool, T., Tiley, J. & Banerjee, R. (2015). Probing the crystallography of ordered Phases by coupling of orientation microscopy with atom probe tomography. *Ultramicroscopy* **148**, 67-74.

Miller, M.K. & Forbes, R.G. (2014). Introduction to Atom-Probe Tomography. In *Atom-Probe Tomography: The Local Electrode Atom Probe*, pp. 1-49. Boston, MA: Springer US.

Nakamura, T., Noguchi, T., Tanaka, M., Zolensky, M.E., Kimura, M., Tsuchiyama, A., Nakato, A., Ogami, T., Ishida, H. & Uesugi, M. (2011). Itokawa dust particles: a direct link between S-type asteroids and ordinary chondrites. *Science* **333**(6046), 1113-1116.

Peterman, E.M., Reddy, S.M., Saxey, D.W., Snoeyenbos, D.R., Rickard, W.D.A., Fougerouse, D. & Kylander-Clark, A.R.C. (2016). Nanogeochronology of discordant zircon measured by atom probe microscopy of Pb-enriched dislocation loops. *Science Advances* **2**(9).

Piazolo, S., La Fontaine, A., Trimby, P., Harley, S., Yang, L., Armstrong, R. & Cairney, J.M. (2016). Deformation-induced trace element redistribution in zircon revealed using atom probe tomography. *Nature Communications* **7**.

Ping, D.-H., Hono, K. & Nie, J. (2003). Atom probe characterization of plate-like precipitates in a Mg–RE–Zn–Zr casting alloy. *Scripta Materialia* **48**(8), 1017-1022.

Reddy, S.M., Van Riessen, A., Johnson, T.E., Saxey, D.W., Fischer, S., Rickard, W.D.A., Fougerouse, D., Prosa, T., Rice, K., Reinhard, D.A. & Chen, Y. (2016). Mechanisms of deformation-induced trace element migration in zircon resolved by atom probe and correlative microscopy. *Geochimica et Cosmochimica Acta* **195**, 158-170.

Rice, K.P., Chen, Y., Prosa, T.J. & Larson, D.J. (2016). Implementing Transmission Electron Backscatter Diffraction for Atom Probe Tomography. *Microscopy and Microanalysis* **22**(3), 583-588.

Schwarz, T., Stechmann, G., Gault, B., Cojocaru-Mirédin, O., Wuerz, R. & Raabe, D. (2018). Correlative transmission Kikuchi diffraction and atom probe tomography study of Cu(In,Ga)Se2 grain boundaries. *Progress in Photovoltaics: Research and Applications* **26**(3), 196-204.

Smith, N.S., Skoczylas, W.P., Kellogg, S.M., Kinion, D.E., Tesch, P.P., Sutherland, O., Aanesland, A. & Boswell, R.W. (2006). High brightness inductively coupled plasma source for high current focused ion beam applications. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **24**(6), 2902-2906.

Stephan, T. (2001). TOF-SIMS in cosmochemistry. *Planetary and Space Science* **49**(9), 859-906.

Stoffers, A., Cojocaru-Mirédin, O., Seifert, W., Zaefferer, S., Riepe, S. & Raabe, D. (2015). Grain boundary segregation in multicrystalline silicon: correlative characterization by EBSD, EBIC, and atom probe tomography. *Progress in Photovoltaics: Research and Applications* **23**(12), 1742-1753.

Sui, T., Song, B., Dluhos, J., Lu, L. & Korsunsky, A.M. (2015). Nanoscale chemical mapping of Li-ion battery cathode material by FIB-SEM and TOF-SIMS multi-modal microscopy. *Nano Energy* **17**, 254-260.

Thompson, K., Flaitz, P.L., Ronsheim, P., Larson, D.J. & Kelly, T.F. (2007a). Imaging of Arsenic Cottrell Atmospheres Around Silicon Defects by Three-Dimensional Atom Probe Tomography. *Science* **317**(5843), 1370-1374.

Thompson, K., Lawrence, D., Larson, D., Olson, J., Kelly, T. & Gorman, B. (2007b). In situ site-specific specimen preparation for atom probe tomography. *Ultramicroscopy* **107**(2), 131-139.

Tytko, D., Choi, P.-P., Klöwer, J., Kostka, A., Inden, G. & Raabe, D. (2012). Microstructural evolution of a Ni-based superalloy (617B) at 700°C studied by electron microscopy and atom probe tomography. *Acta Materialia* **60**(4), 1731-1740.

Valley, J.W., Cavosie, A.J., Ushikubo, T., Reinhard, D.A., Lawrence, D.F., Larson, D.J., Clifton, P.H., Kelly, T.F., Wilde, S.A., Moser, D.E. & Spicuzza, M.J. (2014). Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography. *Nature Geosci* **7**(3), 219-223.

Whitby, J.A., Östlund, F., Horvath, P., Gabureac, M., Riesterer, J.L., Utke, I., Hohl, M., Sedláček, L., Jiruše, J. & Friedli, V. (2011). High spatial resolution time-of-flight secondary ion mass spectrometry for the masses: a novel orthogonal ToF FIB-SIMS instrument with in situ AFM. *Advances in Materials Science and Engineering* **2012,** Article ID 180437, 13 pages..

Yano, H., Kubota, T., Miyamoto, H., Okada, T., Scheeres, D., Takagi, Y., Yoshida, K., Abe, M., Abe, S. & Barnouin-Jha, O. (2006). Touchdown of the Hayabusa spacecraft at the Muses Sea on Itokawa. *Science* **312**(5778), 1350-1353.

Figure 1. BSE image with corresponding EDS and FIB-ToF-SIMS elemental maps for oxygen from a coal sample containing fine kaolinite ($Al_2Si_2O_5(OH)_4$) particles. The white dashed circles denote a particle dectected by BSE imaging but not by FIB-ToF-SIMS indicating that it is below the surface.

Figure 2. BSE image with corresponding FIB-ToF-SIMS elemental maps over a 10 x 10 µm area of a mineral grain from the Itokawa asteroid (RB-CV-0082). The region of interest contains the edge of a Ca pyroxene (Px) crystal and a mottled domain, which is the remnant of an immiscible melt, which exhibits very fine variations in chemical composition. The mass spectra were derived from a 500×500 nm Ca-rich region (black) and a 500×500 nm K-rich region (red). The mass spectra contain a pulser peak from the detection system and a peak associated with the Ga primary ions. These data were collected using a monoisotopic Ga ion source.

Figure 3. Comparison between APT and ToF-SIMS mass to charge state ratio spectra from a sample of San Carlos Olivine. Positive and negative ToF-SIMS spectra are displayed. Gallium peaks are from the FIB primary ion source These data were collected using a natural abundance Ga ion source.

Figure 4. Series of images detailing the button method for high accuracy APT specimen targeting. The region of interest is a refractory metal nugget (containing platinum group elements) located within an ultrarefractory

inclusion in the Allan Hills (ALH) 77307 Carbonaceous chondrite meteorite sample (Daly, et al., 2017). Scale bars represent 1 µm in all images.

Figure 5. Example of a series of buttons placed along a near-linear feature in a shocked zircon ($ZrSiO_4$) from the Vredefort impact structure in South Africa (Cavosie, et al., 2015). In this case, the linear feature is the interface between a {112} lamellar twin and the host grain. The host-twin interface was identified by an increase in the trace element Ca, and was then targeted for APT analysis at multiple locations using the button method.

Figure 6. Example of correlative study involving FIB-ToF-SIMS and APT. The EDS and EBSD (all euler) maps are coincident with the SE image. There are a series of FIB-ToF-SIMS maps (^{39}K intensity maps displayed) overlayed onto an SE image. Ol (olivine), Tr (troilite) and Pl (plagioclase) denotes the minerals identified by EBSD. In the APT reconstruction green spheres represent Na ions, whereas blue spheres represent K ions.