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Best Practices for Reporting Atom Probe Analysis of Geological Materials

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ABSTRACT

The application of atom probe tomography (APT) within the Earth and planetary sciences has produced novel data sets that answer fundamental questions about the near-atomic scale distribution of elements and isotopes within minerals. It involves the incremental evaporation, detection, and subsequent computer reconstruction of charged particles from a needle-shaped specimen. The range of applications is growing such that protocols for reporting are needed for APT data comparison and quality assessment among natural materials. A particular challenge of APT science relates to documenting the instrumental and analyst-dependent conditions that affect the mass spectral and spatial qualities of the data and their interpretation. This contribution outlines recommended data reporting procedures for publication of ATP data in terms of the sample preparation, data collection, and reconstruction phases as well as the characterization and interpretation of the reconstructed volume. Coordinated reporting of this basic information will promote efficient communication of protocols, and aid in the evaluation of published atom probe data as geologists continue to explore atomic compositions and distributions at nanoscale.

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18.1. INTRODUCTION

Recent work has established atom probe tomography (APT) as a unique tool within the geosciences for interrogating material chemistry at the nanoscale. In APT, a needle-shaped specimen with an end-form radius on the order of 50–100 nm is held at high voltage, and constituent atoms are field evaporated through application of a timed voltage pulse (for conductive materials) or laser pulse (for semiconductors and insulators). The voltage bias and small radius of curvature produce a large electric field that is localized around, and diverging from, the end surface of the needle-shaped specimen; evaporated ions are accelerated by the local electric field, leading to divergent trajectories for ions originating from different positions on the specimen surface. A position-sensitive detector records both the hit position of

incident ions and their time of incidence. This information is then converted to identify individual elements and isotopes based on mass-to-charge-state ratios, and to reconstruct individual ion positions based on their incident position on the detector and the specimen geometry [*Gault et al.*, 2012; *Larson et al.*, 2013; *Miller and Forbes*, 2014]. This combination of time-of-flight mass spectrometry and projection microscopy allows characterization of trace and isotope chemistry in three dimensions with sub-nanometer resolution, and presents a novel means to interrogate materials, interfaces, and the processes responsible for elemental and isotopic heterogeneities.

In APT, the needle-shaped specimen is "the primary optic of the atom probe microscope" [*Larson et al.*, 2013], meaning that the field evaporation process and ion flight trajectories are fundamentally affected by the shape, and material properties, of the specimen itself. As a result, characterization of materials by APT requires consideration of numerous variables that influence both data quality and data analysis. A specimen's geometry, crystallography, and physical properties influence specimen yield, as well as spatial and spectral resolution; these in turn influence other aspects of quantitative data analysis, including the detection and characterization of different compositional domains [*Gault et al.*, 2012; *Larson et al.*, 2013; *Miller and Forbes*, 2014]. The detailed description of field evaporation for ceramics and complex oxides remains an active area of research [e.g., *Tsong and Müller*, 1970; *Oberdorfer et al.*, 2007; *Oberdorfer and Schmitz*, 2011, *Silaeva et al.*, 2013; *Vurpillot and Oberdorfer*, 2015; see also *Miller and Forbes,* 2014 and references therein], and optimizing acquisition conditions, such as temperature and voltage pulse magnitude/laser pulse energy, on a material-by-material basis remains important for both acquiring data and ensuring data quality and reproducibility [e.g., *La Fontaine et al.*, 2017]. Interest in precise and accurate reconstructions, quantitative compositional analysis [*Valley et al.*, 2014; *Valley et al.*, 2015; *Reinhard et al.*, chapter 15, this volume], and measurement of isotope ratios for both major [e.g., *Heck et al.*, 2014; *Parman et al.*, 2015; *Lewis et al.*, 2015] and trace components [*Valley et al.*, 2014, 2015; *Peterman et al.*, 2016; *Blum et al.*, chapter 16, this volume; *Saxey et al.*, chapter 14, this volume; *Reinhard et al.*, chapter 15, this volume; *White et al.*, chapter 17, this volume] support continued efforts to understand the complex interaction between spatial and spectral data processing, and associated analytical uncertainties.

As analytical protocols and data mining approaches are developed for geomaterials, we anticipate the need to standardize aspects of data reporting to streamline evaluation, utilization, and expansion of published literature. This note seeks to provide guidelines for APT data reporting within the geosciences in order to (i) maintain effective communication of protocols and techniques within the community, and (ii) provide an efficient means to evaluate published literature. The information to be reported covers sample preparation, sample context, instrument settings, acquisition conditions, reconstruction parameters, and data metrics. We anticipate that information may be included in various ways, including figures, tables, and supplementary materials depending on the stylistic limitation and scientific focus of any given publication.

18.2. REPORTING

18.2.1. Basic Sample Preparation Information

Preparation of APT specimens, as well as previous sample treatment, can influence material properties and data quality. A brief discussion of basic sample preparation information should include any pre-APT analysis processing (e.g., mounting, polishing, and coating for conductivity), as well as APT specimen preparation details (e.g., FIB lift-out, typical vs atypical lift-out geometries, low-voltage cleanup steps, and application/use of coatings) and any correlative microscopy done between APT preparation and APT analysis, such as transmission electron backscatter diffraction [e.g., *Reinhard et al.*, chapter 15, this volume].

18.2.2. Sample Context

Given a single needle-shaped APT specimen typically encompasses a volume $\leq 10^8 \, nm^3$, providing context for APT specimens greatly enhances the utility and interpretability of an APT data set. The importance of the type and scale of sample characterization varies from study to study; however, the material structure (crystallography and mineral group, if applicable), age, and bulk chemistry provide valuable basic specimen information. Imaging of the sample/lift-out locations, and the homogeneity of the sample, is highly encouraged.

18.2.3. Data Acquisition Settings and Data Summary

Basic information concerning specimen analysis is valuable in evaluating data quality. Much of this information can be summarized within a table similar to Table 18.1. "Instrument settings" summarizes the instrument type and basic conditions and controls applicable to data collection. "Data summary" summarizes various aspects of the software used in generating reconstructions (which may or may not be the proprietary IVAS software) as well as select metrics of the data sets. We note that the "percentage of ranged ions" in Table 18.1

Table 18.1 Example Atom Probe Tomography Data Acquisition Settings and Data Summary

Specimen/Data Set	MX1	MX2	MX3
Instrument Model	LEAP 5000 XR	LEAP 5000 XR	LEAP 5000 XR
Instrument settings			
Laser wavelength (nm)	355	355	355
Laser pulse energy (pJ)[a]	200	200	200
Voltage pulse fraction[a] (%)	15	15	15
Pulse frequency (kHz)	125	125	125
Evaporation control	Detection rate	Detection rate	Detection rate
Target detection rate (ions/pulse)	0.01	0.01	0.01
Nominal flight path (mm)	382	382	382
Set point temperature (K)	50	50	50
Sample temperature (K)	55	55	55
Chamber pressure (Torr)	1.3×10^{-10}	1.4×10^{-10}	5.4×10^{-11}
Data summary			
LAS root version	15.41.342j	15.41.342j	15.41.342j
CAMECAROOT version	15.43.393e	15.43.393e	15.43.393e
Analysis software	IVAS 3.6.10a	IVAS 3.6.10a	IVAS 3.6.10a
Total ions:	150,792,481	163,057,160	213,529,143
Single (%)	66.1	69.2	68.1
Multiple (%)	33.1	30.1	31.2
Partial (%)	0.8	0.7	0.7
Reconstructed ions:	140,428,802	155,697,119	194,541,231
Ranged (%)	79.4	75.2	76.7
Unranged (%)	20.6	24.8	23.3
Volt./bowl corr. peak (Da)	16	16	16
Mass calib. (peaks/interp.)	10/Lin.	11/Lin.	11/Lin.
$(M/\Delta M)$ for $^{16}O_2^{+}$[b]	1,130	1,200	1,180
$(M/\Delta M_{10})$[c]	530	550	540
Time-independent background (ppm/ns)	20.5	19.7	18.7
Reconstruction			
Final specimen state	Intact	Intact	Fractured
Pre-/post-analysis imaging	SEM/SEM	SEM/SEM	SEM/n.a.
Radius evolution model	"Shank"	"Shank"	"Shank"
Field factor (k)	3.3	3.3	3.3
Image compression factor	1.65	1.65	1.65
Assumed E-field (V/nm)	28	28	28
Detector efficiency (%)	52	52	52
Avg. atomic volume (nm³)	0.0108	0.0108	0.0108
$V_{initial}$; V_{final} (V)	4,546; 9,608	4,305; 10,383	4,848; 11,719

[a] Entries are mutually exclusive.
[b] ΔM is full width at half maximum.
[c] ΔM_{10} is full width at tenth maximum.

is intended to represent the ranging/reconstruction of the complete data set; the spectra for specific subregions of the data set which are the focus of the scientific inquiry can be presented elsewhere.

18.2.4. Spectral Processing

Time-of-flight data, and the resulting mass/charge ratio spectra, are a critical part of APT data, given they are an input for spatial reconstruction of data and are the basis for visualization and measurement of compositional variation throughout data sets. Publications are therefore encouraged to present a complete mass spectrum, in figure form, for each needle-shaped specimen. These should include hydrogen peaks, labeling of major peak families, and a record of the highest mass-to-charge-state value acquired. This may be more/less involved depending on the importance of ranging and compositional analysis within the study. In certain cases, where large numbers of data sets are included, it may be appropriate to include "representative" spectra so long as the spectra are functionally identical for the given scientific

inquiry, and relevant differences in acquisition settings, charge states, background levels, contaminant levels, and specimen geometries are accounted for. Relevant subregions of the spectra may be highlighted if they are analyzed in the course of the publication; for example, visualization of trace element or isotope peaks can be difficult when viewing the complete spectrum and in instances where they are of particular importance, the local spectrum structure surrounding these peaks may be highlighted in companion images. Indicating the expected peak positions and relative abundances of isotopes may be beneficial in some cases; however, we note that analysis of radiogenic isotopes and/or isotopically doped materials may preclude direct knowledge of "expected" isotope ratios. Other important information includes the bulk specimen composition, including whether this was determined using basic ranging or peak decomposition analysis, and the background correction scheme used. If any other novel analysis was done to treat challenges in spectral analysis (interferences, overlaps, etc.), they may be indicated. An example of how spectral processing may influence measured trace element (isotope) compositions is given in *Blum et al.* [chapter 16, this volume].

We also suggest monitoring a set of peaks representative of two isotopes, in two different charge states: for example, the ion-count ratios, C_{28Da}/C_{29Da}, $C_{14Da}/C_{14.5Da}$, and C_{14Da}/C_{28Da}, corresponding nominally to $^{28}Si^+/^{29}Si^+$, $^{28}Si^{++}/^{29}Si^{++}$, and $^{28}Si^+/^{28}Si^{++}$, allowing for any interferences. This provides some measure of the electric field proximal to the specimen surface. The peaks of interest may vary depending on the material.

18.2.5. Reconstruction

In addition to providing the basic details for the reconstruction (see Table 18.1), papers should include a short statement concerning how the reconstruction was approached: that is, what criteria were used to evaluate an "optimal" reconstruction, and what were the dependent and independent parameters during optimization. For example:

> Standard instrument characteristics (flight path, detector efficiency, etc.) were used in reconstructing data sets (see Table 1). Reconstruction was approached iteratively, with spatial constraints coming from the tip geometry within the pre-/post acquisition images. Final reconstructions utilized spectral ranges refined from preliminary data analysis, and optimized reconstruction parameters to best replicate the inferred evaporated dimensions from pre-/post acquisition imaging, while holding constant those parameters measured as part of pre- and post-acquisition imaging (sphere-cone radius ratio, shank angle, final end-tip radius, etc.).

We encourage presentation of atom map images, both for the entire data set, including one or multiple ions of interest, and images of the regions or features of interest.

In the case that correlative microscopy and/or high-precision reconstructions are a principal component of the study, inclusion of pre-/post-analysis images is desirable.

18.2.6. Spatial Processing

In cases where domains within APT data sets are isolated/defined, we encourage authors to communicate the analysis method utilized (e.g., isoconcentration surfaces and kth nearest-neighbor analysis), and the relevant input parameters (e.g., isoconcentration threshold/value; voxel size and delocalization; or nearest-neighbor order parameters, N_{min}, d_{max}, E, and L). Erroneous results can be generated when input parameters are not selected/calibrated appropriately. Where compositional profiles are of interest, the use of background-corrected data is preferable. The local background levels themselves should also be indicated for mass peaks of interest in cases where the noise contribution may be significant.

18.2.7. Uncertainties

We encourage the inclusion of appropriate uncertainties, including a description or citation indicating how they were calculated. Oftentimes, many uncertainties within the data may be inconsequential to the scientific question of interest, or may be difficult to calculate based on the complex relations between spatial and spectral data types; however, we encourage inclusion and discussion of those uncertainties relevant to the main scientific results and discussion.

18.2.8. Other Information

Broad interest in compositional and isotopic analysis requires consideration of several variables including molecular interferences. Of particular interest are those interferences associated with contamination from the specimen or vacuum environment (e.g., hydrides), and thus may be both variable between different experiments and difficult to constrain through peak deconvolution. The nature and importance of interferences depend on the specifics of a given material and scientific inquiry; at present, there is no framework for a holistic treatment of contaminant interferences. We suggest documenting background corrected counts within each of the 1, 2, and 3 Da peaks, as well as the 16, 17, 18, and 19 Da peaks. These data may generate a database to better understand H, O, H_2O, and so on, signals within APT data sets, and to develop means to monitor and minimize associated interferences. As a better understanding evolves, these reporting suggestions may similarly adapt to provide better reporting practices.

REFERENCES

Blum, T. B., D. A. Reinhard, Y. Chen, T. J. Prosa, D. J. Larson, and J. W. Valley (2018), Uncertainty and sensitivity analysis for spatial and spectral processing of Pb-Pb geochronology by atom probe tomography, in *Microstructural Geochronology: Planetary Records Down to Atom Scale*, edited by D. Moser, F. Corfu, S. Reddy, J. Darling, and K. Tait, John Wiley & Sons, Inc., Hoboken, NJ, *232*, 327–349.

Gault, B., M. P. Moody, J. M. Cairney, and S. Ringer (2012), *Atom Probe Microscopy*, pp. 396, Springer, New York.

Heck, P. R., F. J. Stadermann, D. Isheim, O. Auciello, T. L. Daulton, A. M. Davis, J. W. Elam, C. Floss, J. Hiller, D. J. Larson, J. B. Lewis, A. Mane, M. J. Pellin, M. R. Savina, D. N. Seidman, and T. Stephan (2014), Atom-probe analyses of nanodiamonds from Allende, *Meteorit. Planet. Sci.*, *49*, 453–467.

La Fontaine, A., S. Piazolo, P. Trimby, L. Yang, and J. Cairney (2017), Laser-Assisted Atom Probe of Deformed Minerals: A Zircon Case Study, *Microsc. Microanal.*, 1–10, doi:10.1017/S1431927616012745.

Larson, D. L., T. J. Prosa, R. M. Ulfig, B. P. Geiser, and T. F. Kelly (2013), *Local Electrode Atom Probe Tomography: A User's Guide*, pp. 318, Springer, New York.

Lewis, J. B., D. Isheim, C. Floss, and D. N. Seidman (2015), $^{12}C/^{13}C$-ratio determination in nanodiamonds by atom-probe tomography, *Ultramicroscopy*, *159*, 248–254.

Miller, M. K., and R. G. Forbes (2014), *Atom Probe Tomography: The local Electrode Atom Probe*, pp. 437, Springer, New York.

Oberdorfer, C., and G. Schmitz (2011), On the field evaporation behavior of dielectric materials in three-dimensional atom probe: A numeric simulation, *Microsc. Microanal.*, *17*, 15–25.

Oberdorfer, C., P. Stender, C. Reinke, and G. Schmitz (2007), Laser-assisted atom probe tomography of oxide materials, *Microsc. Microanal.*, *13*, 342–346.

Parman, S. W., D. R. Diercks, B. P. Gorman, and R. F. Cooper (2015), Atom probe tomography of isoferroplatinum, *Am. Mineral.*, *100*, 852–860.

Peterman, E. M., S. M. Reddy, D. W. Saxey, D. R. Snoeyenbos, W. D. A. Rickard, E. M. Fougerouse, and A. R. C. Kylander-Clark (2016), Nanogeochronology of discordant zircon measured by atom probe microscopy of Pb-enriched dislocation loops, *Sci. Adv.*, *2*, e1601318.

Reinhard, D. A., D. E. Moser, I. Martin, K. P. Rice, Y. Chen, D. Olson, D. Lawrence, T. J. Prosa, and D. J. Larson (2018), Atom probe tomography of baddeleyite standard phalaborwa and zircon standard BR266, in *Microstructural Geochronology: Planetary Records Down to Atom Scale*, edited by D. Moser, F. Corfu, S. Reddy, J. Darling, and K. Tait, John Wiley & Sons, Inc., Hoboken, NJ, *232*, 315–325.

Saxey, D. A., S. M. Reddy, D. Fougerouse, W. D. A. Rickard (2018), The Optimization of Zircon Analyses by Laser-Assisted Atom Probe Microscopy: Insights from the 91500 Zircon Standard, in *Microstructural Geochronology: Planetary Records Down to Atom Scale*, edited by D. Moser, F. Corfu, S. Reddy, J. Darling, and K. Tait, John Wiley & Sons, Inc., Hoboken, NJ, *232*, 293–313.

Silaeva, E. P., M. Karahka, and H. J. Kreuzer (2013), Atom probe tomography and field evaporation of insulators and semiconductors: Theoretical issues, *Curr. Opin. Solid State Mater. Sci.*, *17*, 211–216.

Tsong, T. T., and E. W. Müller (1970), Field adsorption of inert-gas atoms on field ion emitter surfaces, *Phys. Rev. Lett.*, *25*, 911.

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

Valley, J. W., D. A. Reinhard, A. J. Cavosie, T. Ushikubo, D. F. Lawrence, D. J. Larson, T. F. Kelly, D. R. Snoeyenbos, and A. Strickland (2015), Nano- and micro-geochronology in Hadean and Archean zircons by atom-probe tomography and SIMS: New tools for old minerals, *Am. Mineral.*, *100*, 1355–1377.

Vurpillot, F., and C. Oberdorfer (2015), Modeling atom probe tomography: A review, *Ultramicroscopy*, *159*, 202–216.

White, L. F., J. R. Darling, D. Moser, D. A. Reinhard, J. Dunlop, D. J. Larson, D. Lawrence, and I. Martin (2018), Trace element nanostructures in shock metamorphosed baddeleyite revealed by atom probe tomography, in *Microstructural Geochronology: Planetary Records Down to Atom Scale*, edited by D. Moser, F. Corfu, S. Reddy, J. Darling, and K. Tait, John Wiley & Sons, Inc., Hoboken, NJ, *232*, 351–367.