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Technical Note

Shorter is Better: The Advantages of Femtosecond Lasers in LA-ICP-MS Analyses

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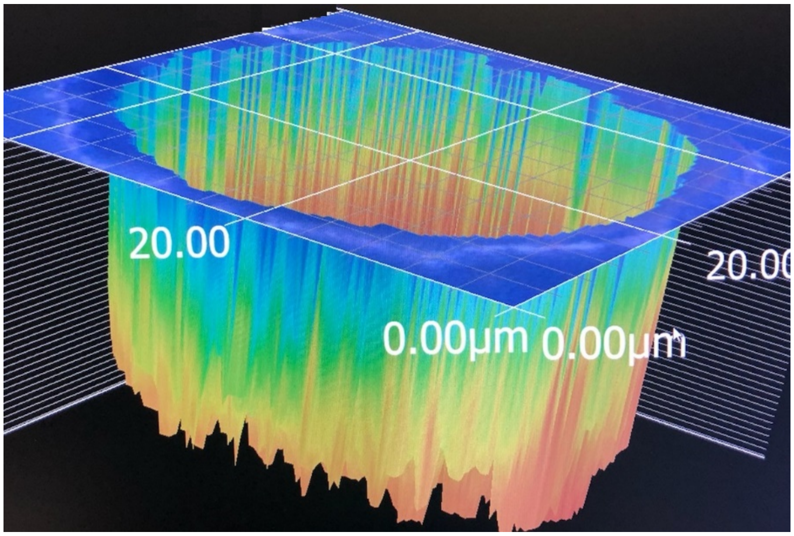


Ablation and post laser ablation imaging courtesy of Michael Pribil (USGS, Denver High Resolution Lab).

It’s been quite a few years since femtosecond (*fs*) lasers appeared on the scene, and the adoption of this technology by micromachining and medical applications in the early 2000s led to a rapid acceleration of the technology providing a range of different systems, wavelengths and overall performance variants that we see today.

Femtosecond lasers have been of interest to the laser ablation ICP-MS community since those early days as the use of ultrashort femtosecond laser pulses was seen as an important advantage for mitigating laser induced fractionation (see Koch & Günther, 2007; Liu et al., 2003; Poitrasson et al., 2003; Russo et al., 2004; and references within). The reason is simple – there are significant differences between the ablation behavior of solids under nanosecond (*ns*) and *fs* regimes that stem from the physical effects initiated by the spread in laser pulse duration. LaHaye et al. (2015) have shown that the plasma that usually accompanies laser-solid interaction tends to form, in the case of *fs* lasers, after the end of the pulse, which means that the individual laser pulses are indeed shorter than thermal pathways within the analyzed solid. This is different compared to *ns* lasers, where the plasma is formed during the duration of the pulse.

As a direct result of this behavior the ablation characteristics of the *fs* lasers are different when compared to *ns* lasers. The aerosol formed during ablation is composed of generally smaller particles which tend to have a narrower particle size distribution (Liu et al., 2003; Poitrasson et al., 2003). This characteristic of the sample aerosol was found to be directly linked to signal quality on ICP MS instruments (Joeng et al., 1999). Furthermore, the significant reduction in thermal effects results in minimal laser-induced fractionation effects observed for *fs* lasers and this allowed researchers to explore the possibilities of non-matrix matched external standardization.

There have always been challenges with the use of *fs* lasers in LA-ICP-MS though. In fact, there were two key areas of concern. One was cost. Early systems were prohibitively expensive for most labs, with price tags often pushing upwards of $1m USD. Thankfully, the competitive nature of the laser business, and the technological advances made have brought these prices down significantly and a highly capable *fs* laser ablation system can now be had for much less than half of that figure. The second issue was performance. Maintenance, energy and beam profile in particular. Many of the early systems required a high level of maintenance and user interaction with the laser itself in order just to be able to turn it on and run it, and even then there was generally only enough energy generated to be of use at a fundamental wavelength often in the infrared spectrum. Although some labs could experiment in the UV, the lack of energy available at these wavelengths severely limited spot size and therefore limited the ability to address the wide range of applications of interest. As with all laser ablation technology, lower UV wavelengths are preferred (Poitrasson et al, 2003).

The final, and most challenging performance barrier was related to the crater geometries created on a sample surface. Previous *fs* laser ablation systems suffered from poor crater geometries that were highly Gaussian in vertical profile with irregular diameters. With *ns* lasers these beam profiles can be improved using homogenizing optics and aperture imaging techniques, but with *fs* laser light the laws of physics dictate that neither of the options are available to us. The result of all of this was that all of these barriers effectively resulted in only very niche and specialized labs taking up the challenge, and even then applications like depth profiling and the use of line/raster ablation were virtually impossible as the extreme Gaussian beam profiles meaning that the volume of ablated material was difficult to control and almost impossible to estimate.

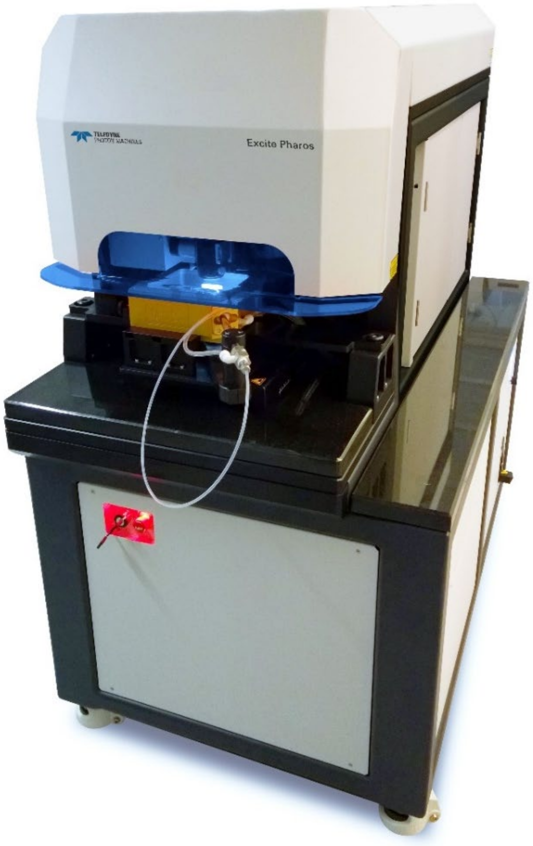


Figure 1. Teledyne Photon Machines Excite Pharos

Fast forward to today and the latest generation of *fs* lasers (Light Conversion's "Pharos") are reliable, robust, and genuinely turnkey in operation requiring little if any maintenance week to week. Energy outputs have also improved and are typically delivering 257nm UV laser output at sufficient intensity to enable spot sizes up to 70µm to be generated at the sample surface. Integrating this laser source into the Teledyne Photon Machines' Excite system we can then incorporate a purposely designed optic beam path (all reflective optics) that now allows for uncompromised laser transmission that provides crater geometries that are far more useable than anything previously seen. Whilst the resulting beam profile could never be regarded as perfectly flat it can now be considered flat enough to allow for volumetric ablation, line scans and rasters in a number of different mineral types.

It is therefore acceptable to claim that the latest generation of *fs* laser systems finally have a place in the wider LA-ICP-MS community. These systems are robust, affordable, and importantly provide a beam profile in the UV range that finally addresses the needs of the analytical user as the unrivaled beam quality now translates into highly symmetric craters, even on problematic matrices (See Figure 2 and Figure 3.)

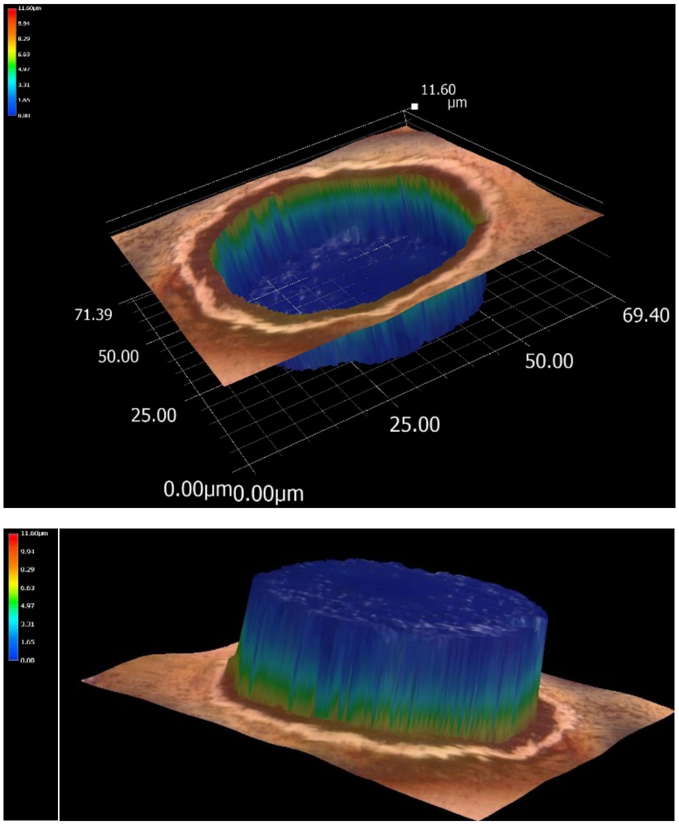
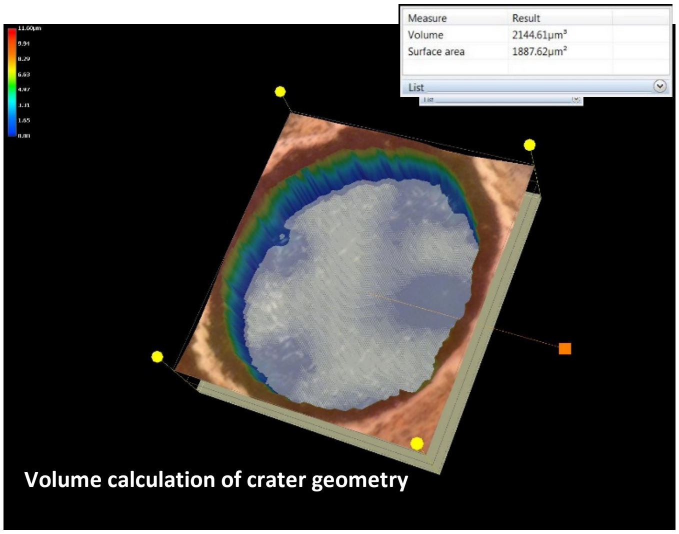


Figure 2. Ablation and crater profile (above and below) of pyrrhotite courtesy of Michael Pribil (USGS, Denver High Resolution Lab).



Measure	Result
Volume	2144.61μm³
Surface area	1887.62μm²

Figure 3. Ablation and crater profile of pyrrhotite courtesy of Michael Pribil (USGS, Denver High Resolution Lab).

References

Joeng, S. H., Borisov, O. V., Yoo, J. H., Mao, X. L., & Russo, R. E. (1999). Effects of particle size distribution on inductively coupled plasma mass spectrometry signal intensity during laser ablation of glass samples. Analytical Chemistry, 71(22), 5123–5130.

Koch, J., & Günther, D. (2007). Femtosecond laser ablation inductively coupled plasma mass spectrometry: Achievements and remaining problems. Analytical and Bioanalytical Chemistry, 387(1), 149–153. https://doi.org/10.1007/s00216-006-0918-z

LaHaye, N. L., Kurian, J., Diwakar, P. K., Alff, L., & Harilal, S. S. (2015). Femtosecond laser ablation-based mass spectrometry: An ideal tool for stoichiometric analysis of thin films. Scientific Reports, 5(April), 13121. https://doi.org/10.1038/srep13121

Liu, C., Mao, X. L., Mao, S., Zeng, X., Greif, R., & Russo, R. E. (2003). Nanosecond and femtosecond laser ablation of brass : Particulate and ICPMS measurements Author : Copyright Information : Nanosecond and Femtosecond Laser Ablation of Brass : Particulate and ICPMS Measurements. 76(2), 379–383. http://dx.doi.org/10.1039/A704169A

Poitrasson, F., Mao, X. L., Mao, S. S., Freydier, R., & Russo, R. E. (2003). Comparison of ultraviolet femtosecond and nanosecond laser ablation inductively coupled plasma mass spectrometry analysis in glass, monazite, and zircon. Analytical Chemistry, 75(22), 6184–6190. https://doi.org/10.1021/ac034680a

Russo, R., Mao, X., Liu, C., & Gonzalez, J. (2004). Laser assisted plasma spectrochemistry: laser ablation. Journal of Analytical Atomic Spectrometry, 19(9), 1084. https://doi.org/10.1039/b403368j.

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