

## Question

Why is the UV laser better for the analysis of minerals?

## Response

In all of our laser research, we have found using progressively shorter wavelength photons (higher energy), improvements in the mass spectral quality and yield for geological (and most really) materials, from IR to Green to UV - the smaller wavelengths created more deposition of energy in thin surface layers - and lower wavelengths also allow a tighter focus, so we are heating a smaller volume, allowing the tip apex to cool more rapidly.

## Extra

Kelly, T. F. et al. Laser pulsing of field evaporation in atom probe tomography. *Current Opinion in Solid State and Materials Science* 18, 81–89 (2014). Blum, T. et al. Best Practices for Reporting Atom Probe Analysis of Geological Materials. *Microstructural Geochronology* 232, 369 (2017).

Are there good review articles that can be a good place to start?

Here are the references cited during the webinar

[Saxey, D. W., Moser, D. E., Piazzolo, S., Reddy, S. M. & Valley, J. W. Atomic worlds: Current state and future of atom probe tomography in geoscience. \*Scripta Materialia\* 148, 115–121 \(2018\).](#) 1. [Valley, J. W. et al. Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography. \*Nature Geoscience\* 219 \(2014\) doi:10.1038/NGEO2075.](#) 1. [Reddy, S. M. et al. Atom Probe Tomography: Development and Application to the Geosciences. \*Geostandards and Geoanalytical Research\* 44, 5–50 \(2020\).](#) 1. [Blum, T. et al. Best Practices for Reporting Atom Probe Analysis of Geological Materials. \*Microstructural Geochronology\* 232, 369 \(2017\).](#)

Great talk so far! Will this and the previous talk be publicly available to share?

Please see <https://www.atomprobe.com/keyaplinks/webinars>

Sorry I missed the detail before, but is APT able to identify oxidation states of elements? incredible tech, please thank Robert for his time :)

Ions that leave the specimen apex can leave in more than one charge state (Tungsten prefers +3 and +4, but will evaporate at +2 under warmer/lower-field conditions in laser pulsing, Silicon prefers +2, but will evaporate at +3 from a high-field oxide region) and can leave as a single ion, or as a molecular ions like SiO or SiO<sub>2</sub>. There is likely bonding information in APT mass spectra, but the signal is clouded by many factors and is not well understood. So, no, if you get Si and O, or SiO, or SiO<sub>2</sub>, there is no simple relation as to how they were bonded in the specimen, just that those elements were on the surface at the same time during evaporation - You can get molecules that don't make much sense, like hydrogen Da 1,2,3 and Water related 18,19, 37, 55

Müller, E. W. & Tsong, T. T. Field Ion Microscopy, Field Ionization and Field Evaporation. *Progress in Surface Science* 4, 1 (1973). 1. [Kingham, D. R. The Post-Ionization of Field Evaporated Ions: A Theoretical Explanation of Multiple Charge States. \*Surface Science\* 116, 273–301 \(1982\).](#)

<p>How are the limits of detection for individual elements determined for the atom probe?</p>	<p>Detection limits for individual peaks have very different modalities, an isolated peak (As+), two nearby peaks (&lt; 1Dalton 61Ni++ and 92Mo+++), a peak in the tail of a larger peak (Co after Ni) and two peaks directly overlapped (&lt; 0.1 Da Si++, N+). For isolated peaks, the detection limit is simple calculated from the noise floor - the counts that would be in the range of a peak down to perhaps 10% of the peak maximum. A practical review can be found at : Currie, L. A. Limits for Qualitative Detection and Quantitative Determination: Application to Radiochemistry. Analytical Chemistry 40, 586–592 (1968) - which addresses both the detection limit within certain confidence intervals, and the quantification limit. "DETECTION LIMIT LDL – the true net signal (number of counts) which may be expected to lead to a detection. This is the lowest level of detection which will lead to a true signal (95% of the time) and is typically used when no net signal is observed. Note LC and LDL overlap. <math>LDL = 4.65 \sqrt{\text{Background}}</math>" . A more detailed (and more complex) method is presented here - 1.Haley, D., London, A. J. &amp; Moody, M. P. Processing APT Spectral Backgrounds for Improved Quantification. Microscopy and Microanalysis 26, 964–977 (2020).</p>	<p>CRITICAL LIMIT LC – the net signal level (number of counts) above which an observed signal may be reliably recognized or detected. When a net signal is above this level, it is true (95% of the time). <math>LC = 2.33 \sqrt{\text{Background}}</math> or 3.29 for 99%</p>
<p>Can you use the APT effectively to analyze total organic and inorganic carbons?</p>	<p>There are several different applications of this. One way is to identify C12/13 ratios if the source of the carbon is extraterrestrial, others might be what elements do they co-evaporate with. Both of these applications are challenging for lots of different reasons (see the references), 1.Gordon, L. M. &amp; Joester, D. Mapping residual organics and carbonate at grain boundaries and the amorphous interphase in mouse incisor enamel. Front. Physiol 6, 57 (2015). 1.Lewis, J. B., Isheim, D., Floss, C. &amp; Seidman, D. N. Distinguishing Meteoritic Nanodiamonds from Disordered Carbon Using Atom-Probe Tomography. Microscopy Today 26, 18–23 (2018).</p>	
<p>These samples need to be prepared with the FIB. Have there been studies on how FIB (specifically Ga-based) influences the observed structure/clustering?</p>	<p>Focused beams of ions can obviously change materials - it is why they are so useful for making specimens, but they can also damage relevant parts of the region of interest. The same challenges exist in TEM as in APT specimen preparation and there are great techniques like capping materials, low energy final milling, low energy noble gas ion bombardment 'cleaning', preparation under cryo conditions. So, yes, you can cause changes in clustering, but with a careful design, you can avoid it. You can request our FIB technical notes here: <a href="https://www.atomprobe.com/keyaplinks/aptdownloads">https://www.atomprobe.com/keyaplinks/aptdownloads</a> A nice recent references can be found here - that highlights overall problems as well as those specific to Aluminum alloys: 1.Unocic K.a., Mills M.j. &amp; Daehn G.s. Effect of gallium focused ion beam milling on preparation of aluminum thin foils. Journal of Microscopy 240, 227–238 (2010). - another very practical article - 1.Thompson, K. et al. In-Situ Site-Specific Specimen Preparation for Atom Probe Tomography. Ultramicroscopy 107, 131–139 (2007). - an excellent overview of using cryo to minimize specimen alteration. 1.McCarroll, I. E., Bagot, P. A. J., Devaraj, A., Perea, D. E. &amp; Cairney, J. M. New frontiers in atom probe tomography: a review of research enabled by cryo and/or vacuum transfer systems. Materials Today Advances 7, 100090 (2020).</p>	

what is the detection efficiency possible with latest instrument configuration?

The latest APT systems (LEAP 5000) can achieve up to 80% detection efficiency, while the reflectron based systems have a metal mesh that the ions pass through twice, reducing the DE to about 50%. The detectors are sensitive to the incoming ions H to Uranium and even heavy molecules after about 3kV of specimen voltage, so generally APT is a standardless technique, some specimens have ions that preferentially like to evaporate in multiples and this can lower the detection for those species (B in Si is the classic, as much as 50% of the Boron can be lost in heavily doped specimens) True DE is difficult to measure within a few percent accuracy.

1.Meisenkothen, F., Samarov, D. V., Kalish, I. & Steel, E. B. Exploring the accuracy of isotopic analyses in atom probe mass spectrometry. *Ultramicroscopy* 216, 113018 (2020). Prosa, T. J., Geiser, B. P., Lawrence, D., Olson, D., & Larson, D. J. (2014). Developing detection efficiency standards for atom probe tomography. In M. T. Postek (Ed.) (p. 917307). Presented at the SPIE NanoScience + Engineering, San Diego, California, United States. <https://doi.org/10.1117/12.2062211>

you mentioned APT being 'standardless'--can you expand on this a bit?

When careful specimen preparation is complete, carefully chosen analysis conditions are used, and proper data reduction techniques are used, quantitative compositional information comes from simply counting the atoms detected in a peak or set of peaks and dividing by the total number of atoms detected. The detector is an MCP + delay line detector that in the LEAP 5000 XS (straight flight path, no mesh) detects up to 80% of the incoming ions without bias on a wide variety of applications. If careful work is NOT done, you can collect data with compositional biases - especially in some noted semiconductor examples - Boron in Silicon, measuring III/V semiconductors. These biases come from evaporation in-between pulses (DC evaporation) and from multiple event dead-time errors, as well as disassociation/neutralization after leaving the tip. In some materials the biases are difficult to avoid, so then you would need to run some carefully planned standard analysis on well documented standards - as is done in almost EVERY quantitative analysis techniques, calibration curves, Relative Intensity Factors, etc..

1.Kitaguchi, H. S., Lozano-Perez, S. & Moody, M. P. Quantitative analysis of carbon in cementite using pulsed laser atom probe. *Ultramicroscopy* 147, 51–60 (2014). Russo, E. D. et al. Compositional accuracy of atom probe tomography measurements in GaN: Impact of experimental parameters and multiple evaporation events. *Ultramicroscopy* 187, 126–134 (2018). 1.Meisenkothen, F., Samarov, D. V., Kalish, I. & Steel, E. B. Exploring the accuracy of isotopic analyses in atom probe mass spectrometry. *Ultramicroscopy* 216, 113018 (2020).

From a Geo perspective - "The quantification of APT data, while not perfect (or within the variation of counting statistics) in every case, is different from the situation with standard geoanalytical methods (SIMS, LA-ICP-MS, EPMA). In these cases, there are relative sensitivity factors, that often vary by several orders of magnitude, and tend to be matrix dependent. For APT data, any necessary corrections are on a smaller scale, though they may be difficult to quantify without a some amount of systematic testing or published literature related to the mineral of interest. The other important difference to note is that the volume of atoms detected in APT is typically much smaller than in other geo methods. This means that the statistical uncertainties are necessarily greater due to the smaller number of atoms counted, but the APT uncertainty is very close to the fundamental atomic limit due to the high detection efficiency of APT compared with conventional geoanalytical methods."

Question

Response

Extra

Why has the geoscience community adopted APT in just the last 5 or 10 years?

The wide availability of the UV laser available in the LEAP systems after 2010 is the basic reason. Laser pulse atom probe tomography has been available since 2006 or 2007, but the data quality for some materials - especially those with poor thermal/electrical conductivity was sometime quite poor - long thermal tails that give a high overall noise floor, reducing sensitivity dramatically. The UV laser with the tight focus and stronger absorption reduces the heated volume of the sample dramatically and speeds the cool down period. (50K -> 300K for ~ 1nsec) The nature geoscience paper in 2014 which was able to confirm the age of the oldest intact minerals known on earth from Dr. Valley really opened the eyes of the community .... And the community really came together quickly and had a multi group paper put together on standards in data collection and analysis lead by Tyler Blum in 2017 and 2018 - these collaborative efforts continue yet today with the review paper which includes a summary of run conditions for a wide variety of minerals - I am not sure of any other community that has come together so quickly - so this all adds for fast adoption.

Valley, J. W. et al. Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography. *Nature Geoscience* 219 (2014) doi:10.1038/NGEO2075.

Reddy, S. M. et al. Atom Probe Tomography: Development and Application to the Geosciences. *Geostandards and Geoanalytical Research* 44, 5–50 (2020).  
Blum, T. B., Darling, J. R., Kelly, T. F., Larson, D. J., Moser, Desmond. E., Perez-Huerta, A., et al. (2018). Best practices for reporting atom probe analysis of geological materials. In D. E. Moser, F. Corfu, J. R. Darling, S. M. Reddy, & Kimberly. T. Tait (Eds.), *Microstructural Geochronology: Planetary Records Down to Atom Scale* (Vol. 232, pp. 369–373). AGU/Wiley Publishing.

And also to the shorter review paper: Saxey, D. W., Moser, D. E., Piazzolo, S., Reddy, S. M., & Valley, J. W. (2018). Atomic worlds: Current state and future of atom probe tomography in geoscience. *Scripta Materialia*, 148, 115–121. <https://doi.org/10.1016/j.scriptamat.2017.11.014>

Are there any particular problems with specimen Preparation of these materials which are mostly very poor conductors?

Much like semiconductors, or organic materials, these materials often need a thin layer of metal sputtered on them – and there are sometimes problems with charging as you get to the final milling, so site specific targeting can be challenging, but with most specimens it can be overcome. Some recent work looking at hydrogen and water content of some mineral phases has shown definite advantages using cryo preparation and transfer – so the recent availability of commercial transfer systems (like the VCTM-LEAP and VCTM-FIB and VCTM-Glove box) has really assisted this work.

There can also be some issues in getting homogenous ion milling in all crystal directions, particularly for some asymmetric or particularly hard mineral phases such as diamond, calcite, or phyllosilicates.”

Do you have a recommendation for the ranging method used when looking at geologic materials (full width or constant width), particularly with complex spectra?

The reference has some good advice, but it is really dependant upon the dataset - the most important thing is to come up with a method and use it constantly. One common error when trying to quantify isotopic ratios, for example, is to use a ranging method that sets the width of the range relative to where the peak emerges from the noise. This results in wider ranges being used for the higher peaks, introducing bias in the quantification. A better approach is to take a constant width across all peaks that require direct comparison, while choosing a range width that is no so large that it captures too much noise in the smaller peaks.”

1. Blum, T. et al. Best Practices for Reporting Atom Probe Analysis of Geological Materials. *Microstructural Geochronology* 232, 369 (2017).

Do you have difficulty with magnetic samples during FIB preparation of APT samples?

Similar to insulative materials, imaging in the FIB can be affected, especially using 'in-lens' high-resolution modes, but of the hard and soft magnets we have analyzed, there were no dramatic problems that prevented creating viable APT specimens

1. Alam, T. et al. Influence of niobium on laser de-vitrification of Fe-Si-B based amorphous magnetic alloys. JOURNAL OF NON-CRYSTALLINE SOLIDS 428, 75–81 (2015).

please comment on optimal specimen geometry of geoscience samples (seemingly often getting >40M ions) [apex to (Pt?) weld distance, 1/2-shank angle, Half-Grid or coupon, substrate type?]

There is not much to add beyond standard suggestions of a non zero shank angle (~ 15 degree full angle) and a full touch down of the wedge onto the carrier - be it a microtip coupon, wire, or TEM grid. Welds in the FIB should be orientated away from the laser. There have been reports that the laser will sometimes preferentially locate down the shank/weld of the specimen, in this case, a taller wedge (increase from ~ 3 microns to 6) may be necessary, but geological specimens behave similarly to any APT specimen

Some discussion here: 1. Daly, L. et al. Developing Atom Probe Tomography of Phyllosilicates in Preparation for Extra-Terrestrial Sample Return. Geostand Geoanal Res ggr.12382 (2021) doi:10.1111/ggr.12382.

Thanks for an interesting overview! You mentioned that APT doesn't need reference materials. In the previous slide you have shown that it is indeed important to use ref materials as some isotope ratios are not what expected, something that can be only verified with ref materials.

When careful specimen preparation is complete, carefully chosen analysis conditions are used, and proper data reduction techniques are used, quantitative compositional information comes from simply counting the atoms detected in a peak or set of peaks and dividing by the total number of atoms detected. The detector is an MCP + delay line detector that in the LEAP 5000 XS (straight flight path, no mesh) detects up to 80% of the incoming ions without bias on a wide variety of applications. If careful work is NOT done, you can collect data with compositional biases - especially in some noted semiconductor examples - Boron in Silicon, measuring III/V semiconductors. These biases come from evaporation inbetween pulses (DC evaporation) and from multiple event dead-time errors, as well as dissociation/neutralization after leaving the tip. It is good to compare the peak height ratios in single detector events versus multi evaporation events. If you see higher peaks for species in the multis, you can investigate further to see if there is signal loss due to multiple events on the detector. In some materials the biases are difficult to avoid, so then you would need to run some carefully planned standard analysis on well documented standards - as is done in almost EVERY quantitative analysis techniques, calibration curves, Relative Intensity Factors, etc..

The data showing a discrepancy between the APT and bulk isotopic results is still a work in progress. The reason for this discrepancy is not understood, and it may be an artefact of the data analysis method used here, or could even be a real isotopic difference in the sample, so it is not necessarily saying that APT data 'can be only verified with ref materials'."

Has any experiment been made with Atom Probe to optimise the extraction of minerals in complex mineral structures? Optimisation of REE elements extraction for example which would directly support the mining industry.

The talk discussed the analysis of the distribution of gold in gold ore - in which the local chemistry can make it more or less expensive to extract the gold from the ore, we are not aware of similar studies on REE ores

APT has strengths in measuring isotopes, though Meisenkothen's 2020 Ultramicroscopy paper (re. isotope msrmt fidelity) mentions 'deadtime effects', what's this?

See the answer above 1. Meisenkothen, F., Samarov, D. V., Kalish, I. & Steel, E. B. Exploring the accuracy of isotopic analyses in atom probe mass spectrometry. Ultramicroscopy 216, 113018 (2020).